We are now engaged in isolating the aldehyde and the insoluble chromium compound in quantities sufficient to enable us to investigate them still further.

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AKRON, OHIO.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE RED AND WHITE SILVER SALTS OF 2,4,6-TRIBROMOPHENOL.[1]

BY HENRY A. TORREY AND W. H. HUNTER.

Received December 16, 1910.

Only one silver salt of 2,4,6-tribromophenol was mentioned in the chemical literature at the time we took up this research. This was prepared by Purgotti[2] from the calcium salt, and described as an orange-red precipitate. In preparing this salt by precipitation of a solution of the sodium salt with silver nitrate in excess, we happened to leave a partly washed red precipitate standing on the filter for some hours; when we came to finish the washing, we found it had become completely decolorized, with the exception of some particles which had dried on the edge of the filter. A determination of silver in the air-dried white salt indicated that it was isomeric with the red salt, which was amply confirmed by later analyses of pure specimens.

A study of the conditions under which the white isomer was formed showed that it could be obtained from the red compound by carrying on the precipitation from very dilute solutions, or from a boiling solution, or by solution of the red salt in a little ammonia, and precipitating the white salt from this solution by the addition of more silver nitrate solution. Of these methods, the last is the only one which gives us a pure white salt, and can be used to advantage as a method of preparation. It also furnishes us with a probable explanation of the formation of the white salt from the red when exposed to the air of the laboratory, which may well have contained ammonia.

At this point of our work, a preliminary paper was published,[3] and this called forth immediately a paper[4] from Hantzsch's laboratory, in

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[1] This research was suggested by the late Professor Henry A. Torrey and the experimental work was done under his direction but the explanation of the observations and the writing of the paper were deprived of the benefit of his supervision by his too early death. C. L. JACKSON.

The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy by William Hammett Hunter.

[2] *Gazz. chim. ital.*, 16, 527 (1886).

[3] *Ber.*, 40, 4332 (1907).

[4] *Ibid.*, 40, 4875 (1907).

which he confirmed our results, added another case of the kind which he had discovered, and courteously left the field to us.

In continuing the work, a method of preparing the white salt without previous formation of the red one was worked out, based on the change produced by ammonia, which was more economical of time and silver nitrate. It consisted in adding to the solution of the sodium salt of tribromophenol a few drops of ammonia, which prevented the formation of the red salt, but allowed the precipitation of the white on the addition of rather more silver nitrate than would be required to precipitate the red salt in a solution free from ammonia. This method also helps to prove that the white salt is the stable, and the red salt the labil form.

Since the appearance of the paper of Furcht and Lieben,[1] who describe a white and yellow levulinate of silver, but ascribe the color of the yellow salt to an impurity, it is worth while to point out the reasons for believing that the red color of the silver tribromophenolate is not due to an impurity. Our analyses of both salts agree with the theoretical percentages. The white salt is made from the red without the appearance of any colored by-products. Moreover, some white salt was converted into tribromophenol, and from this sample the red salt was obtained just as easily as from a sample of the phenol freshly prepared.

Nor are the salts of tribromophenol the only case of the kind known. In the paper mentioned, Hantzsch describes two forms, a white and an orange, of the silver salt of dibromoparacresol, in addition to corroborating our work on the salts of tribromophenol. He investigated a number of other phenols, finding white salts in some cases, colored salts in others, but in no other case did he find both forms.

On our part, we have been able to find two other cases in which a red precipitate occurs first, rapidly becoming spontaneously converted into a white form, but we could only isolate the white forms for analysis, as the velocity of transformation of the red salts was too great to permit of their isolation. In view of the purity of the materials used, and of the white salt isolated in each case, there can be no doubt that the red salts formed were strictly analogous to those of tribromophenol and dibromoparacresol. An additional piece of evidence is that ammonia hastens the change in exactly the same manner as that of the tribromophenol salts.

