

A STUDY
OF THE
PREPARATION OF THIOBENZOIC ACID
BY NEW METHODS

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Introduction:

Thiolbenzoic acid (C_6H_5COSH) has long been known, but little work has been done on it since 1910. The amount of work done before that time does not seem adequate when we consider the significance of a simple method of preparing this acid. Such a method would prove to be the basis for numerous researches on substituted thiolbenzoic acids and their derivatives. The purpose of this paper is to describe efforts toward production of thiolbenzoic acid by new methods.

Historical:

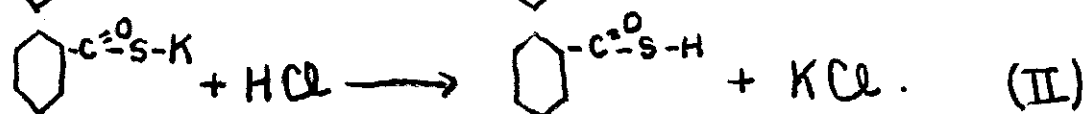
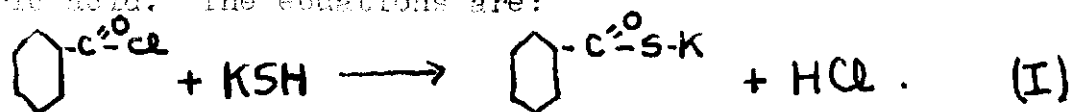
Thiolbenzoic acid (1) has usually been prepared by action of benzoyl chloride on alcoholic potassium hydrosulphide. This method of Kym has been regarded as the best method of obtaining the potassium salt. The free acid may be obtained by dissolving this salt in water and adding dilute hydrochloric acid.

Other methods of preparation are: by the action of benzoyl chloride on an alcoholic solution of potassium sulfide (2); by the action of carbon oxysulfide on phenyl magnesium bromide in ether (3); by shaking a solution of benzoyl chloride in water-alcoholic potash with sulfur (4); by boiling benzoic acid-phenyl ester or benzoic anhydride with alcoholic potassium hydrosulfide (5); by the action of benzoyl disulfide on al-

coholic potassium hydrosulfide (6); by the action of a water solution of potash on a boiling alcoholic solution of benzoyl disulfide (7); by dissolving benzoyl disulfide in an alcoholic solution of potassium hydrosulfide (8); on the addition of ammonia to a solution of dibenzoyl disulfide in chloroform (9).

Experimental:

For purposes of comparison thiolbenzoic acid was prepared by the method of Kym (1). An alcoholic solution of potassium hydrosulfide was made by passing hydrogen sulfide gas in excess through a cold alcoholic solution of 20 grams of potassium hydroxide. To this solution 20 grams of benzoyl chloride were added, the precipitated potassium chloride filtered off and the filtrate evaporated to dryness on a water bath. The crude potassium thiolbenzoate, 25 grams, was dissolved in the least possible amount of water and the free acid precipitated by the addition of (3 N) hydrochloric acid. The equations are:



The thiolbenzoic acid comes down as a yellow oil which solidifies in the cold and melts at 24°. One troublesome thing about this method is the ready oxid-

ation of the acid to benzoyl disulfide, as shown by the following equation (10):

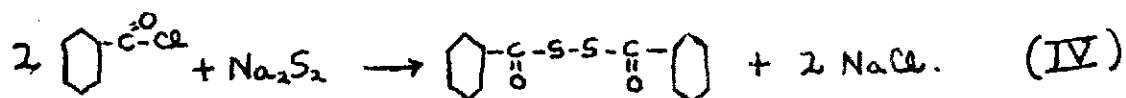


For this reason it should be kept out of contact with air as far as possible. This method is not entirely satisfactory as a means of preparing thiolbenzoic acid. Sodium salts should be used instead of potassium. An objection to the use of the alcohol is the formation of more or less ethyl benzoate.

