[Contribution from the Goodyear Tire and Rubber Company]

RESEARCHES ON MERCAPTOTHIAZOLES. I

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Introduction

Since the discovery of 2-mercaptobenzothiazole by Hofmann,[1] who prepared this compound from *o*-amidothiophenol and carbon disulfide, further research on this compound and its possible derivatives was desirable when its value as an accelerator of rubber vulcanization was discovered.

The synthesis of 2-mercaptobenzothiazole from aniline, sulfur and carbon disulfide[2] not only offered a commercial preparation but made it possible to prepare several derivatives, using a substituted aniline according to the same method. This method, however, is limited in its application, as only six substituted 2-mercaptobenzothiazoles could be prepared. Another disadvantage is the necessity of carrying out the reaction in a closed system whereby pressures as high as 1000 lbs. per sq. in. (7.03×10^5 g./sq. cm.) were obtained.

For laboratory use it seemed very desirable to develop a simple method of preparing 2-mercaptobenzothiazole which could be extended to several new derivatives. The present paper outlines a method of preparing 2-mercaptobenzothiazole in one step from *o*-nitrochlorobenzol, a comparatively cheap material. The method is capable of extension to the preparation of other derivatives such as the halogen, amido and carboxyl derivatives from the corresponding *o*-nitrochlorobenzol derivatives. It has been shown by Blanksma[3] that *o*-nitrochlorobenzol reacts easily with sodium disulfide to give dinitrodiphenyl disulfide.

Bogert and Snell[4] have developed a method for the reduction of this disulfide using zinc and acetic acid, resulting in the formation of the zinc salt of *o*-amidothiophenol, from which Bogert and his co-workers have prepared a large number of phenylbenzothiazoles. From the zinc salt of *o*-amidothiophenol the diaminodiphenyl disulfide was obtained by passing air through its ammonia solution. The best yield obtained by Bogert and by ourselves is approximately 65–75%; the isolation of the pure material is tedious and the loss through crystallization large.

It has been found that the alkaline hydrosulfides are efficient reducing agents for dinitrodiphenyl disulfide, giving a good yield of the corresponding diamino compound.

Several examples are described in the literature whereby alkali hydro-

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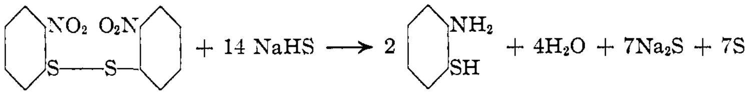
[1] Hofmann, *Ber.*, **20**, 1788 (1887).

[2] Sebrell and Boord, This Journal, **45**, 2396 (1923).

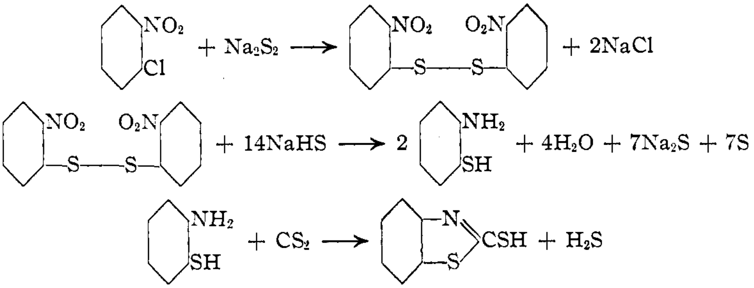
[3] Blanksma, *Rec. trav. chim.*, **20**, 121 (1901).

[4] Bogert and Snell, This Journal, **46**, 1308 (1924).

sulfides are used for the reduction of the nitro compounds to the corresponding amino compounds[5] and usually the reaction can be accomplished in water solution when the final product is soluble in alkali. In our case the reduction scheme is represented by the following reaction.



Instead of alkali hydrosulfides, sodium hydrosulfite, $Na_2S_2O_4$, can be used, either alone in alcohol, or in water solution in the presence of alkali. The third step in the preparation of 2-mercaptobenzothiazole from *o*-nitrochlorobenzol is the interaction of carbon disulfide with *o*-aminothiophenol. Hofmann obtained it by refluxing *o*-aminophenyl mercaptan with carbon disulfide for 12–14 hours. No data about yields are given, so that the reaction was carried out for the same length of time with *o*-diaminodiphenyl disulfide, giving a low yield of 2-mercaptobenzothiazole. Considering the three reaction schemes by which 2-mercaptobenzothiazole is formed from *o*-nitrochlorobenzol,



it occurred to us that these reactions could be accomplished in one step.

