THESIS

Some Silver Salts of Brominated Phenols and Naphthols.
The Action of Potassum and Butyl Alcohol on Amines.

by

Charles Fillmore Simpson

Class of Nineteen Hundred and Twenty One

Department of Chemistry

CALIFORNIA INSTITUTE OF TECHNOLOGY
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PART 1

SOME SILVER SALTS OF BROMINATED PHENOLS AND NAPHTHOLS.

Introduction

In 1910 Torry and Hunter while working in the Harvard laboratory discovered that the red silver salt of symmetrical tribrom phenol turned white on standing. Analysis showed the two forms to be isomeric. At the time it was assumed that ammonia in the air of the laboratory had caused the transformation. These two investigators also found two forms of silver salts of 3, 4, 6 tribromguaiacol and 2, 4, 6 tribromresorcinol monomethyl ether. In the two cases, however, the red form was so unstable that it could not be analysed.

Somewhat later Hanzsch[2] confirmed this work and made the silver salts of a large number of halogenated phenols. It has since been shown that Hanzsch's work was not entirely correct. However, Kemp has since shown that two isomeric silver salts of pentabromphenol do exist. Basing their theory on Kemp's work and that previously done by Torry and Hunter, Lucas and Kemp[3] have advanced a new theory of chromoisomerism as follows: 1. As has been shown by recent X-ray work on the structure of crystals, the atoms or atom groups that form in solution, thus the sodium and chloride atoms in sodium chloride, maintain in most crystalline substances their separate identity and still carry the same charge that they do in aqueous solution. It is evident, however, that powerful electrostatic fields which accompany the atoms in the ionized condition will be weaker in the crystalline state; for instead of existing in the solution more or less independently of other atoms each atom is now closely surrounded by atoms carrying charges of opposite sign. The intensity of vibration of the electrons will therefore be less and the frequency of vibration shorter, so that the absorption is displaced toward the violet end of the spectrum and the crystalline substance may become of a paler red or yellow than that of its ions in solution or it may even become colorless. 2. On passing over into the solid state the ions may no longer retain their separate identity; but the atoms or atom groups constituting them may become chemically united, in other words may become as intimately associated as the atoms within the atom groups that constituted the ion in the solution. In this case the electrostatic field would be weakened to a much greater extent than in the former case and the absorption would be still more diminished and further displaced toward the violet end of the spectrum. A solid substance which was still colored while its ions retained their identity in the crystal might become colorless when its ions were more intimately associated.

The work of the writer was done to find if possible other silver salts of brominated phenols of higher molecular weight. It was thought that in the larger molecules the period of vibration would be greater and that if two forms did exist they might both be colored one deeper than the other.

Discussion of Results.

Compounds Investigated.

Tribrombetanaphthol was prepared (According to Smith) and crystallized from benzene. The silver salt was prepared by dissolving in sodium hydroxide and making almost neutral with dilute accetic acid. The sodium salt is quite soluble. The addition of silver nitrate produced the insoluble silver salt. This salt was almost white at first but became almost black on standing, which was probably due to the reduction of silver ion by the organic part of the molecule. There was no evidence of either yellow or pink colors.

Smith calls this compound tetrabrombetanaphthol while Armstrong and Rossiter[5] call it the tribrom derivative. An analysis made of this compound indicates that Armstrong and Rossiter were correct.

2. Pentabrombetanaphthol was prepared and purified by dissolving in sodium hydroxide and then reprecipitating by acidifying with hydrochloric acid. The sodium and potassium salts are white and quite insoluble. The silver salt prepared from the very dilute solution of the potassium salt is also white.

3. Tetrabrom pp' dihydroxy biphenyl was prepared from pp' biphenol. Attempts to prepare a sodium or potassium salt were unsuccessful owing to the formation in alkaline solution of a bluish green amorphous substance which was supposed to be a meriquinone. Sodium carbonate would not dissolve an equivalent amount of the tetrabrom pp' biphenol.

4. Two attempts to replace hydrogen in one hydroxyl group by other groups which would prevent the easy oxidation to a quinone or meriquinone were unsuccessful. The first of these attempts was aimed at the introduction of the group CH_2 CH_2 OH into the compound. It was thought that the presence of the alcoholic hydroxyl group would increase the solubility of the salts. The possibility of forming a disilver salt would also be eliminated. The method used was to add together molecular amounts of the brom derivative, ethylene chlorohydrim and 6 normal sodium hydroxide solution. Only a green amorphous precipitate was produced which was supposed to have been a meriquinone.

