

A STUDY OF SOME SALTS AND ESTERS
OF TRIOLBENZOIC ACID

A THESIS

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FOREWORD

Thiolbenzoic acid and its derivatives present certain interesting problems upon which little work has been done since 1910. The work done prior to that time was not extensive, and some of the work done earlier than 1870 has not been checked.

The purpose of this work is to check some of that previously reported, to develop methods of preparation of certain salts and esters of thiolbenzoic acid, and to study their properties.

THIOLBENZOIC ACID

Historical:

Thiolbenzoic acid has been prepared by a variety of methods, the most important of which have been summarized by Calaway (1). The most convenient method at the present time is Calaway's modification of a method first suggested by Engelhardt, Latschinoff, and Malyschieff (2). The latter investigators prepared the acid by the addition of benzoyl chloride to an alcoholic solution of potassium sulfide with subsequent acidification.

Since the ethyl alcohol would tend to form more or less ethyl benzoate, Calaway suggested that a mixture of water and acetone consisting of three volumes of the former and four volumes of the latter be used as the solvent. The purpose of the acetone was to decrease the rate of hydrolysis of the benzoyl chloride.

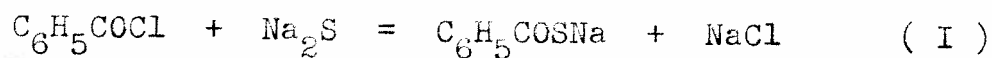
Calaway recommended that thirty-five grams of hydrated sodium sulfide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) be dissolved in the smallest possible amount of the water-acetone mixture, fourteen grams of benzoyl chloride added, the solution acidified, and the acid precipitated by the addition of water.

Experimental:

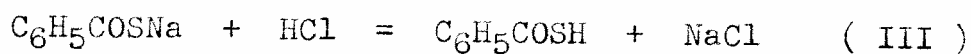
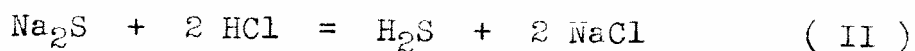
Thiolbenzoic acid was prepared by Calaway's method, both

- (1) Calaway, (Unpublished Thesis), Georgia School of Technology, 1933.
- (2) Engelhardt, Latschinoff, and Malyschieff, *Zeitschrift fur Chemie*, 1863, pp. 353-9.

in the cold and at room temperature, the yield in both cases comparing favorably with that reported by him (slightly above 90%). Since the amount of solvent required was rather large, several runs were made in which the thirty-five grams of sodium sulfide were dissolved in 150 cc. of water, and 200 cc. of acetone added. On standing, two phases separated, but by maintaining vigorous agitation the separation was prevented. Upon the addition of benzoyl chloride the reaction progressed smoothly, according to the following equation:

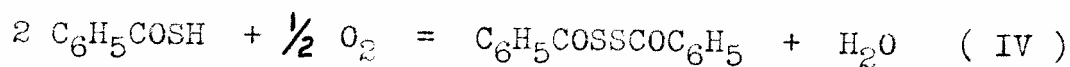


Upon acidification with hydrochloric acid, the two reactions which took place were the liberation of hydrogen sulfide from the excess sodium sulfide, and the liberation of the acid, thus:



Upon dilution of the water-acetone solution of thiolbenzoic acid with water, the acid separated. However, the formation of a colloidal solution often prevents complete separation even after several days.

Long standing often causes a loss of thiolbenzoic acid through its oxidation to benzoyl disulfide by atmospheric oxygen, thus:



To avoid this loss, the solution was allowed to stand for a

short time, the acid layer separated, and the water layer extracted with ether. The separated acid was dissolved in ether and the ether solutions were washed several times with water to remove HCl, H₂S, any traces of benzoic acid, and any other water soluble impurities. The ethereal solutions were then extracted with just less than the equivalent amount of sodium hydroxide solution, the aqueous solution evaporated, and the yield obtained as the more stable sodium salt. The yield was approximately ninety percent of the theoretical, the same as that reported by Calaway.