It is known that sodium sulfide solutions absorb carbon disulfide, forming trithiocarbonates, which decompose on heating,[6]

$$CS_2 + Na_2S \rightleftharpoons Na_2CS_2 \qquad (1)$$

so we may assume that also in the case of sodium hydrosulfide we have the reaction,

$$NaHS + CS_2 \rightleftharpoons NaHCS_3 \qquad (2)$$

and as sodium sulfide is always present in a sodium hydrosulfide solution, Reactions 1 and 2 must take place simultaneously.

This shows that carbon disulfide is converted into a water-soluble trithiocarbonate, which will give carbon disulfide in the nascent and more reactive form.

Another factor that facilitates the formation of 2-mercaptobenzothiazole from diaminodiphenyl disulfide is the use of hydrogen sulfide for the formation of sodium hydrosulfide from sodium sulfide throughout the re-

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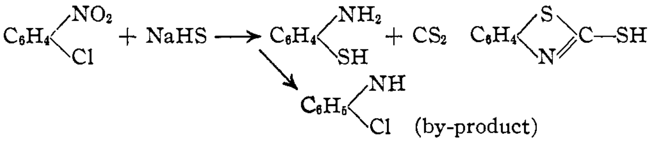
[5] Teppema, *Rec. trav. chim.*, **42**, 40 (1923).

[6] Victor Meyer and Jacobson, *Org. Chem.*, I (2), 1367.

action, whereby the free *o*-amino thiophenol will be present instead of the corresponding disulfide. Experiments confirmed this theory.

It was also possible to combine Reaction 1 with 2 and 3. Blanksma[3,7] and Wohlfahrt[8] state that by the action of sodium disulfide on *o*-nitrochlorobenzol, some *o*-chloro-aniline is formed, and the best yield of dinitrodiphenyl disulfide obtained by ourselves did not exceed 75%. Several modifications in the reactions either cut down or did not affect the yield of final product. To eliminate the loss caused by the reducing action of sodium disulfide on an alcoholic solution of *o*-nitrochlorobenzol, the three reactions were carried out in one step from *o*-nitrochlorobenzol, sodium hydrosulfide and carbon disulfide. The result was an 87.5% yield of 2-mercaptobenzothiazole, based on the *o*-nitrochlorobenzol used; m. p. of the crude material, 173–174°. One crystallization from alcohol gave needles; m. p., 177–178°. The combined reactions may be represented as follows.



As already mentioned, substituted 1-chloro-2-nitrobenzol compounds can be used as starting material. The yields are best for the halogen derivatives. The nine following substituted 2-mercaptobenzothiazoles were prepared according to the method described: 5-chloro-2-mercaptobenzothiazole, 5-bromo-2-mercaptobenzothiazole, 2-mercaptobenzothiazole-5-sulfonic acid (sodium salt), 5-amido-2-mercaptobenzothiazole, 7-methyl-2-mercaptobenzothiazole, 5-methyl-2-mercaptobenzothiazole, 2-mercaptobenzothiazole-5-carboxylic acid, 2-mercaptobenzothiazole-4-carboxylic acid and 2-mercapto-5-oxybenzothiazole.

The combined reaction could not be applied in all cases, as will be shown in the Experimental Part.

Attempts to prepare dichloro-substituted 2-mercaptobenzothiazoles from the corresponding nitrotrichlorobenzols failed and the constitution of the resulting compounds is still in doubt.

The melting points given in this work are all uncorrected. However, they were all made with the same thermometer under identical conditions.

Experimental Part

(a) **Alkali Hydrosulfide Reduction. 2-2'-Diaminodiphenyl Disulfide (Reaction 2).**—A mixture of 5 g. of 2,2'-dinitrodiphenyl disulfide, 150 cc. of water and 30 cc. of concd. aqueous ammonia was saturated with hydrogen sulfide and then heated under reflux for two hours. To the solution was added another 30 cc. of concd. aqueous ammonia and it was again saturated with hydrogen sulfide. After refluxing for two

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[7] Blanksma, *Rec. trav. chim.*, **28**, 108 (1909).

[8] Wohlfahrt, *J. prakt. Chem.*, [2] **66**, 553 (1902).

hours more, the solution was acidified with hydrochloric acid and evaporated on a steam-bath until all of the sulfur had coagulated and a clear solution was obtained. The solution was filtered hot and the residue washed with hot water. The filtrate contains the reduction product, mostly in the form of the hydrochloride of the mercaptan. To oxidize this to the disulfide, two methods were applied.