These two cases were the silver salts of 2,4,6-tribromoresorcinol monomethyl ether, and of 3,4,6-tribromoguaiacol.[2]

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[1] *Bull. soc. chim.*, [4] 5, 1069 (1909).

[2] The position of the bromine in this substance has never been determined beyond question, but as it is formed from the 4,6-dibromoguaiacol there seems little doubt that the third atom of bromine has taken the 3, rather than the 5 position, which stands between the two atoms of bromine already present. It may be added that the position of this third atom of bromine seems in no way important in our work.

The silver salt of tetrabromoguaiacol behaves in the same way, except for the fact that at the very instant of precipitation, the silver salt seems to be white. This appearance is evanescent, however, the red salt appearing immediately, and changing rapidly in its turn to a permanent white. This salt was not analyzed, as it seemed useless to analyze any more white salts.

We next tried precipitation in acetone instead of water, in the hope of isolating the red salts of the two phenols whose white salts had been analyzed. We were not able to get an acetone solution of the potassium salt of tribromoresorcinol monomethyl ether, but we obtained a noteworthy compound from tribromoguaiacol, a yellow potassium derivative, giving a yellow solution in acetone. Further, this yellow solution gave a red precipitate with an acetone solution of silver nitrate which, however, blackened from decomposition before it could be isolated. No formation of a white silver salt was observed, possibly because the red compound decomposed before this change began. This yellow potassium derivative seems as if it might be nearly related to the red silver salt. Analyses for bromine and potassium pointed toward its having the composition of a potassium salt with one molecule of crystal water, or of an addition product of tribromoguaiacol and potassium hydroxide. It was prepared by the action of solid caustic potash on an acetone solution of tribromoguaiacol and was a yellow solid giving a yellow solution in pure dry acetone, which was immediately decolorized by the addition of a little water. The dry yellow substance also dissolved slowly in water, giving a colorless solution. It is intended to investigate this interesting compound in the near future.

We were unable to obtain any difference in chemical behavior between the two salts, acids, alkalies, alkyl iodides, and other compounds with more or less reactive halogen atoms all acting in the same way with each isomer. Hantzsch, indeed, found a difference of a degree or two in the melting points of the ethers obtained from the two salts, but it is our opinion that it was accidental, as suggested by him. Experimental work along this line was abandoned only when there seemed no obvious point of attack left untried. Kruyt[1] has recorded his inability to solve this problem along physico-chemical lines.

In the course of the work with alkyl halides, we found that alkyl iodides, if used without a solvent, gave with the silver salts of tribromophenol a very strange series of reactions consisting in the appearance of a green color in the solid salt, accompanied by a blue color in the alkyl iodide, which in a few minutes became light yellowish brown, the solid in the meantime having taken on the appearance of silver iodide. The product of the reaction found in solution in the alkyl iodide, and making up part

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[1] *Ber.*, 43, 543 (1910).

of the precipitate, was a white organic compound, containing neither silver nor an alkyl group, and on analysis yielding about 64 per cent. of bromine, but no iodine. The same product was obtained with methyl, ethyl, or allyl iodide. Only enough work was done on it to show that there was no difference in the behavior of the two silver salts, but it is proposed to study it in much further detail at a later date.

Any explanation of the two salts must show that they can behave in the same manner toward reagents; for instance both give tribromophenol with acids, normal ethers with diluted alkyl iodides, and even the same abnormal reaction with the undiluted iodides.

Our present knowledge of the facts may be summed up as follows: in the case of five phenols, we have a colorless compound giving two silver salts, one red and one white, and these two salts have not been shown to act differently toward any reagents.

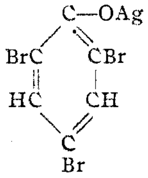
In determining the type of isomerism represented by these salts, the fact of their forming identical reaction products precludes the idea that they are chemical isomers, and leaves as the only probable explanations physical isomerism, polymerism, or tautomerism.