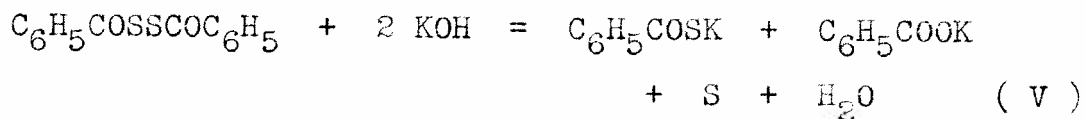
As has been reported (3), the sodium thiolbenzoate formed upon evaporation of its aqueous solution is reddish in color. However, the red color is removed by washing repeatedly with ether, leaving the salt a very light yellow.

A small amount of benzoyl disulfide was formed in every case when the precipitated acid was allowed to stand. This was purified by recrystallization from ether, which gave a white solid melting to a red liquid between 128.0° and 128.5°. The melting point previously reported was 128°. None of the light yellow color reported by Mitchell (3) was noticed in the purified disulfide. Indeed, upon slow evaporation of a carbon disulfide solution of benzoyl disulfide, large perfectly colorless hexagonal crystals were formed.

Purification of the benzoyl disulfide by heating with aqueous sodium hydroxide was also attempted, but the disulfide

(3) Mitchell, (Unpublished Thesis), Georgia School of Technology, 1932.

itself dissolved slowly. A large amount of sodium benzoate and smaller amounts of sodium thiolbenzoate and free sulfur were formed. Hydrogen sulfide was liberated upon acidification. The following equation is given in the literature (4):



In this reaction, however, the disulfide was in alcoholic solution, and Mulliken (5) states that aqueous alkali will not react with benzoyl disulfide if the latter is not in alcoholic solution. After consideration of the amounts and identity of the products obtained, it is evident that equation (V) does not accurately express the true course of the reaction in aqueous solution.

In every batch of thiolbenzoic acid prepared by the method of Calaway, there appeared a red color which remained in the ether after the alkali extraction. There seemed to be more of this red by-product formed when the temperature was not kept low and when the benzoyl chloride was added rapidly. In an attempt to identify the red material, the ether was evaporated, leaving a red oil and a solid which proved to be benzoyl disulfide. The red oil was subjected to distillation under reduced pressure, and a constant boiling fraction obtained. When extracted with alkali, thiolbenzoic acid was obtained, indicating that this constant boiling fraction was a mixture. Benzoic

(4) Fromm and Schmoldt, *Berichte*, 40, 2861, (1907).

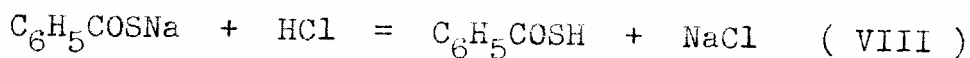
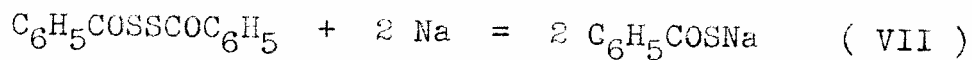
(5) Mulliken, *Identification of Pure Organic Compounds*, John Wiley and Sons, Vol. IV, page 110.

acid and a sulfide were also present in the lower fractions of the distillate. Benzoyl disulfide crystallized out of the thiolbenzoic acid fraction on standing, formed probably by the oxidation of the thiolbenzoic acid. More benzoic acid and thiolbenzoic acid were formed when the distillate was redistilled after the alkali extraction.

Another method used by Calaway (1) for the preparation of thiolbenzoic acid was suggested by the work of Moses and Reid (7) on the action of metallic sodium on alkyl disulfides. They found that in certain cases sodium would react with the disulfides in an inert solvent in the following manner:



Calaway prepared sodium thiolbenzoate by adding sodium to benzoyl disulfide in absolute alcohol until no further change in color occurred. The acid was obtained in 56% yield upon acidification. The equations are:



It was thought that a more complete conversion would be obtained if an inert solvent was used instead of the absolute alcohol used by Calaway. Accordingly, toluene dried over sodium was used as the solvent. A preliminary run was made using 33% excess benzoyl disulfide, but since subsequent runs with only 15% excess disulfide gave almost identical yields, the latter is recommended.

(7) Moses and Reid, J.A.C.S., 48, 776, (1926).