(1) The acid solution was neutralized by a sodium carbonate solution and air was drawn through the solution to oxidize the free mercaptan to the disulfide.

(2) An alcoholic solution of iodine was added to the acid solution until the iodine color remained. The solution was filtered and the filtrate neutralized with sodium carbonate. The yield of the first product of the diamido compound was 3.9 g.; m. p., 75–80°. Redissolving in hydrochloric acid solution, boiling with charcoal and reprecipitating with sodium carbonate gave 3.4 g.; m. p., 80°. According to the literature, the melting point of the *o*-diaminodiphenyl disulfide is 93°. As another purification of the obtained product by redissolving in hydrochloric acid and reprecipitating with sodium carbonate did not raise the melting point, a sulfur analysis was made.

Anal. Calcd. for $C_{12}H_{12}N_2S_2$: S, 26.68. Found: 25.81.

Once recrystallized from dilute alcohol the melting point was 87°. Twenty-five g. of crude product gave 20 g. by recrystallization from dilute alcohol.

Instead of ammonium hydrosulfide, sodium hydrosulfide could be used. With the same procedure, 10 g. of *o*-dinitrodiphenyl disulfide gave 7.6 g. of *o*-diaminodiphenyl disulfide. This product was redissolved in hydrochloric acid, charcoal added, and the solution refluxed for two hours. Reprecipitation gave 7.2 g. of *o*-diamidodiphenyl disulfide; m. p., 80–85°. Recrystallization from dilute alcohol gave 5.5 g. of 2,2′-diamidodiphenyl disulfide; m. p., 87°.

(b) **Reduction with Sodium Hydrosulfite.**—A mixture of 10 g. of *o*-dinitrodiphenyl disulfide and 150 cc. of alcohol was boiled under reflux, and to the hot solution 50 g. of sodium hydrosulfite was added in portions, through the condenser. At each addition 5–10 cc. of water was added; total addition time, one hour; total added water, 100 cc. After two hours' more heating the solution was filtered and the residue (inorganic salts) washed with hot alcohol. The filtrate was acidified and evaporated until dry. The residue was treated with hydrochloric acid and filtered hot. A small amount of tar remained on the filter. The filtrate was rather dark colored and was boiled with charcoal for two hours. After filtering and cooling, the solution was neutralized with sodium carbonate; first product, 8 g.; m. p., 70–75°. Once reprecipitated 7 g. was obtained. Five g. of *o*-diamidodiphenyl disulfide was obtained by recrystallization from dilute alcohol; m. p., 87°.

The reduction of the *o*-dinitrodiphenyl disulfide could also be accomplished by sodium hydrosulfite in water solution if a small amount of alkali was added to increase the solubility of the final product. The melting points given for the *o*-diamidodiphenyl disulfide, that is, 87°, are lower than those usually given for this compound. However, material of this purity was entirely suitable for use in other reactions described later in this paper. Small samples on further recrystallization showed a melting point of 92–93°, but the loss on crystallization is high.[4]

Reaction of *o*-Diamidodiphenyl Disulfide and Carbon Disulfide (Reaction 3).—Five g. of *o*-diamidodiphenyl disulfide, m. p. 87°, and 30 cc. of carbon disulfide were refluxed for 15 hours and carbon disulfide was evaporated on the water-bath. The residue was acidified with hydrochloric acid and filtered hot.

Neutralization with sodium carbonate gave 3 g. of unchanged *o*-diamidodiphenyl disulfide. The residue on the filter was heated with hot, dilute, aqueous ammonia and filtered. A small amount of black tar (sulfur) was left. Filtrate treated with hydrochloric acid gave 2 g. of mercaptobenzothiazole; yield, 32%.

Reduction with Ammonium Hydrosulfide with Carbon Disulfide Present.—A mixture of 5 g. of *o*-dinitrodiphenyl disulfide, 200 cc. of water and 30 cc. of concd. aqueous ammonia was saturated with hydrogen sulfide previously passed through a wash bottle containing water and carbon sulfide. The solution was boiled under reflux at the same time for two hours. After this, the heating was stopped, 30 cc. of concd. aqueous ammonia was added and hydrogen sulfide again bubbled through until the mixture had cooled to room temperature. The mixture was then refluxed again for two hours.

The dark red solution was acidified and evaporated until the sulfur had coagulated and a clear solution was obtained. The white precipitate was filtered and extracted twice with hot aqueous ammonia. Precipitation with hydrochloric acid gave 5.2 g. of mercaptobenzothiazole; m. p., 176°; yield, 96%. The residue on the filter proved to be pure sulfur; m. p., 118°.