The second attempt was to substitute a methyl group for the hydrogen. Tetrabrom pp' dihydroxy biphenyl was heated to 220° with potassium methyl sulfate and sodium hydroxide in a closed bottle for several hours. But after treatment of the product with alkali only unchanged tetrabrom pp' dihydroxy biphenyl was found. Extraction of the reaction product with alkali would not of course give the dimethyl ether of tetrabrom pp' dihydroxy biphenyl which might have been formed.

5. The octobrom derivative of pp' dihydroxy biphenyl was prepared by brominating in liquid bromine with aluminum bromide as a carrier. After crystallizing repeatedly from benzene colorless prisms were obtained which melted at 286-290°. The number of bromine atoms was determined by the method of Carius. This compound is not mentioned in the literature although the corresponding chlor[6] compound has been prepared.

The compound is not very soluble in sodium hydroxide. The silver salt comes down as a light brown precipitate from a slightly alkaline solution and soon becomes almost black due probably to the reduction of the silver ion to metallic silver by the organic part of the molecule.

7. The results of the experiments showed that the brom derivatives of beta naphthol and pp' dihydroxy biphenyl are too unstable to be worked with in the manner that this problem requires. However, it does not seem from what was observed that a red or yellow silver salt is formed by these brominated phenols and naphthols.

The instability of the pp' dihydroxy biphenyl is undoubtedly due to its easy oxidation to a quinone or a meriquinone. A mono hydroxy biphenyl would be more stable but might have other unfavorable characteristics.

It is not plain why the naphthols should be so unstable though naphthols are more reactive than phenols.

Experimental Part.

Smith [4] prepared what he called tetrabrom beta naphthol by dissolving beta naphthol in glacial acetic acid and adding an excess of bromine. The reaction was allowed to proceed for a day. The crystals were then filtered off and washed with a minimum of glacial acetic acid and then crystallized from glacial acetic acid. Acetic acid did not appear to be very satisfactory so benzene was used and after four crystallizations a gray mass of needles was obtained which had a constant melting point of 152-155°. A determination of the bromine confirmed the statement of Armstrong and Rossiter[5].

Determination of Bromine by the Method of Carius.

Wt. of Sample	Wt. of Ag Br.	Found	Percent of Bromine. Calc. from $C_{10} H_5 O Br_3$
.1859	.2772	63.45	62.99

Pentabrom Betanaphthol

Pentabrom betanaphthol was prepared by Flessa[7] by adding the naphthol to sufficient bromine to keep the mass liquid. The bromine was anhydrous and contained about one percent of aluminum bromide which was obtained by adding small pieces of aluminum to the bromine. After allowing to stand for a day the flask was broken open and the excess bromine blown off. No solvents were recommended but turpentine and nitrobenzene recommended for the pentabrom alpha naphthol, were tried, and found rather poor. Chlorbenzene is also unsatisfactory. The compound appeared to decompose at the boiling point of these solvents. The color was now removed by dissolving in dilute sodium hydroxide and reprecipitating with hydrochloric acid. The colorless impure compound melted at 236-260 which is much too high. Flessa[7] gives 237° as the melting point.

The silver salt of this compound was made by adding a dilute silver nitrate solution to a slightly alkaline solution of the sodium salt. The sodium and potassium salts are white and appear crystalline and rather insoluble. The silver salt is white and even more insoluble.

Tetrabrom pp' Dihydroxy Biphenyl.

The tetrabrom compound was obtained by brominating biphenol which was prepared from benzidin. The "technical" benzidin was purified by crystallizing from hot water. The benzidin came down in needles and white glittering plates, melting at 123-124° C. The biphenol was prepared by diazotizing the benzidine and decomposing with steam. The product crystallized from water , melted at 263-264°. It was a light ochre color.

The dry biphenol was dissolved in glacial acetic acid and an excess bromine added. After it has been allowed to stand for a day the precipitated tetrabrom pp' dihydroxy biphenyl was filtered off and dried. It was recrystallized from 95% alcohol. The product melted at 260-265°. It was a bright yellow crystalline mass.