The most satisfactory method used was the addition of two grams of sodium to 24.7 grams (0.1 mol) of benzoyl disulfide in 150 cc. of dry toluene. The mixture was then heated to the boiling point of toluene (111°) and maintained at that temperature until reaction was complete. The solid was separated at the pump, the sodium thiolbenzoate dissolved in water, the excess disulfide filtered, and the aqueous solution evaporated. The yield of the dry yellow sodium salt was as follows:

<u>Run</u>	<u>Grams sodium</u>	<u>Grams salt</u>	<u>Theoretical</u>	<u>% yield</u>
1	1.3	7.3	9.0	81.1
2	2.0	11.0	13.9	79.1
3	2.0	11.2	13.9	80.6

As a means of preparing thiolbenzoic acid, the reaction between sodium and benzoyl disulfide is less convenient, less efficient, and more expensive than the method previously discussed.

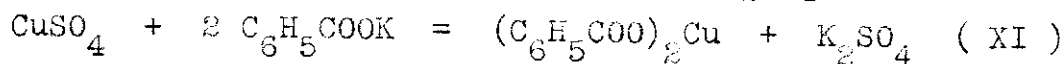
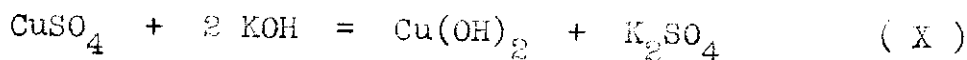
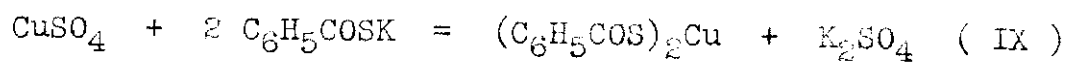
SALTS OF THIOLBENZOIC ACID

Historical:

Engelhardt, Latschinoff, and Malyschieff (2) reported that a water solution of the potassium salt of thiolbenzoic acid gave a greenish yellow precipitate with cupric sulfate. Upon standing for a time, this precipitate became a bright red, and benzoyl disulfide was obtained by extracting with carbon disulfide. In a private communication Dr. E. Emmet Reid suggested that by analogy to copper xanthate the final product might be cuprous thiolbenzoate.

Experimental:

In order to determine the identity of the precipitate, it was prepared by addition of aqueous cupric sulfate to a solution of the potassium thiolbenzoate purified as previously discussed. The precipitate so formed was yellow with no trace of green, but a greenish yellow precipitate had been previously obtained when a less carefully purified sample of potassium thiolbenzoate was used. The greenish color was probably caused by the formation of cupric hydroxide or cupric benzoate, both of which are blue and insoluble. The blue precipitate formed from the free alkali or from a salt of benzoic acid would impart a greenish tinge to the yellow precipitate of cupric thiolbenzoate. The equations for the three possible reactions are as follows:



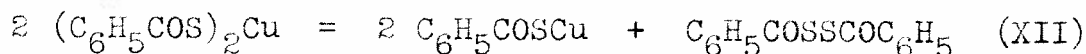
Samples of cupric thiolbenzoate prepared from the sodium and potassium salts of thiolbenzoic acid of varying degrees of purity were allowed to stand for several days. The color change was invariably from yellow to orange. In no case was a bright red color formed as reported by Engelhardt and his coworkers.

When the purest sample of cupric thiolbenzoate seemed to have completed its color change from yellow to orange, it was filtered, dried, and the benzoyl disulfide extracted with carbon disulfide. Portions of the residue were then dissolved in nitric acid and analyzed for copper content by electrolysis.

Calculated: $\text{C}_6\text{H}_5\text{COSCu}$ - 31.70% Cu; $(\text{C}_6\text{H}_5\text{COS})_2\text{Cu}$ - 18.84% Cu.

Found: 31.11% Cu, 31.08% Cu.

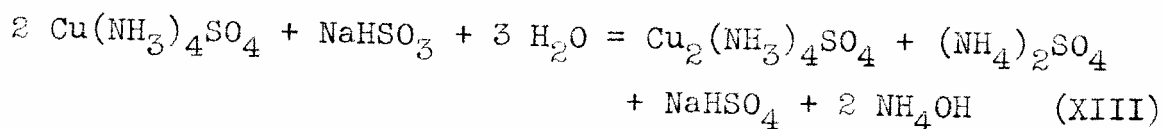
The average of the two runs was approximately 0.6% lower than that calculated for cuprous thiolbenzoate, but was close enough to prove that cupric thiolbenzoate changes spontaneously to cuprous thiolbenzoate:



After long standing, the orange cuprous thiolbenzoate darkened slowly, finally forming a very dark brown solid.