Reduction with Sodium Hydrosulfide in the Presence of Carbon Disulfide.—The procedure followed was the same as in the case of ammonium hydrosulfide. Twenty-five g. of sodium sulfide was used instead of ammonia. The advantage of this method lies in the fact that sodium sulfide is regenerated from the sodium hydrosulfide, while in the case of ammonium hydrosulfide the ammonia escapes, forming crystals of ammonium hydrosulfide in the condenser. The yield of mercaptobenzothiazole was identical with the yield obtained above.

In the case of the sodium hydrosulfite reduction the two reactions could not be combined in water solution. Addition of carbon disulfide to the alcoholic solution with sodium hydrosulfite gave a very small amount of mercaptobenzothiazole after a long time of heating. This fact led to the assumption that the easy way in which carbon disulfide reacts in the sodium hydrosulfide reduction method must be explained by the formation of a water-soluble carbon disulfide compound, which decomposes on heating to give carbon disulfide in the nascent state. This assumption is verified by the following experiments.

(a) Five g. of *o*-diamidodiphenyl disulfide and 30 cc. of carbon disulfide were refluxed for 6.5 hrs. The excess of carbon disulfide was evaporated and the residue treated with hot dil. hydrochloric acid to extract unchanged *o*-diamidodiphenyl disulfide. The residue, a mixture of mercaptobenzothiazole and sulfur, was extracted with hot dil. aqueous ammonia and the extract precipitated with hydrochloric acid; yield, 0.5 g.

(b) Five g. of *o*-diamidodiphenyl disulfide, 50 cc. of water and 9 g. of $Na_2S.9H_2O$ were saturated with hydrogen sulfide, the latter previously having been passed through a wash bottle containing water and carbon disulfide. After 6.5 hours' reaction, the solution was cooled and acidified with hydrochloric acid, evaporated until the sulfur had coagulated completely, and filtered hot.

The filtrate did not give a precipitate with sodium carbonate solution, an indication that no unchanged *o*-diamidodiphenyl disulfide remained. The residue on the filter was extracted with hot, dilute, aqueous ammonia and precipitated with hydrochloric acid. Six and one-tenth g. of mercaptobenzothiazole was obtained; yield, 98%.

The difference between Expts. (a) and (b) is that in Expt. (b) both carbon disulfide and *o*-amidothiophenol are formed in the nascent state. In

Expt. (a) the free *o*-aminothiophenol is probably formed as an intermediate product.

After a further study it did not appear that the above experiments were sufficiently conclusive since in Expt. a the disulfide must undergo reduction to the free mercaptan before it can react with carbon disulfide.

To prove further the validity of the previous conclusions the following experiments were carried out.

(c) Five g. of *o*-aminothiophenol was refluxed with 25 cc. of carbon disulfide for six hours. After this the cardon disulfide was evaporated and the residual liquid treated with dil. hydrochloric acid. No residue remained after heating on a water-bath.

It seems, therefore, that *o*-aminothiophenol as such reacts very slowly with carbon disulfide. Hofmann claims that 2-mercaptobenzothiazole is formed after 24 hours' refluxing but does not mention the yield obtained.

(d) Five g. of *o*-aminothiophenol and 2 g. of sodium hydroxide were mixed with 50 cc. of water. Carbon dioxide, which had been saturated with carbon disulfide, was bubbled through the mixture, which was then refluxed for six hours. Acidification gave 6 g. of 2-mercaptobenzothiazole (98%). These experiments show that either *o*-aminothiophenol or carbon disulfide in the nascent state causes a complete reaction within reasonable time.

We are thus unable to say definitely that the success of our new method for making 2-mercaptobenzothiazole is entirely dependent upon the formation of nascent carbon disulfide from sodium trithiocarbonate. However, it may be equally dependent upon the presence of nascent *o*-aminothiophenol formed by the action of hydrogen sulfide on the sodium salt.

Combination Reactions 1, 2 and 3.—A solution of 250 g. of $Na_2S.8H_2O$ in 1 liter of water was saturated with hydrogen sulfide, the latter previously having been passed through a wash bottle containing water and carbon disulfide. After complete saturation, 100 g. of *o*-nitrochlorobenzol was added and the mixture refluxed for 20 hours on a sand-bath, while hydrogen sulfide saturated with carbon disulfide was bubbled through the solution. It is essential that in the beginning of the reaction the mixture be not heated too strongly. After the reaction was complete, a dark red solution was obtained. The reaction mixture was steam-distilled and the steam distillate extracted with ether. The ether solution was dried over anhydrous potassium carbonate and gave 8.5 g. of *o*-chloro-aniline; b. p., 207°. If the reaction were not carried out to completion, the *o*-chloro-aniline was mixed with unchanged *o*-chloronitrobenzene. These could be separated by extracting the *o*-chloronitrobenzene from the acid-water mixture. The residual water solution was made alkaline and again ether-extracted.