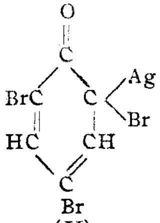
The question next arises, are they physical isomers? The hypothesis that they are simply two different solid modifications of the same compound accounts for all the chemical relationships, even to the change of the red salt into the white by ammonia solutions, but there are two valid objections to it. First, it should be possible to go from the white salt to the red, and if this is possible, the conditions for doing it have not yet been found. Second, and more important, not a case could be found in the literature, in which such a change is accompanied by a change in color. Obviously, phase changes accompanied by a change in water of crystallization do not come into this class.

Polymerism, on the other hand, is considered by Hantzsch to be a plausible explanation of the case. But Hantzsch himself has pointed out that the colorless derivative in cases of chromoisomerism may be safely presumed to have the normal formula, and it has been observed that in cases of polymerism, the monomolecular form appears first, and is less stable than its polymer, while if our salts are polymeric, the reverse is the case, the red salt appearing first, and being less stable than the white.

Again, this explanation would seem to require such a great difference in chemical activity as to preclude the likelihood of a duplication of the chemical action in the two cases. Especially is this probable in the case of the abnormal reaction with alkyl iodides discovered by us, which is so different from the normal behavior of silver salts as to lead to the conclusion that two molecules which give it must be far more like than polymers usually are. Nor can a supposed conversion of one form into the other during the reaction be used to avoid this difficulty, as it can hardly be supposed that cold methyl iodide could turn a polymer into the monomolecular form, or *vice versa*.

If these objections to the other theories are of sufficient weight, tautomerism is left as the sole explanation of the phenomenon, and if we ascribe the normal formula I to the white silver salt of tribromophenol, the best formula for the red salt is II. The para form of this arrangement is also possible, but seems less probable, since the red color resembles the ortho rather than the para quinones, and all the five phenols which show this peculiarity have a bromine atom ortho to the hydroxyl, while Hantzsch's dibromoparacresol does not possess a para bromine atom. This is, however, a matter of slight importance, as the same arguments apply to both forms.


(I)


(II)

The chief objection to this formula was raised by Hantzsch after the formula was proposed tentatively in our preliminary paper: it contains silver tied directly to carbon, and to the same carbon atom as bromine. If silver could behave thus, he pointed out that mercury would have an even greater tendency to attach itself in a similar way, and therefore, should give colored salts, and yet the mercury salts of tribromophenol and other phenols studied by Hantzsch and Auld[1] were white. The analogy is not complete, however, for the salts mentioned were mercuric salts, which resemble silver salts only remotely. A much better experiment for the case in hand would be to take the mercurous salts of phenols, as mercurous mercury is very like silver, and we have still the great tendency which mercury shows to unite to carbon. This experiment was tried by us, and yellow salts were obtained from trobromophenol and tribromoresorcinol, and an orange salt from triiodophenol. It was proved further by analysis that these colors were not due to the presence of basic salts. Moreover, yellow precipitates were obtained under like conditions with tetrabromoguaiacol and with tribromoresorcinol monomethyl ethers, though these were not analyzed. Hantzsch's argument, therefore, from the analogy between our red salts and the corresponding mercury salts, is converted from an objection into a confirmation of formula II, since colored mercurous salts were obtained from phenols which gave red silver salts.

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[1] *Ber.*, 39, 1105 (1906).

Another objection to this formula is that it would seem as if it could not give the same reaction products as the normal salt; for instance, different ethers would be expected from the two salts, whereas both salts give the same ether and the same abnormal reaction with alkyl iodides. It must be remembered, however, that in the case of compounds having the quinoid-benzenoid isomerism indicated by our formulas, it is the rule rather than the exception that they give identical chemical reactions. The difficulty is rather to find reactions which will prove a difference between the two isomers, and usually the simple fact of one form being colorless, the other colored, has been taken as sufficient for ascribing such an isomerism as the cause of the difference in color.

It is fully recognized that arguments such as the above do not and can not prove the correctness of the explanation given for the structures of the two salts, but it would seem that it can be claimed with safety that the formula proposed for the red salt is open to less serious objections than any of the other explanations of the phenomena which we have considered.[1]

Experimental Part.