For purposes of comparison cuprous thiolbenzoate was prepared. In order to do so, cupric sulfate was reduced to cuprous sulfate by means of sodium bisulfite. Mellor (6) states that an ammoniacal solution is necessary for the reduction to take place. The equation for the reaction is then:

(6) Mellor, Comprehensive Treatise on Inorganic and Theoretical Chemistry, Longmans and Co., Vol. III, page 232.



Upon addition of varying amounts of the pink cuprous solution to one gram of potassium thiolbenzoate in aqueous solution, precipitates were formed of a slightly lighter yellow color than that formed by the addition of cupric sulfate. As in the case of the cupric thiolbenzoate, the yellow color changed to a bright orange on standing, with the difference that much less time was required for the change to be complete. The run in which the largest amount of the cuprous solution was used underwent the most rapid color change, turning orange almost immediately. In this case the color changed to a very dark brown before filtration could be completed, in spite of the use of a "Hy-Vac" pump. The slowest color change was complete in less than half an hour, whereas the color change of the cupric thiolbenzoate required several hours. All the runs were filtered and allowed to stand under water for several days, during which time all darkened. They were then filtered and analyzed for copper by electrolysis. The dark brown solid, by very rough analysis, gave 67.6% and 68.9% copper, checking fairly closely with 66.5%, the value calculated for cupric sulfide. One of the samples which had darkened only slightly gave results of 34.9% and 34.6% copper, not much higher than the value calculated for cuprous thiolbenzoate, which is 31.7%.

Another sample of cuprous thiolbenzoate was prepared using only a small amount of the cuprous solution, filtered as rapidly as possible using a "Hy-Vac" pump, dried, and analyzed.

Calculated: C_6H_5COSCu - 31.7% Cu. Found: 30.4%, 30.7% Cu.

The low value of the copper content was perhaps due to insufficient time for the complete change from yellow to orange to take place. If the yellow material could be shown to contain a lower percentage of copper than cuprous thiolbenzoate the discrepancy might be explained. It was hoped that the yellow compound could be analyzed, but its rapid change to the orange material prevented.

Salts of various other metals were added to solutions of potassium thiolbenzoate to determine if peculiarities similar to those above were exhibited by any other salts of thiolbenzoic acid. The following ions were added and the precipitates allowed to stand under the solutions from which they were precipitated:

Ferrous and Ferric; The former gave no precipitate upon addition, whereas the latter gave a deep wine red coagulating to a very dark red. Both subsequently formed additional light brown precipitates on standing.

Mercurous and Mercuric; The former gave a gray precipitate, and the latter a white one, both turning black on standing.

Stannous and Stannic; The former gave a yellow precipitate and the latter a white one. On standing, the former turns slowly to a deep brown, and the latter takes on a slight yellow hue.

Barium, Calcium, and Magnesium; No precipitate was given immediately, but on standing a sparse yellow-white precipitate developed in each case.

Lead, Antimony, and Cadmium; All three gave white flocculent precipitates. On standing, the first took on a creamy

tinge, the second developed a slight yellow color, and the third became a bright canary yellow at the surface, and turned black on the side exposed to the light.

Aluminum, Arsenic, and Chromic; A faint cloudiness formed in each case, settling slowly, the first two to yellow precipitates, and the third to a green-white precipitate.

Zinc; Formed a white precipitate composed of silky platelets, resembling those formed by benzoic acid.

Bismuth; Formed a pale yellow granular precipitate.

Nickel; Formed a deep orange color on addition, deepening in color and coagulating to a deep red precipitate.

Several of the precipitates mentioned above showed a tendency to undergo a color change upon standing, but none exhibited as rapid or as complete a color change as did the cupric salt. Accordingly, it was not thought advisable to investigate them more thoroughly.

It was thought that the silver salt of thiolbenzoic acid could be used in the preparation of esters, but such a reaction would probably have to be performed in the absence of light, as silver thiolbenzoate is very sensitive to light. This salt seems to darken even more rapidly than silver chloride when exposed to light while wet.