The alkaline residue of the steam distillation was acidified with hydrochloric acid and evaporated until all of the sulfur had coagulated and a clear solution was obtained.

The precipitate, consisting of sulfur and mercaptobenzothiazole, was twice extracted with warm aqueous ammonia and reprecipitated with hydrochloric acid. The water filtrates were concentrated to regain the water-soluble mercaptobenzothiazole; total yield, 92.5 g., or 87.5%.

A modification of this experiment was made by using alcohol as a solvent instead of water. The yield was only 73.5% and the product darker colored than in the reaction where water was used.

If commercial *o*-nitrochlorobenzol (containing a small amount of the *para* derivative) was used, the yield of 2-mercaptobenzothiazole was 84%. The procedure outlined above was followed in the synthesis of the derivatives of 2-mercaptobenzothiazoles described in this paper, where reference is made to the general procedure.

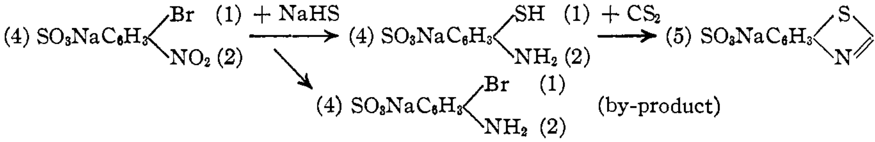
5-Chloro-2-mercaptobenzothiazole.—Following the same procedure as described for 2-mercaptobenzothiazole, a yield of 87% of 5-chloro-2-mercaptobenzothiazole was obtained. From 250 g. of $Na_2S.9H_2O$ dissolved in 500 cc. of water, hydrogen sulfide, carbon disulfide and 100 g. of 1,4-dichloro-2-nitrobenzol, reacted for 20 hours, 91 g. of 5-chloro-2-mercaptobenzothiazole was obtained.

This compound, not previously mentioned in the literature, has an enormous absorption capacity for water and alcohol when first precipitated from these solutions. The best way to obtain it in a dry state is to press it out in a piece of fine-woven cloth. After drying, it was crystallized from alcohol, giving colorless needles; m. p., 192°.

Anal. Calcd. for $C_7H_4NS_2Cl$: Cl, 17.60; N, 6.94. Found: Cl, 17.18; N, 6.98.

Pressure Reactions.—If the reaction was carried out under pressure, the time for complete reaction was shortened noticeably, but the highest yield obtained did not exceed 62%.

2-Mercaptobenzothiazole-5-sulfonic Acid (Sodium Salt).—This compound was prepared successfully from 2-nitrobromobenzol-4-sulfonic acid. The reaction scheme is as follows.



The reaction product, consisting of sulfur and the sodium salt of 2-mercaptobenzothiazole-5-sulfonic acid, was extracted with boiling alcohol, leaving most of the sulfur behind.

One hundred g. of 2-nitro-1-bromobenzol-4-sulfonic acid gave 70 g. of small, white needles. This material was purified by crystallizing it twice from boiling water, whereby most of the alcohol-soluble sulfur is left behind.

Anal. Calcd. for $C_7H_4O_3NS_3Na$: S, 35.68; N, 5.20; Na, 8.55. Found: S, 35.86; N, 4.82; Na, 8.0.

This compound is quite soluble in water and hot alcohol, insoluble in ether, benzene and chloroform.

Properties.—(a) A solution of the sodium salt of 2-mercaptobenzothiazole-sulfonic acid in alcohol gives a precipitate with iodine, proving its nature as a mercaptan.

In water solution no precipitate is formed by the addition of iodine, showing that the sodium salt of the acid is soluble in water.

(b) A water solution of the sodium salt treated with zinc acetate does not give a precipitate. On evaporation to a smaller volume, the unchanged sodium salt is recovered.

(c) A water solution of the sodium salt treated with a water solution of the equivalent amount of lead acetate gave an instantaneous color change to yellow, which disappeared quickly with the formation of a colorless precipitate.