The reduction of benzoyl disulfide:

Since benzoyl disulfide has been prepared by a simple method (10) the reduction of this substance was suggested as a possible means of preparing thiolbenzoic acid. A quantity of benzoyl disulfide was prepared according to the method of Mitchell (10). 240 grams of crystalline sodium sulfide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) were dissolved in 140 grams of water, 32 grams of finely powdered rhombic sulfur added, and the mixture warmed until all was dissolved. The resulting reddish solution was sodium disulfide (Na_2S_2). The solution was kept at a temperature of 30° while 260 grams of freshly distilled benzoyl chloride were added, with intense mechanical stirring. The crude benzoyl disulfide separated out at once (10). The equation for this preparation is as

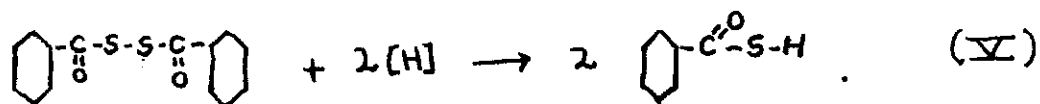
follows:



The purity of the substance was increased by filtration and washing with aqueous (3 N) sodium hydroxide. The benzoyl disulfide so prepared was used in subsequent attempts at reduction to thiolbenzoic acid.

Several acid reducing mixtures were tried, namely: iron turnings and dilute acetic acid; iron turnings and dilute sulfuric acid; granulated zinc and dilute acetic acid; granulated zinc and dilute sulfuric acid; tin and dilute acetic acid; tin and dilute sulfuric acid.

The sample of benzoyl disulfide was placed in a flask fitted up for steam distillation, and the reducing mixture to be studied added. Steam was then blown through the mixture. Thiolbenzoic acid, being volatile in steam, passed over. The yellow, oily drops of the acid were extracted by dissolving in ether. The water portion of the distillate was then shaken with ether to remove any small traces of the thiol acid. The ether was then evaporated, the thiolbenzoic acid weighed and the yield calculated. The equation for this reduction is as follows:



With all acid reducing mixtures tried the yield was disappointingly small. Several runs were made using the aforementioned combinations of acids and metals. Iron and dilute sulfuric acid gave an average yield of about 10 per cent. Zinc and dilute sulfuric acid gave a slightly smaller yield, 9 per cent being the average. The same metals with dilute acetic acid yielded about 3 per cent less than with dilute sulfuric acid. Tin, with both acids, gave only traces of thiolbenzoic acid. Results are given in the following table:

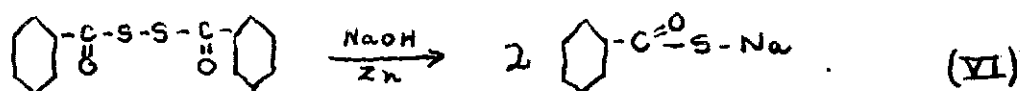
<u>Acid reducing mixture</u>	<u>B. disulfide (grams)</u>	<u>Thiol acid^u (grams)</u>	<u>Per cent yield</u>
Fe+HAc	5	0.38	7.6
Fe+H ₂ SO ₄	5	0.52	10.4
Zn+HAc	5	0.32	6.4
Zn+H ₂ SO ₄	5	0.47	9.4
Sn+HAc	5	traces	
Sn+H ₂ SO ₄	5	traces	

^uThe figures in the third column represent the average yield for five runs.

From the yields obtained it is readily seen that this method of preparation of thiolbenzoic acid is not satisfactory.

Reduction of the benzoyl disulfide in alkaline solution was tried. With such a reducing mixture the

thiolbenzoic acid would remain as a salt. Hence the disulphide and the alkaline reducing mixture were boiled in a flask with a return condenser. When the disulfide dissolved the solution was filtered and acidified. The alkaline reducing agents used were zinc and caustic soda, and arsenious acid with excess of strong caustic soda. The reaction was expected to take place in this manner:

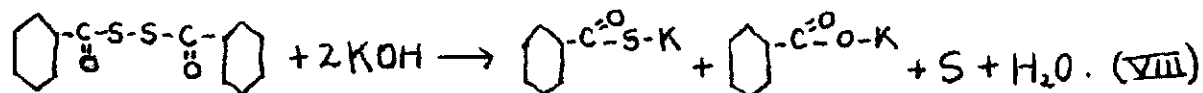


Acidification of the sodium thiolbenzoate would give the free acid. As shown by the equation:



The results of these investigations were disappointing. The addition of hydrochloric acid gave, instead of the expected thiolbenzoic acid, a bulky, flocculent, precipitate of benzoic acid. Traces of thiolbenzoic acid were noticed but the greater bulk of the precipitate was benzoic acid. Varying the concentration of the hydrochloric acid added did not affect results to any noticeable extent. More than a dozen runs were made using sodium hydroxide and zinc dust as the reducing materials and in no case was an appreciable amount of thiolbenzoic acid formed.