ESTERS OF THIOLBENZOIC ACID

Historical:

Esters of thiolbenzoic acid have been prepared by a variety of methods. Engelhardt, Latschinoff, and Malyschieff (2) reported that Tuttschieff had prepared the ethyl ester by the action of benzoyl chloride on lead ethyl mercaptide, $\text{Pb}(\text{SC}_2\text{H}_5)_2$. The same workers prepared isoamyl thiolbenzoate from benzoyl chloride and isoamyl mercaptan, the yield being quantitative. Esters of thiol acids in general have been prepared by the action of magnesium bromo mercaptide, RSMgBr , on the acid chloride or anhydride (8), and this method was used by Hepworth and Clapham (9) in preparing ethyl thiolbenzoate. The most convenient method, however, is that used by Wheeler (10), which is the well known reaction between the sodium salt of the acid and an alkyl halide:



Experimental:

The known ethyl and isoamyl esters of thiolbenzoic acid were prepared with a double purpose: firstly, to determine if the esters could be made in good yield using aqueous solutions of the salt, avoiding the evaporation of the solution to obtain the dry salt; secondly, to check the boiling point of the former, concerning which there have been conflicting reports.

- (8) Taboury, Ann. Chim. Phys., 15, 5-66.
- (9) Hepworth and Clapham, J.C.S., 119, 1188-98, (1921).
- (10) Wheeler, Am. Chem. J., 24, 69, (1900).

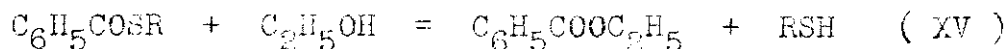
In an attempt to prepare the ethyl ester, eighty grams of sodium thiolbenzoate (33% excess) in aqueous solution were refluxed with forty-one grams of ethyl bromide. The layers were separated, and the non-aqueous layer dried and distilled three times at thirty-one millimeters pressure. A final fraction was obtained, boiling at 142.5°-144.5° (corr.) at the above pressure. The boiling point of ethyl thiolbenzoate is recorded in the literature as 146° at the pressure mentioned. The final product weighed 9.0 grams, a yield of only 14.5%! The ester was redistilled at 740 mm. pressure, with a boiling point of 243°-245°, uncorrected, being raised to 246°-248° when corrected for emergent stem. The boiling points recorded in the literature are: 241°-243° (2); 243° (11); and 252°-253° (10). The latter value seems to have been quite a careful determination, an Anschütz thermometer having been used which was probably much more accurate than the uncalibrated instrument used in this case. In an endeavor to obtain a better check, the thermometer was checked against a calibrated Anschütz thermometer at ten degree intervals in the range 240°-280°. At a thermometer reading of 240° the correction was +7.4°. A micro boiling point was then taken on the ester according to the method described by Shriner and Fuson (12), using the calibrated thermometer. The uncorrected boiling point was 243.5°-244.5°, which was raised by the correction factor 7.4° to 251°-252°, checking Wheeler's value fairly closely.

(11) Seifert, J. Prakt. Chem., (2), 31, 471.

(12) Shriner and Fuson, Identification of Organic Compounds, John Wiley and Sons, page 54.

The isoamyl ester was made by refluxing thirty-two grams of sodium thiobenzate in water solution with 22.5 grams of isoamyl bromide for one and one-half hours. The ester layer was separated, dried, and distilled twice at thirty mm. pressure, with a definite fraction at 177-9° (corr.). A micro boiling point was taken as above, giving a value of 278-4°, uncorrected, and 281-2° after the 8.2° correction was made. Engelhardt, Latschinoff, and Malyschiew (2) reported a boiling point of 271° for the isoamyl ester. The fact that their boiling points for the ethyl and isoamyl esters were both some ten degrees low suggests that the stem correction was neglected. It will be noticed that in each case their value is within two degrees of the uncorrected value recorded here.