In attempting to make the monomethyl ether of the tetrabrom pp' dihydroxy biphenyl the same general directions were followed as are used in making guaiacol. In this case four grams of this tetrabrom pp' dihydroxy biphenyl was thoroughly mixed with .5 grams of sodium hydroxide and 1.2 grams of, potassium methyl sulfate and was heated up to 220° for three hours in a closed bottle. The mixture was purified by dissolving in sodium hydroxide solution and reprecipitating with an acid. The resulting product washed free of salts proved to be unchanged tetrabrom pp' dihydroxy biphenyl.

Without attempting to obtain the potassium salt by itself .2 grams of tetrabrom pp' dihydroxy biphenyl was treated with one cubic centimeter of ethylene chlorohydrin and .05 grams of potassium hydroxide dissolved in water. The mixture was allowed to stand for a few days and then some of the solution was evaporated under vacuo. A green flocculent precipitate which was supposed to be a meriquinone was formed.

It was noticed that sodium carbonate dissolved the tetrabrom pp' dihydroxy biphenyl , but it was found that one mole would not dissolve in one half mole of sodium carbonate solution to form the mono sodium salt.

Alcoholic potassium hydroxide solution was added to an alcoholic solution of the tetrabrom derivative. After allowing it to stand for a day it was concentrated to a few cubic centimeters. A crystalline substance finally appeared on evaporating almost all of the alcohol. The crystals were filtered off and dried. They showed a tendency to become green due to oxidation. They melted at 262° showing them to be unchanged tetrabrom pp' dihydroxy biphenyl and not the mono potassium salt.

Since the tetrabrom derivative was much more soluble in propyl alcohol than in ethyl alcohol it seemed reasonable to expect a greater solubility in butyl alcohol. .2 grams of this compound dissolved in a minimum amount of butyl alcohol and the exact amount of potassium necessary to form the mono potassium salt in the form of potassium butylate were mixed. Upon heating a green flocculent precipitate appeared. This was too highly colored to work with.

Octobrom pp' dihydroxy Biphenyl.

This compound was prepared by adding the biphenol to a very large excess of bromine containing one percent of aluminum bromide. The aluminum bromide was obtained as in other cases of this nature, i.e., by adding aluminum to anhydrous bromine in small pieces . The flask containing the bromine should stand in cold water. After allowing the flask to stand over night the excess bromine was blown off. It was then crystallized from benzene. After four crystallizations colorless prismatic crystals separated out. The compound was analyzed for bromine by the method of Carius. It proved to be very refractory. Over thirty hours heating at a temperature of about 320° was necessary to entirely decompose the compound, although it appears to be very easily attacked by fuming nitric acid since it turned red after a very brief contact with the fumes.

Determination of Bromine by the Method of Carius.

Wt. of Sample	Wt. of Ag. Br.	% of Bromine Found	Calc. from $C_{12} H_2 O_2 Br_8$
.1319	.2361	76.18[1]	78.22
.1133	.2051	78.55	

The octobrom derivative is slightly soluble in sodium hydroxide solution probably because the sodium salt has only small solubility in water. The addition of silver nitrate to the aqueous solution gives a light brown precipitate rapidly turning black.

[1] Heated for only twenty hours at 300-320°.

Attempt to Prepare 2,3 Dihydroxy Naphthalene.

The contemplated method of making 2,3 dihydroxy naphthalene was to sulfonate beta naphthol with sulphuric acid preferably fuming at 100-110°. The solution was then neutralized with barium carbonate and after filtering off the barium sulphate the solution was evaporated to dryness. The sulfonation produces two isomeric sulfonic acids whose barium salts have different solubilities in cold water. The barium salt of 6,8 naphthalene disulfonic acid was abstracted with cold water while the 3,6 salt remained undissolved. After treating the mixture with successively smaller amounts of water the residue was considered pure and treated with enough water to dissolve the entire amount. The solution was now treated with just enough sodium carbonate to completely precipitate the barium as the carbonate and thus give the sodium salt. After filtering off the barium carbonate the solution was evaporated down to a much smaller volume. The first two crops of crystals that separated were used for the next step. This step consisted of fusing the sodium salt of the 3,6 disulfonic acid with 5-6 parts of sodium hydroxide and a little water at 200-220°C which was supposed to give 2,3 dihydroxy naphthalene 6 sulfonic acid. Friedlander[9] says that the 2,3 dihydroxy 6 sulfonic acid will crystallize out in white shining plates after the fused mass is dissolved in water and almost neutralized. It was found, however, that no crystals (white and shining), separated out when the temperature was only 220°. When the temperature of the fusion was as high as 260° it darkened probably due to charring. After adding water and acid white plates did separate from this darkened mass. But at the lower temperatures the compound was always colored and amorphous. The next step consisted of heating the sodium salt of the dihydroxy naphthalene 6 sulfonic acid in a tube to 180-190° with dilute sulfuric acid which should give the 2,3 dihydroxy naphthalene but this step was never attempted. The failure to get better results in the first two steps may have been due to not working with large amounts.