Upon acidification traces of sulfur were found in the mixture and some hydrogen sulfide was evolved. The following reaction is recorded in the literature (11):



According to this reaction only one half of the disulfide molecule would be converted into sodium thiolbenzoate if 100 per cent yield were secured. Actual results, however, showed that the greater part of the final product was benzoic acid, a reaction difficult to explain. It was first thought that sodium thiolbenzoate was formed, and when hydrochloric acid was added the following reaction took place:



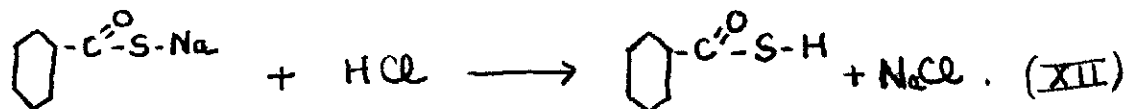
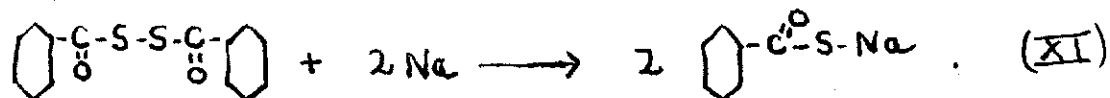
Later results showed that a water solution of sodium thiolbenzoate does give the thiol acid when hydrochloric acid is added. The obvious conclusion would seem to be that sodium thiolbenzoate is not formed in any quantity, but that sodium benzoate is formed instead. After repeated trials this method was abandoned as a means of preparing thiolbenzoic acid.

The next method tried was suggested by the work of Moses and Reid (12) on the action of sodium on alkyl disulfides. They found that sodium would, in

some cases, react with alkyl disulfides in the following manner:



It was thought advisable to study the effect of sodium on an alcoholic solution of benzoyl disulfide. Absolute alcohol, sodium and benzoyl disulfide were shaken together in a small flask. The solution turned reddish-brown in color; this change evidently being due to the formation of sodium thiolbenzoate which is soluble in alcohol. This solution was then evaporated to dryness, the red-brown residue dissolved in the least possible amount of water and acidified with hydrochloric acid. Thiolbenzoic acid was formed at once. The reactions are:



To get some idea of the yield of thiolbenzoic acid runs were made using approximately four grams of benzoyl disulfide in 100 cc. of absolute alcohol with addition of sodium until the color of the solution remained unchanged. The results are shown below:

No.	<u>B. disulfide (grams)</u>	<u>Thiol acid (grams)</u>	<u>% yield</u>
1	4.0162	2.9062	72
2	4.0067	2.2257	56
3	4.0082	2.5076	58
4	4.0059	2.2396	56
5	4.0085	2.2180	55

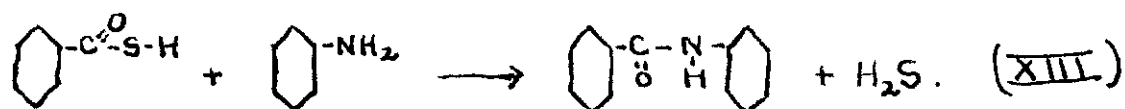
In the last four runs shown in the table the yield of thiol acid was approximately 56%. The first yield of 72% seemed to be an exception and was not considered in calculating the average yield.