The tribromophenol was recrystallized from dilute alcohol till it showed the constant melting point 92°, which is that given by Post,[2] who also could not reach the higher temperature given by Körner[3] and Sintenis.[4]

The ordinary method used for making sodium salts of phenols in this work was to dissolve the phenol in a slight excess of alkali containing only a trace of chloride, and add very dilute acetic acid until a slight permanent precipitate was formed, when the mixture was shaken to coagulate the fine precipitate, and filtered. The solution of the tribromophenol sodium salt made in this way was always alkaline to phenolphthalein.

Red Silver Salt of Tribromophenol.—This salt, which was discovered by Purgotti, was made by adding a dilute solution of silver nitrate to the solution of the sodium salt prepared in the manner just described. The orange-red precipitate, after thorough washing on a plaited filter, was sucked dry in a Buechner funnel, pressed out on a porous plate, and dried *in vacuo* over calcium chloride, as it was found that these silver salts blackened if dried *in vacuo* over sulphuric acid. In silver determinations by the method of Carius, nitric acid alone was used, as the substance contains three atoms of bromine to one of silver.

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[1] Work is now in progress at the Chemical Laboratory of the University of Minnesota, on the abnormal reaction of alkyl iodides on phenol silver salts, and also on the yellow potassium derivative of tribromoguaiacol.

[2] *Ann.*, 205, 66 (1880).

[3] *Ibid.*, 137, 208.

[4] *Ibid.*, 161, 340.

Calculated for $C_6H_2Br_3OAg$: Br, 54.79; Ag, 24.7.
Found: Br, 54.12; Ag, 24.9.

It seemed necessary to confirm Purgotti's work by these analyses in order to establish beyond question that the two salts were isomers.

White Silver Salt of Tribromophenol.—Three methods have been discovered for converting the red salt into the white one. If a dilute solution of the sodium salt is heated to boiling and treated with a fairly dilute solution of silver nitrate, a pale orange precipitate appears at first, which on longer boiling and stirring gradually becomes white. A very slightly reddish specimen prepared in this way was washed thoroughly with water, then quickly with boiling alcohol, dried, and analyzed (I).

The second method consisted in forming the precipitate in very dilute solutions. It gave better results, but like the preceding, yielded in one operation not more than one gram. Moreover, the product in either case was apt to be contaminated with small quantities of the red isomer or of silver oxide. The third method gave a white product, and could be used with large quantities of material. It consisted in dissolving the freshly precipitated, well washed red salt in a little strong ammonia, diluting to about five times its volume to keep the rather insoluble ammonium salt from separating, and then adding dilute sulfuric acid till the solution was only faintly alkaline. A slight white precipitate was formed here, which was dissolved by adding more water, and then a concentrated solution of silver nitrate was added in small portions at a time until a precipitate begins to appear. If this was reddish, an attempt was made to whiten it by stirring it with the solution. If this did not succeed, strong ammonia was added drop by drop until the precipitate had turned white or was dissolved. In the latter case it was diluted again with water, and silver nitrate added, when a white precipitate appeared. After a white precipitate had been obtained, the addition of silver nitrate was continued with constant stirring until the reaction had come to an end. A specimen of salt prepared in this way was washed thoroughly and dried *in vacuo* over phosphoric anhydride for analysis II. The salt prepared in this way showed no trace of the red isomer, even under the microscope.

The methods described above had the disadvantage of starting from the red salt; this was avoided by the following process, which was, therefore, the most convenient, if large amounts were required. A few drops of ammonia added to the sodium salt led to the exclusive formation of the white salt. If sufficient ammonia was present to prevent an immediate red precipitate on the addition of silver nitrate, further slow addition with stirring produced a white precipitate or a reddish precipitate becoming white. If the red color was persistent, not enough ammonia had been added, and a drop or two more was used. The white salt was collected on a plaited filter for washing as it clogged the filter if suction were applied. When washed, it was sucked dry, and finally dried *in vacuo* over calcium chloride.