SUMMARY

1. The silver salt of tribrom beta naphthol was found to be white and to become black on standing.
2. The silver salt of pentabrom beta naphthol was found to be white.
3. An attempt to prepare the monomethyl ether of tetrabrom pp' dihydroxy biphenyl was unsuccessful.
4. The attempt to substitute the group CH_2 CH_2 OH for the hydrogen in one hydroxyl radical was also unsuccessful owing to the formation of a green amorphous substance.
5. Octobrom pp' dihydroxy biphenyl was prepared and the bromine determined.
6. The silver salt of octobrom pp' dihydroxy biphenyl came down as a light brown precipitate rapidly turning black.
7. The preparation of 2,3 dihydroxy naphthalene from beta naphthol was started but never finished.

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PART 11.

The Action of Potassium and Butyl Alcohol On Amines.

Introduction.

The common method of obtaining a qualitative test for nitrogen in organic compounds is to allow a small quantity of the substance under examination to fall on fused sodium. The product is dissolved in water and then treated with sodium hydroxide, ferrous sulfate and ferric chloride. The formation of Prussian blue indicates the presence of nitrogen.

It was thought that amines might be reduced by hydrogen formed by the action of potassium on butyl alcohol. If this could be done it might be applicable to several different classes of nitrogen compound such as nitro and nitroso compounds, amids and perhaps substituted amines. Nitriles, azo and hydrazo compounds and other classes of nitrogen compounds will probably act similarly.

Nessler's[1] reagent seemed to be the proper reagent to detect the presence of small amounts of ammonia. No mention of the action of amines on Nessler's reagent was found when these experiments were started but after considerable work had been done an abstract[2] was found which gave some valuable information. "All amines react with Nessler's reagent to form complex compounds. Some particularly the higher insoluble amines and cyclic amines react only in Nascent condition when solutions of their salts are added to the reagent. Of the primary amines only methyl amine and propyl amine give colored compounds, of secondary amines diphenyl amine, while tertiary amines do not give colored compounds. All these compounds are insoluble in water but dissolve in potassium iodide with the exception of the isobutylamine compound."

DISCUSSION OF RESULTS.

The alkyl amines alone give a very large precipitate immediately with Nessler's reagent while the aromatic amines do not except on long standing. With potassium and butyl alcohol a different result is obtained.

In the case of aniline two procedures were followed. In one the reaction mixture was treated directly with Nessler's reagent while in the other the reaction mixture was heated to boiling for two minutes and then to the distillate Nessler's reagent was added. In the latter case where the reagent was added to the distillate a very small red crystalline precipitate appeared after several hours. This precipitate was entirely different from the one obtained by adding Nessler's reagent directly to the reaction product which was a yellow flocculent precipitate. Even the use of larger amounts of butyl alcohol and potassium never increased the amount of the precipitate thus showing that the reduction to ammonia was very slight if any. When Nessler's reagent was added to the portion which had not been distilled a large flocculent yellow precipitate was formed.

A large number of amines were investigated and it was found that in the case of methyl aniline, dimethylaniline, ethylaniline, diethyaniline, para toluidine, diphenylamine, nitroso dimethylaniline, methyl benzylaniline, alpha naphthylamine and ortho, meta, and para nitroaniline, the reaction products from treatment with potassium and butyl alcohol all gave precipitates though some only small amounts. If Nessler's reagent is added to the butyl alcohol solution of these nitrogen compounds only a slight cloudiness appears. However, in the case of aniline, if to the butyl alcohol solution of the amine, some sodium hydroxide is added then the addition of a few drops of Nessler's reagent gives a heavy yellow precipitate similar to the precipitate obtained after treatment of the amine with potassium and butyl alcohol.

This seemed to indicate that the presence of an excess of alkali is a necessary condition for the formation of a precipitate with Nessler's reagent. With sodium hydroxide present other compounds which gave only a slight cloudiness in the absence of excess alkali formed good precipitates with the reagent. For instance nitrobenzene gave a red precipitate and azobenzene a yellow cloudiness when concentrated sodium hydroxide was added.