To prove that the substance prepared by this method, and by the reduction of benzoyl disulfide in acid solution, was thiolbenzoic acid it was compared with the thiol acid obtained by the method of Kym (1). All properties were identical. The true molecular weight of thiolbenzoic acid is 138.11. The molecular weight of the suspected thiol acid was obtained by the freezing point lowering method using m-dinitrobenzene as the solvent. The resulting weight, 136.1 checked the true weight within the limits of experimental error. The substance was oxidized and benzoyl disulfide was formed.

The equation for this reaction has been given as number (III).

The disulfide so obtained was identified by its melting point and properties. The thiol acid was found to be

very soluble in alcohol and ether, and relatively insoluble in water. It was readily volatile in steam. The odor was very characteristic and exceptionally unpleasant. After purification the melting point of the product checked exactly the M. P. of 24° given in the literature for thiolbenzoic acid. Wheeler (13) found that when thiolbenzoic acid was treated in the cold with aniline, benzanilide was obtained quantitatively and hydrogen sulfide evolved according to the following equation:



Identical results were secured with the thiolbenzoic acid prepared from benzoyl disulfide.

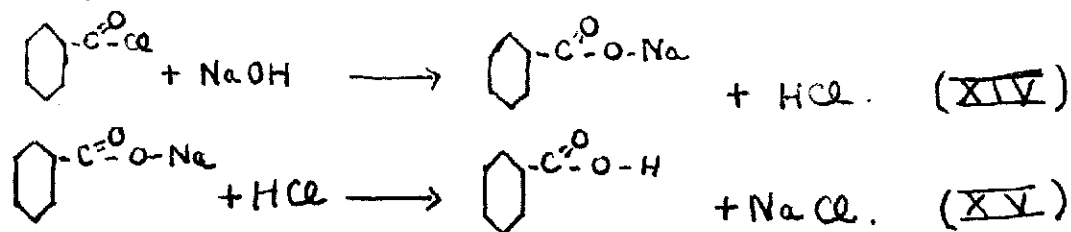
The action of sodium sulfide on benzoyl chloride:

Since thiolbenzoic acid has been prepared by acidification of a water solution of sodium thiolbenzoate, and since we have been told that benzoyl chloride hydrolyzes only slightly with cold water, it seemed reasonable to expect a good yield of sodium thiolbenzoate when a water solution of sodium sulfide reacted with the proper amount of benzoyl chloride. If this reaction would take place we would have a direct method for preparation of thiolbenzoic acid, since acidification of the sodium salt gives the free acid.

This reaction has been carried out by Mitchell (10), who found that acidification of the supposed sodium thioibenzoate solution gave only traces of the expected thiol acid and large quantities of benzoic acid. The same reaction was carried out and results identical with those of Mitchell were secured. 35 grams of sodium sulfide were dissolved in 70 cc. of water and 14 grams of benzoyl chloride added, with intense mechanical stirring. When this reaction was complete acidification of the resulting solution gave benzoic acid in large quantities along with traces of thiolbenzoic acid. This reaction was repeated several times with the hope of obtaining some explanation for the unexpected results. The temperature was kept low in each case since benzoyl chloride hydrolyzes readily in hot water. The reaction proceeded very slowly since there was little contact surface. The benzoyl chloride formed oily drops in the mixture hence exposing only the surface of these drops to the sodium sulfide solution.

Because the reaction occurred slowly and was rapidly stirred, it was thought that more and more benzoyl chloride was hydrolyzed as the contact surface was increased by breaking up the drops of the acid chloride. Since the solution was alkaline the final product of the reaction would be sodium benzoate, the acidifica-

tion of which would give benzoic acid. The reactions would be:



An alcohol solution of benzoyl chloride and sodium sulfide reacts readily to form sodium thiolbenzoate. The alcohol is objectionable in that it forms more or less ethyl benzoate with the benzoyl chloride.

A search was made for a solvent that would dissolve both sodium sulfide and benzoyl chloride, but would not react with them. It was believed that such a solvent would cause the reaction to take place as desired and would prove the factor necessary to make this reaction a good method for the preparation of thiolbenzoic acid. A water-acetone mixture was found to give the desired results.