Since the yields were very poor when a water solution of the salt was used in the preparation of the ester, it was decided to use a solvent which would dissolve both the salt and the alkyl halide. Such a solvent is ethyl alcohol, but in this case there is danger of re-esterification of the thiol ester by the ethyl alcohol as shown:



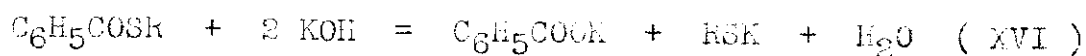
In order to determine if the re-esterification would take place, thirty grams of allyl bromide and fifty-three grams of the sodium salt were placed in five hundred cc. of alcohol and refluxed for twelve hours. After refluxing, the alcohol was distilled off from the water bath. When the separation of solid began to cause bumping, ether was added, the solid fil-

tered, the distillation continued, and the process repeated until all the solid was removed. The ether was distilled, and the residual liquid distilled twice at seven mm., with a fraction at 120.5°-121.5°, weighing 20.6 grams, a 46.5% yield. The ester was redistilled at 15.5 mm. pressure, practically all distilling between 136.5° and 137.0°, giving a product with a very light yellow color. Upon heating, preparatory to taking a micro boiling point, the color began darkening at 120°, deepened to orange at the boiling point, and continued deepening as that temperature was maintained. The uncorrected boiling point was 260.5°-261.5°, which was raised to 268.5°-269.5° when the 7.8° correction was applied.

The boiling point shows that this compound could not possibly be either ethyl benzoate formed as in equation (XV), allyl benzoate, or ethyl thiolbenzoate, as the boiling points of these three compounds are respectively 211-2°, 250°, and 251-2°. Unsaturation was shown by the ready decolorization of bromine water and potassium permanganate solution. A strong qualitative test for sulfur was obtained. The fact that the boiling point is some sixteen degrees higher than that for the ethyl ester adds to the evidence that it is the allyl ester of thiolbenzoic acid, as in many cases (benzoate, cinnamate, isovalerate, butyrate, etc.) the allyl ester boils some twenty degrees higher than the corresponding ethyl ester, the difference in boiling points being less in the case of esters of aromatic acids. The analysis of this compound for carbon and hydrogen content was attempted, using the semi-micro combustion chain

described by Fieser (13), a simple modified procedure using ordinary analytical balances being used. For some reason, possibly an error in procedure, four combustions failed to give satisfactory results. No two runs checked, and no run checked the calculated value.

In another attempt to prove the identity of this compound, a small sample of it was refluxed for several hours with 25% potassium hydroxide solution:



However, the hydrolysis was only partially completed, the reaction being quite slow. Upon acidification, extraction with ether, and evaporation of the ether, a white solid and a small amount of a yellow liquid were left. The former was identified as benzoic acid. In order to separate the liquid from the benzoic acid, both were dissolved in a small excess of potassium hydroxide solution and the liquid distilled. Mulliken (14) states that under these conditions the potassium mercaptide hydrolyzes and the mercaptan distills. The distillate had the odor of garlic, and gave a white flaky precipitate upon addition of mercuric chloride. The amount of the precipitate was too small to allow recrystallization, and could not be identified as $\text{CH}_2=\text{CHCH}_2\text{SHgCl}$ which should begin to decompose at 100° . However, the separation of the mercaptan from the benzoic acid seemed to be incomplete, as the residue from the alkali distillation retained a yellow color.

(13) Fieser, Experiments in Organic Chemistry, page 350.

(14) Mulliken, *ibid.*, page 17.

In spite of the failure to prove definitely that the ester is allyl thiolbenzoate, there seems to be little reason to doubt its identity, as it was shown to be an ester containing sulfur, at least one point of unsaturation, and a benzene nucleus. The boiling point eliminated allyl benzoate, ethyl benzoate, and ethyl thiolbenzoate as possibilities, leaving allyl thiolbenzoate as the only remaining possibility.

In order to determine if a thiol ester could be formed by the reaction of a salt of thiolbenzoic acid upon an alkyl halide using no solvent, 16.6 grams of potassium thiolbenzoate and 16.7 grams of benzyl chloride were refluxed for five hours at the boiling point of benzyl chloride (179°). The mixture was allowed to cool, ether added, and the solid filtered. No potassium thiolbenzoate remained in the reaction mixture, as no precipitate was formed upon adding cupric acetate to a water solution of the residual solid. When the ether was distilled, and distillation of the residual oil attempted under reduced pressure, difficulty was encountered because of the excessive ease with which the lowest fraction solidified in the apparatus, causing clogging. The apparatus was simplified and the material distilled rapidly enough to prevent solidification, all being caught in one receiver. Three fractions were noticed, the lowest being an almost white solid, the second an orange liquid, and the highest being a very small amount of a heavy red oil, solidifying in the tube as it distilled.