Since most of the blanks were run without excess of alkali present comparison between these results and the results obtained from tests with potassium have but little significance. From these experiments it appeared that the treatment of amines, nitro compounds and azo compounds with potassium and butyl alcohol and Nessler's reagent could hardly be used as a test for nitrogen in these forms. The test was especially unreliable because of the slight difference which exists between the cloudiness which is always present with butyl alcohol, water and Nessler's reagent, and the precipitate which such compounds as nitrobenzaldehyde and alpha naphthylamine produce with the same reagents.

It was found that Shiff's reagent gave a positive test for aldehydes when a small amount was added to a little butyl alcohol. A drop of formaldehyde gave a slight pale precipitate with Nessler's reagent with no excess alkali which resembled the precipitate formed when Nessler's reagent was added to butyl alcohol alone and also to the alcoholic solution of a nitrogen compound. It is probable that the pale cloudiness was produced by the butyl aldehyde which the Shiff's reagent showed was present.

EXPERIMENTAL PART.

In testing ammonia or amines with Nessler's reagent one drop of liquid or .05-.1 gram of solid was added to .5-1.cc of butyl alcohol and a piece of potassium (a cube 3 mm on a side) was then added. Upon the completion of the reaction 6-7cc of water was added and then a few drops of Nessler's reagent. The precipitate appeared in the aqueous layer.

When the vapors were driven out of the aniline reaction product by heat they were passed through rubber tubes to the water in which they were to be dissolved. After heating for about two minutes the connecting tubes were washed out and a few drops of Nessler's reagent added to both the wash water and the water into which the ammonia was supposed to pass.

COMPOUND	PRECIPITATE WITH POTASSIUM & BUTYL ALC. & NESSLER'S REG.	PRECIPITATE WITH BUTYL ALC. & NESSLER'S.REG	PRECIPITATE WITH BUTYL ALC NAOH & NESSLER
ANilene	Large Yellow ppt.	Slightly cloudy	Large Yellow
Methylaniline	" " "	" "	
Di " "	Slight " "	" "	
Ethyl "	Small " "	" "	
Di " "	" " "	" "	
P Toluidine	Moderate" "	" "	
Diphenylamine	Very slight " "	" "	
Nitrosodimethylaniline	Moderate Yel."	" "	
Methylbenzylanil.	Slight "	" "	
P Nitraniline	Moderate " "	" "	
Alpha Naphthylamine.	Slight cloudiness[1]	" "	Light Yellow
Benzylaniline	Slight Yellow ppt.	" "	
O Nitraniline	Light Orange ppt.	" "	
M "	Moderate Yellow ppt.	" "	
P "	" " "	" "	
Beta Naphthylamine	Cloudy solution	" "	
Phthalimide	" "	" "	
Nitrophenol	Slight ppt.	" "	
Nitrobenzene	Very slight ppt.	" "	Moderate ppt.
Di "	" " ppt.[1]	" "	
P Nitranisol	" " "	" "	
O Nitrobenzaldehyde	" " "	" "	
P "	" " "	" "	
Benzonitrile	" " "	" "	Very slight[1]
Azobenzene	" " "	" "	" "[1]
Nitrophenylhydrazine	Slight cloudiness	" "	None

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[1] Precipitates appeared after half hour .

Precipitates appeared within 10 minutes or less ordinarily.

An aqueous solution of methylamine hydrochloride gave a large red precipitate with no excess of alkali.

SUMMARY

1. An attempt to reduce aniline to ammonia with butyl alcohol and potassium was only slightly successful.
2. It was found that Nessler's reagent reacted with nitrogen compound ~~only~~ under the following conditions:-
    - a. Alkylamines alone.
    - b. Simple aromatic amines and some substituted amines even as high as diethylaniline in the presence of a large amount of alkali and butyl alcohol.
    - c. Nitro compounds in the presence of butyl alcohol and excess alkali.
    - d. Azo compounds and nitriles upon treatment with potassium and butyl alcohol.

BIBLIOGRAPHY.

1. Potassium mercuric iodide .5 normal in K_2 Hg I_4 by dissolving 115 grams Hg I_2 and 80 grams KI in enough water to make the volume 500 cc; add 500 cc 6 normal Na OH; decant the solution from any precipitate that may form on standing.

2. Chem. Abs. 1-2355.
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