Calculated for $C_6H_2Br_3OAg$: Br, 54.79; Ag, 24.65.
Found: Br, 54.67, 54.48; Ag, 25.06, 24.66.

Silver Salt of the Monomethyl Ether of Tribromoresorcinol.—The monomethyl ether of resorcinol was made by the method of Tiemann and Parrisius.[1] It showed the boiling point 243–244°, and was then converted into the tribromo derivative as directed by the same authors. On adding silver nitrate to the solution of the sodium salt, prepared as in the case of tribromophenol, a distinctly yellow precipitate fell, which rapidly became white, especially if shaken with the liquid. The tendency to pass over into the white form was so great that we could not isolate the orange modification. The white salt was filtered, washed with distilled water, and dried *in vacuo* over calcium chloride for analysis. The dry salt is almost pure white.

Calculated for $C_6HBr_3(OCH_3)OAg$: Br, 51.27. Found, 51.10.

Silver Salt of Tribromoguaiacol.—Tribromoguaiacol was made by the method of Hill and Jennings.[2] An aqueous solution of the potassium salt was treated with silver nitrate solution, when a copious precipitate fell, yellowish red at first, but rapidly growing redder and more gelatinous, until it became as clear red and transparent as currant jelly. When an attempt was made to filter some of it immediately after precipitation, in this transparent stage the filter paper was clearly visible through the gelatinous mass. The transparent precipitate soon turned white and opaque, but if allowed to stay in the solution, this change was accompanied by a general decomposition, shown by blackening. Many schemes were tried without avail to isolate the red salt.

The white salt was obtained best by the ammonia method used in the case of tribromophenol, avoiding the appearance of the red salt. It was washed with a little very dilute ammonia, which seemed to prevent decomposition, perhaps by dissolving the finer particles, and finally with distilled water. It was dried *in vacuo* and analyzed for bromine.

Calculated for $C_6HBr_3(OCH_3)OAg$: Br, 51.27. Found, 51.22.

A Yellow Potassium Derivative of Tribromoguaiacol.—As it was desired to try to form the red silver salt in another solvent than water, acetone was chosen for this purpose. Some tribromoguaiacol was dissolved in dry acetone, and as potassium hydroxide is almost insoluble in it, a lump of this alkali free from halogen, weighing about a gram, was placed in the test-tube. Its corners had been previously rounded

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[1] *Ber.*, **13**, 2362 (1880).

[2] *Am. Chem. J.*, **15**, 164.

off by water, which had then been washed off with several amounts of dry acetone. No action was apparent at first, but on shaking, the solution became yellow, and yellow flakes were peeled off the lump of caustic potash. The solution was allowed to stand for awhile to allow any potash which might be contained in the flakes to react with the excess of tribromoguaiacol, and then the lump was removed, the flakes of salt filtered off, washed with dry acetone, dried over phosphoric anhydride, *in vacuo*, and analyzed.

	Calculated for		
	$C_6HBr_3(OCH_3)OK$.	$C_6HBr_3(OCH_3)OK.H_2O$.	Found.
Br	60.11	57.52	57.93
K	9.81	9.38	9.15

From these analyses it would appear that the substance contains one molecule of water of crystallization, or is an addition product of potassium hydroxide and tribromoguaiacol. Unfortunately, a direct determination of water could not be made as the compound decomposed very readily on heating. Analyses like these of a substance which could not be purified must be accepted with caution.

The addition of a little water to the yellow acetone solution of the salt or addition product causes an immediate decolorization. Water slowly dissolves the dry compound to a clear colorless solution from which carbon dioxide precipitates the tribromoguaiacol.

A saturated dry acetone solution of silver nitrate gives a red precipitate with the yellow solution of the potassium derivative, but all attempts at isolation of this precipitate, which we suspected to be identical with the red salt obtained in water solution, resulted in failure, owing to the very rapid blackening of the precipitate.