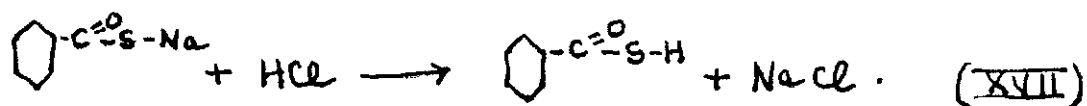
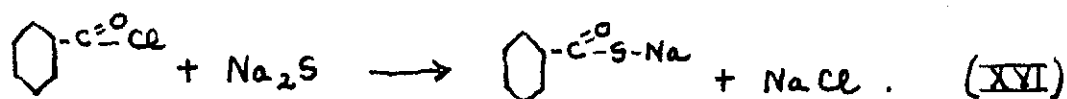
35 grams of sodium sulfide were dissolved in the least possible amount of a water-acetone solution (4 volumes acetone to 3 volumes of water) and 14 grams of benzoyl chloride added. The solution turned brown at once and acidification gave thiolbenzoic acid. This acid is soluble in acetone but was thrown out of solution as water was added. The yield of thiol acid was quite satisfactory as results given below would indi-

cate:

No.	B. Chloride (grams)	Thiol acid (grams)	% yield
1	14	11.213	81
2	14	12.197	89
3	14	12.321	89
4	14	12.246	89
5	140	140.	95

Since excess sodium sulfide was used the first action with acid was the liberation of hydrogen sulfide gas.

Equations are as follows:



Conclusions:

- (1) Thiolbenzoic acid has been prepared by the reduction of benzoyl disulfide with acid reducing mixtures. The yield of thiol acid (10%) was very small.
- (2) No appreciable amount of thiolbenzoic acid was formed in the reaction between zinc, caustic soda, and benzoyl disulfide. Similar results were obtained using arsenious acid with caustic soda as the alkaline reducing medium.
- (3) Sodium thiolbenzoate has been prepared by the action of sodium on an alcoholic solution of benzoyl disulfide. Acidification of this salt gave the free acid.

The yield was 56%.

(4) The sodium salt of thiolbenzoic acid has been prepared in a simple and direct manner by the action of a water-acetone solution of sodium sulfide with benzoyl chloride. The yield of the free acid by this method varied from 89 to 95%.

Suggestions for further work:

Two of the procedures outlined in this paper have proven good methods for the preparation of thiolbenzoic acid. The last named is superior in that it is simple and has given good yields of the acid. It was planned to carry out a number of reactions of the acid but lack of time forced its postponement.

It is suggested that the esters of thiolbenzoic acid be prepared either from the potassium salt or the silver salt. The silver salt should be particularly useful for making esters from the higher alkyl halides from C₁₀ on up.

Another experiment to try would be the coupling of phenyl diazonium chloride with the thiolbenzoic acid. The product should be phenyl thiolbenzoate which is a crystal solid melting at 56°. The hydrolysis of this would give thiophenol, which is rather difficult to prepare otherwise. If this should work well with good yields we would have a good method of preparation which

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should be applicable to substituted thiophenols, many of which are difficult to obtain.

REFERENCES

- 1 - Kym, Berichte, 32, 3533 (1899), footnote.
- 2 - Engelhardt, Latschinoff and Malyscheff, Zeitschrift für Chemie (1868), 355.
- 3 - Weigert, Berichte, 36, 1010 (1903).
- 4 - Fromm, de Seixas Palma, Berichte, 39, 3324 (1906).
- 5 - Engelhardt, Latschinoff and Malyscheff, *ibid.*, 354.
- 6 - Engelhardt, Latschinoff and Malyscheff, *ibid.*, 357.
- 7 - Fromm and Schmoldt, Berichte, 40, 2863 (1907).
- 8 - Engelhardt, Latschinoff, and Malyscheff, *ibid.*, 359.
- 9 - Busch and Stern, Berichte, 29, 2150 (1896).
- 10 - Mitchell, (Unpublished Thesis) Georgia School of Tech, 1932.
- 11 - Fromm and Schmoldt, Berichte, 40, 2861 (1907).
- 12 - Moses and Reid, J. A. C. S., 48, 776 (1926).
- 13 - Wheeler, J. A. C. S., 23, 443 (1901).