This was filtered, washed with water and dried,

Anal. Calcd. for $C_7H_3O_3NS_3Pb$: Pb, 45.80. Found: Pb, 43.66.

5-Amido-2-mercaptobenzothiazole.—The preparation of this compound from 1-chloro-2,4-dinitrobenzol or 2,4-tetranitrodiphenyl disulfide with sodium hydrosulfide and carbon disulfide was not successful.

Forty-five g. of 1-chloro-2,4-dinitrochlorobenzol, 200 g. of $Na_2S.9H_2O$, carbon disulfide, and 500 cc. of water were reacted according to the general procedure for 48 hours. The final dark red solution was steam-distilled and the residue of the steam distillate acidified with dil. acetic acid.

The yellow-brown precipitate was filtered and dried; yield, 35 g.

Anal. (Crude product). Calcd. for $C_7H_6N_2S_2$: S, 35.2. Found: 38.9.

This crude product could not be crystallized from the common organic solvents. The product was extracted with alcohol leaving a considerable amount of residue. The alcohol solution was treated with bone black. On evaporation of the alcohol a yellow solid was obtained which was crystallized from aniline.

The yield of this material was very small. It proved to be 5-amido-2-mercaptobenzothiazole; m. p., 215°.

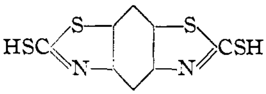
Anal. Calcd. for $C_7H_6N_2S_2$: S, 35.2; N, 15.35. Found: S, 35.40; N, 15.45.

If the crude product was not extracted with alcohol but was dissolved in hot pyridine and left standing for 24 hours, colorless rosets had separated out. They were filtered and washed first with pyridine and then with ether.

For further purification this compound was once more crystallized from pyridine, as it proved to be insoluble in other solvents tried. It did not melt up to 270°.

Anal. Found: S, 50.60; N, 10.47.

This analysis checks for the following formula: dimercaptobenzodithiazole. Calcd. for $C_8H_4N_2S_4$: S, 50.00; N, 10.93.



The formation of this compound by the interaction of 2,4-dinitrochlorobenzol, sodium hydrosulfide and carbon disulfide is explained by assuming that the sulfur, formed by the violent reduction of the nitro groups, is introduced in *ortho* position to the nitro group in Position 4. This assumption is justified as it is known that sulfur reacts with certain organic amines to form aryl disulfides.[9]

Since it has already been shown that 5-amido-2-mercaptobenzothiazole cannot be formed by treating 2,4-dinitrochlorobenzol with sodium hydrosulfide and carbon disulfide, an attempt was made to prepare 2,4-diamidothiophenol as an intermediate product.

2,2′,4,4′-Tetranitrodiphenyl Disulfide.—One hundred g. of 2,4-dinitro-1-chlorobenzol was dissolved in 1 liter of alcohol and a melt of 65.5 g. of $Na_2S.8H_2O$, and 9 g. of sulfur was added in small portions. A violent reaction took place and the 2,4,2′,4′-tetranitrodiphenyl disulfide separated. To complete the reaction the mixture was heated under reflux on a sand-bath for three hours.

After cooling, the solution was filtered and the residue washed first with alcohol, then with warm water until free from sodium chloride; yield, 86 g. This compound decomposes at 280°, in agreement with Willgerodt.[10]

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[9] Schultz and Beyschlag, *Ber.*, **42**, 743 (1909).

[10] Willgerodt, *Ber.*, **17R,** 352 (1884).

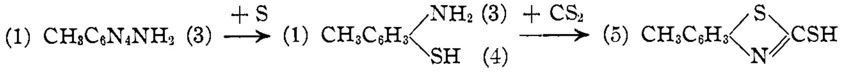
Reduction of 2,4,2',4'-Tetranitrodiphenyl Disulfide and Formation of 5-Amido-2-mercaptobenzothiazole.—Eighty-six g. of 2,4,2',4'-tetranitrodiphenyl disulfide is mixed with 350 g. of tin, and a mixture of 750 cc. of concd. hydrochloric acid and 750 cc. of water added. The solution is slowly heated on a sand-bath until the reaction is completed. Finally the solution is heated for two more hours to complete the reduction. The solution obtained is diluted with its own volume of hot water and filtered. The filtrate is evaporated to a small volume until crystals separate out and most of the excess of hydrochloric acid is evaporated. It is then diluted with seven times its volume of hot water and the solution de-tinned with hydrogen sulfide. The de-tinned solution is evaporated to a smaller volume and neutralized with sodium hydroxide; 150 g. of $Na_2S.9H_2O$ is then added to the cold solution and hydrogen sulfide, previously saturated with carbon disulfide, is bubbled through until saturated. The solution is then heated on a sand-bath under reflux for 20 hours, while hydrogen sulfide, previously saturated with carbon disulfide, is bubbled through.