The solid from the red oil was recrystallized from ether, giving very pale yellow needles, melting at 182.0° - 182.5° (uncorr.).

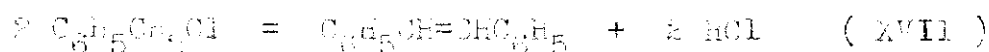
This was probably tetraphenyl thiophene (thionessal), which is reported as melting at 184°. Fromm and Schmoldt (4) reported that thionessal was formed by the dry distillation of sodium thiolbenzoate. The same effect as in the dry distillation of the salt could very easily have been obtained to a small extent, as the volume of the benzyl chloride was insufficient to keep the whole bulk of the potassium thiolbenzoate moistened.

The fraction containing the white solid was separated by distilling at a somewhat higher pressure, as the boiling point is further removed from the freezing point by an increase in pressure. The remainder of the mixture was then distilled at a pressure of five mm., and an orange colored fraction obtained which distilled between 183° and 186° at this pressure.

The white solid was recrystallized several times from ether, but in each case the product had a wide melting range. Redistillation did not improve the product. However, when petroleum ether was used as the recrystallizing solvent, a white compound crystallized in glistening needles, leaving benzoic acid in the solvent. After three recrystallizations from petroleum ether, this compound melted sharply at 99.5°, with no change on further recrystallization. A determination of the boiling point by the micro method gave a value of approximately 257° after applying the correction. It was shown qualitatively that the compound contained neither halogen nor sulfur.

After the compound melting at 99.5° stood for some time, its melting point was no longer sharp, but ranged up to 115°. Sodium hydroxide then extracted benzoic acid from the solid,

leaving a white residue melting at 124°. This was thought to be stilbene (M.P. 124°), formed thus:



The bromine addition compound, however, instead of melting at 237°, gave a wide decomposition range, beginning around 200°, and melting between 225° and 229°. Possibly further purification might have raised the melting point to 237°, but the amounts of the materials on hand were insufficient.

The orange fraction (boiling at 183-6° at 5 mm.) solidified completely when placed in a freezing mixture (ice and conc. HCl), and melted at 30-32°. Ether does not serve well as the recrystallizing solvent for this compound, but petroleum ether will serve if the freezing mixture is also used. Five or six recrystallizations were necessary to remove the pink color which was visible after the first crystallization, the compound then melting sharply at 33°. The presence of sulfur was known qualitatively, and the compound was shown to be the benzyl ester of thiobenzic acid by analysis for carbon and hydrogen in the combustion chain.

Calculated for $\text{C}_{14}\text{H}_{12}\text{SO}$: 5.3% H; 73.7% C.

Found: 5.0% H; 73.3% C.

No percentage yield was calculated because of the incompleteness of the separation and purification, but the yield of the ester seemed to be not more than 10%. It is evident, therefore, that a solvent is essential if the ester is to be obtained in good yield, free from by-products.

CONCLUSIONS

- (I) The sodium salt of thiolbenzoic acid has been prepared from benzoyl disulfide in improved yield (eighty percent), by the action of metallic sodium in dry toluene.
- (II) It has been shown, both by analysis and by comparison to cuprous thiolbenzoate prepared directly, that cupric thiolbenzoate is converted spontaneously into cuprous thiolbenzoate upon standing, forming also benzoyl disulfide.
- (III) Eighteen other metallic ions were added to solutions of potassium thiolbenzoate in an effort to obtain another salt which undergoes a change similar to that exhibited by cupric thiolbenzoate. None were found which underwent nearly as rapid or as complete changes.
- (IV) The known ethyl and isoamyl esters of thiolbenzoic acid were prepared. The boiling point of the ethyl ester checked with that reported by Wheeler. The boiling point of the isoamyl ester did not check with that reported by Engelnarat, Latschinoff, and Malyschieff.
- (V) The allyl and benzyl esters of thiolbenzoic acid were prepared.
- (VI) It was shown that in the reaction between sodium thiolbenzoate and alkyl halides a poor yield is obtained if no solvent is used, that a slightly better (though still less than 15%) yield is obtained if water is used as the solvent, and that a still better (about 45%) yield is obtained if ethyl alcohol is the solvent.