It is the intention of the junior author to pursue the study of this compound, with a view to proving its composition and investigating its constitution, as well as comparing it with the salt prepared in aqueous solution. It is also hoped that it may be found possible to prepare other compounds of like nature.

Silver Salt of Tetrabromoguaiacol.—Tetrabromoguaiacol was made by the method of Jackson and Torrey,[1] and its action tried. On adding the silver nitrate to its potassium salt, an immediate white precipitate was formed, which quickly turned red. The red product had the same appearance as the red silver salt from tribromoguaiacol, and went through the same changes; it became transparent and gelatinous, and then white and opaque, but it decomposed even more readily.

A pure white salt was obtained by the usual ammonia treatment, which could be washed free from silver without decomposition.

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[1] *Proc. Am. Acad.*, 33, 165 (1898).

Mercurous Salts of Phenols.

Mercurous Salt of Tribromophenol.—The sodium salt was precipitated by a slightly acid solution of mercurous nitrate. The yellow precipitate was washed with water till dilute hydrochloric acid gave no reaction for mercurous chloride in the filtrate, then as it contained tribromophenol it was boiled with alcohol, filtered, washed with cold alcohol, and finally with ether. It was dried *in vacuo* and analyzed for bromine. The dry salt was a full yellow.

Calculated for $C_6H_2Br_3OAg$: Br, 45.45. Found, 45.24.

A yellow salt, presumably identical with the one described here was precipitated when the acid mercurous nitrate solution was added to an alcoholic solution of the free phenol.

Mercurous Salt of Triiodophenol.—To a dilute alcoholic solution of triiodophenol, prepared by the method of Körner,[1] was added a slightly acid solution of mercurous nitrate. A very heavy granular orange-yellow precipitate fell immediately, which was filtered off, washed well with alcohol, brought to constant weight *in vacuo* over phosphoric anhydride, and analyzed. The dry salt was a deep orange-red.

Calculated for $C_6H_2I_3OHg$: I, 56.77. Found, 57.80, 57.22.

Mercurous Salt of Tribromoresorcinol. — A slightly acid solution of mercurous nitrate gave a heavy yellow precipitate with a dilute solution of tribromoresorcinol in alcohol. The precipitate was filtered off, washed with alcohol, dried *in vacuo* to constant weight, and analyzed. The dry salt had a full yellow color.

Calculated for $C_6HBr_3(OH)OHg$: Br, 43.94. Found, 43.56.

Under the same conditions, yellow precipitates were obtained from alcoholic solutions of tribromoresorcinol monomethyl ether and tetrabromoguaiacol.

Work on the Constitutions of the Two Salts.

Experiments were tried on the behavior of the two salts with iodine, bromine, chloroformic ester, chloroacetic ester, and acetobromoamide, $CH_3CONHBr$, without our obtaining any definit compounds, or being able to trace any differences in action between the two salts. Treatment with acids, alkalies, or zinc and acetic acid showed no perceptible difference. Acetic acid set free tribromophenol, recognized by its melting point, from each modification.

In trying the result of alkylation, no differences could be detected in the action of the two salts; the interesting observation was made that if undiluted ethyl bromide or diluted alkyl halides were used, the normal ethers appeared, but with dry, undiluted alkyl iodides the silver salts

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[1] *Ann.*, 137, 213.

were converted into amorphous compounds, which will be investigated more fully later. At present, just enough work has been done to show that the same compound was formed by all the iodides used, and that this reaction did not distinguish between the two salts.

Action of Ethyl Bromide.—Undiluted ethyl bromide was poured over the dry, white salt in an Erlenmeyer flask, and allowed to stand three days, with occasional shaking. It gave the known tribromophenetole, melting at 72–73°.

The same experiment on the red salt gave an identical result.

Action of Ethyl Iodide in Alcohol on the Salts.—Purgotti obtained the tribromophenetole from the red salt by ethyl iodide in alcohol.