The solution is acidified with dil. acetic acid and the precipitate filtered off and washed with water. The residue is extracted with warm, aqueous ammonia and reprecipitated with dil. acetic acid.

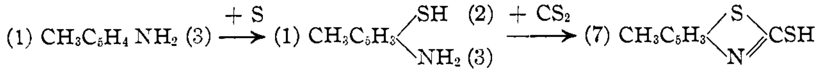
The precipitate is filtered, washed, dried and finally crystallized from freshly distilled aniline; yield, 38 g. of colorless needles; m. p., 216°.

Anal. Calcd. for $C_7H_6N_2S_2$: S, 35.2; N, 15.35. Found: S, 35.00; N, 14.97.

7-Methyl-2-mercaptobenzothiazole.—Sebrell and Boord[2] described the preparation of 3-monomethyl derivatives of 2-mercaptobenzothiazole, respectively, 4-, 5- and 6-methyl-2-mercaptobenzothiazole from the corresponding toluidines. They assume that 5-methyl-2-mercaptobenzothiazole is formed according to the following reaction scheme.



Theoretically, it would be possible for the following reaction to take place simultaneously.



In this case, the compound assigned as 5-methyl-2-mercaptobenzothiazole would be a mixture of 5- and 7-methyl-2-mercaptobenzothiazole.

To investigate this, an attempt was made to prepare 7-methyl-2-mercaptobenzothiazole. This is possible according to the new method of preparing substituted 2-mercaptobenzothiazoles from the corresponding *o*-nitrochlorobenzol compounds.

Commercial *o*-toluidine was purified by distillation and the mixed oxalates were prepared from the distillate separated according to the method of Holleman.[11]

The preparation of 2-chloro-3-nitrotoluene from acetyl-*o*-toluidine is described by Cohen and Dakin.[12] An improvement of the latter part of the reaction is given by Holleman.[11]

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[11] Holleman, *Rec. trav. chim.*, **27**, 458 (1908).

[12] Cohen and Dakin, *J. Chem. Soc.*, **79**, 1127 (1901).

Reaction of 2-Chloro-3-nitrotoluene with Sodium Hydrosulfide and Carbon Disulfide.—Seven g. of 2-chloro-3-nitrotoluene, 30 g. of $Na_2S.9H_2O$, and carbon disulfide were reacted according to the general procedure for four hours.

The final light red colored solution was steam-distilled, whereby some oil distilled (2-chloro-3-aminotoluene) and the residue acidified with dil. acetic acid.

The precipitate was filtered, washed with water and treated with warm aqueous ammonia. The sulfur was filtered off and the filtrate acidified with dil. acetic acid. The precipitate of 7-methyl-mercaptobenzothiazole was filtered, washed and dried; m. p. (dry), 176–180°. It was crystallized from aniline and then melted at 184°; yield, 2 g.

Anal, Calcd. for $C_8H_7NS_2$: S, 35.36; N, 7.73. Found: S, 35.75; N, 7.47.

As a by-product in this reaction 2-chloro-3-aminotoluene is formed, analogous to the formation of *o*-chloro-aniline from *o*-nitrochlorobenzol.

5-Methyl-2-mercaptobenzothiazole.—This compound could be prepared from 3-nitro-*p*-chlorotoluene, using *p*-toluidine as the starting material.[13]

Reaction of 3-Nitro-4-chlorotoluene with Sodium Hydrosulfide and Carbon Disulfide.—Five and one-half g. of 3-nitro-4-chlorotoluene, 20 g. of $Na_2S.9H_2O$, hydrogen sulfide and carbon disulfide were reacted according to the general scheme. The next procedure was identical with the one described for 7-methyl-2-mercaptobenzothiazole; yield of dried, crude material, 3.2 g. It was crystallized from toluene, giving colorless needles; m. p., 171–173°.

This melting point is higher than indicated by Sebrell and Boord for the same compound prepared from *m*-toluidine. The assumption that their compound was a mixture of 5- and 7-methyl-2-mercaptobenzothiazole seems, therefore, to be justified.

Anal. Calcd. for $C_8H_7N_2S_2$: S, 35.36; N, 7.73. Found: S, 35.85; N, 7.42.