Some of the white salt was treated with a mixture of one part of ethyl iodide to about two of alcohol. On slight warming, silver iodide formed, which was filtered off after standing three hours. Crystals were found by evaporation, which melted at 69–71.5° without purification. This is obviously the normal ether, tribromophenetole, and the white salt acts like the red.

Undiluted Ethyl Iodide on the Red Salt.—2.8 g. of red silver salt, dried over phosphoric anhydride, were covered with dried, freshly distilled ethyl iodide, in a stoppered flask, and the mixture well shaken during the whole experiment. At first no action could be observed, but after a time the salt appeared to darken, and then became a bright green, whereupon the liquid began to grow blue. When the solution was a bright blue, there was a sudden change in the somewhat voluminous greenish precipitate, which became yellow and curdy, having every appearance of silver iodide. The blue color of the solution immediately began to fade, and after a few minutes had turned to a light yellowish brown. The mixture was then allowed to stand about ten minutes, after which the precipitated silver salt was filtered off, and washed well with dry chloroform, in which the reaction product was known to be soluble. Upon adding 95 per cent. alcohol to the filtrate, a white powdery precipitate was produced which, after drying, commenced to shrink at 260°, and sintered and decomposed between 270° and 290°.

This amorphous precipitate was purified for analysis by repeated solution in chloroform and precipitation by alcohol, as it had been found that evaporation of the solution deposited the substance in the form of a varnish.

One fraction, air-dried only, was analyzed.

0.1535 g. gave 0.2312 g. AgBr = 64.10 per cent. Br.

Another fraction was dried by heating an hour at 100–110°, and standing over phosphoric anhydride.

0.1538 g. gave 0.2315 g. AgBr = 64.05 per cent. Br.

The silver salt from the analysis was shown to contain no iodine.

The filtrates from this compound yielded needles, estimated at less than a decigram in amount, which gave the melting point of the normal ether. It is indeed surprising that such a small percentage of the tribromophenetol should be formed by this reaction.

Action of Undiluted Methyl Iodide on the Red Salt.—Methyl iodide under the same conditions gave an identical action, noticeably slower than with the ethyl iodide. It was allowed to stand two hours, though apparently complete long before this, and was worked up in the same manner. The product was identical in appearance with that from ethyl iodide, and analysis showed it to have the same halogen content:

0.1545 g. gave 0.2323 g. AgBr = 63.98 per cent. Br.

Action of Allyl Iodide on the Red Salt.—The allyl iodide used was freshly distilled and, when used, was nearly colorless. In this case the reaction was very vigorous when started, so the red salt was moistened with a little dry benzene, and after pouring off all that was possible, the allyl iodide was added. The action was apparently identical, but a rather poor yield of the amorphous compound was obtained, possibly on account of the presence of the benzene.

0.0822 g. gave 0.1244 g. AgBr = 64.40 per cent. Br.

Action of Methyl Iodide Undiluted on the White Salt.—The phenomena observed were identical with those with the red salt. The amorphous substance was isolated and analyzed.

0.1564 g. gave 0.2328 g. AgBr = 63.34 per cent Br.

Although this result is over 0.6 per cent. lower than that from the red salt, there is little doubt that the products are the same.

Hantzsch had already shown in his paper that the normal ether was given by both the red and white salts, on treatment with methyl iodide diluted with ether.

Tribromoresorcinol Dimethyl Ether.—This compound, hitherto undescribed, was chosen to try the behavior of diluted methyl iodide on the white silver salt of tribromoresorcinol monomethyl ether. The salt was treated with the mixture of methyl iodide and alcohol on the steam bath with a reflux condenser, till the action apparently ceased.

The filtered solution was then heated again and water added till the precipitate barely dissolved, when cooling gave a powdery precipitate which became crystallin on scratching and stirring. It was recrystallized in the same way from alcohol and water to the constant melting point 68–69°; insoluble in water and alkalies, soluble in alcohol, ether, acetone, benzene, ligroin.

Calculated for $C_6HBr_3(OCH_3)_2$, 63.81. Found, 63.95