2-Mercaptobenzothiazole-5-carboxylic Acid.—2-Nitro-4-cyano-1-chlorobenzol was prepared from *p*-chloro-aniline according to Mattaar.[14]

The saponification of 2-nitro-4-cyano-1-chlorobenzol was accomplished by dil. sulfuric acid (1:1).[15] The yield of 4-chloro-3-nitrobenzoic acid is almost quantitative. 4-Chloro-3-nitrobenzoic acid was treated with sodium hydrosulfide and carbon disulfide according to the general procedure described for previous *o*-chloronitrobenzol compounds.

Ten g. of 4-chloro-3-nitrobenzoic acid, 50 g. of $Na_2S.9H_2O$, hydrogen sulfide and carbon disulfide reacted for six hours gave 6 g. of 2-mercaptobenzothiazole-5-carboxylic acid.

After cooling, the solution was acidified with dil. acetic acid and the precipitate filtered, washed and while still wet digested with warm aqueous ammonia. The solution was filtered from undissolved sulfur and the filtrate acidified with dil. acetic acid. The precipitate was filtered and dried; yield, 6 g.

This compound was difficultly soluble in water and cold alcohol and slightly soluble in warm glacial acetic acid.

It was crystallized from glacial acetic acid, giving white needles which did not melt up to 270°.

Anal. Calcd. for $C_8H_5O_2NS_2$: S, 30.33; N, 6.63. Found: S, 29.88; N, 7.01.

To prove the presence of a carboxyl group this compound was titrated in 50% alcohol-water solution, with 0.1 *N* sodium hydroxide solution, using phenolphthalein as an indicator.

Titration. Calcd. for $C_8H_5O_2NS_2$: 28.43 cc. Found: 28.40 cc.

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[13] Gattermann, *Ber.*, **18**, 2600 (1885).

[14] Mattaar, *Rec. trav. chim.*, **41**, 24 (1922).

[15] Claus and Kurz, *J. prakt. Chem.*, [2] **37**, 200 (1888).

Attempts to Prepare Dichloro-2-mercaptobenzothiazole.—Attempts were made to prepare dichloro-substituted 2-mercaptobenzothiazoles by the general procedure described above from (1) 1,2,4-trichloro-*o*-nitrobenzol, prepared as described by Lesimple;[16] (2) 2,2′-dinitro-4,5,4′,5′-tetrachlorodiphenyl disulfide, obtained from *o*-dichlorobenzol as described by Blanksma.[17]

In both cases compounds were obtained which indicated that one chlorine atom was replaced by a mercaptan group. However, the yields of the products were very poor and no effort has been made to clear up their exact structure.

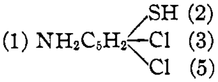
(3) *p*-NITRO-ANILINE.—It was thought that a dichloro-2-mercaptobenzothiazole could be formed from 2,2′,4,4′-tetrachloro-6,6′-dinitrodiphenyl disulfide, which is obtained from *p*-nitro-aniline as described by Holleman and Blanksma.[18]

Seventy g. of this material, m. p., 190°, and 200 g. of $Na_2S.9H_2O$ dissolved in 500 cc. of water and treated according to the general procedure gave 22 g. of a colorless, amorphous powder.

This material was crystallized from xylene and gave 18.5 g. of colorless needles; m. p., 213°.

Anal. Found: N, 7.12; S, 15.10; Cl, 36.52.

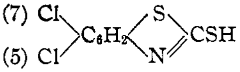
The analysis checks for the formula



$$(1)\ NH_2C_5H_2\begin{cases}SH & (2)\\ Cl & (3)\\ Cl & (5)\end{cases}$$

Calcd. for $C_5H_5NSCl_2$: N, 7.12; S, 16.5; Cl, 36.60

and not for the expected compound



Calcd: N, 5.93; S, 27.12; Cl, 30.00.

We have here a remarkable case where the ring closing of the *o*-amidothiophenol to the thiazole ring is prevented by the other substituents present. Under what conditions the ring closing can occur will be investigated later. As a substituted thiophenol this compound is new in its class.

Summary

A new method for the preparation of 2-mercaptobenzothiazole is described, which is especially suitable for laboratory use. This method was extended to several new derivatives and is especially suitable for the monohalogen derivatives. The general synthesis could not be applied for the dihalogenated 2-mercaptobenzothiazoles.

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[16] Lesimple, *Ann.*, **137**, 123 (1866).

[17] Blanksma, *Rec. trav. chim.*, **21**, 419 (1902).

[18] Holleman and Blanksma, *ibid.*, **23**, 366 (1904); **27**, 48 (1908).