method of preparation, properties, and analyses of fluorotetra-acetylfructose and bromotetra-acetylfructose are given.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF OHIO STATE UNIVERSITY]

THE PREPARATION AND PROPERTIES OF 1-MERCAPTO-BENZOTHIAZOLE, ITS HOMOLOGS AND DERIVATIVES[1,2]

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The present paper comprises a study of the synthesis of 1-mercapto-benzothiazole and its derivatives which was made in connection with an investigation of the role played by these compounds when functioning as accelerators of vulcanization. Eight different mercapto-benzothiazoles were prepared and studied. Each of these substances excepting where the quantity of material was limited, were prepared by four separate methods. These methods were alike in that the reaction mixture was heated in an autoclave under pressure. The reaction mixtures were as follows: (1) the corresponding disubstituted thio-urea and sulfur; (2) the zinc salt of the corresponding aryl dithiocarbamic acid and sulfur; (3) the ammonium salt of the same acid and sulfur; (4) a mixture of the corresponding aryl amine, carbon disulfide and sulfur.

The first method has been described by Romani.[3] The last three methods are new.

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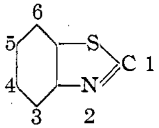
[1] This paper and one entitled: "A Study of 1-Mercapto-benzothiazole and its Derivatives as Accelerators of Vulcanization" being published in a current number of *J. Ind. Eng. Chem.* [**15**, 1009 (1923)] have been abstracted from the dissertation presented by L. B. Sebrell to the Graduate School of Ohio State University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, September, 1922.

[2] The system of nomenclature as outlined in *C. A. Decennial Index*, **1–10**, 2345, namely, omitting the sulfur and beginning the numbering with the carbon atom of the thiazole ring has been followed throughout this article.



[3] The four methods of preparation described in the following pages as applied to 1-mercapto-benzothiazole and its three monomethyl derivatives, together with their disulfides and metallic salts were reported before the Organic Division of the American Chemical Society at the Birmingham meeting, April 6th, 1922. [(a) See *Science,* **56,** 55 (1922).] Shortly afterward, an article by Romani, [(b) *Gazz. chim. ital.,* **52,** 29 (1922)] became available, describing the preparation of the three methyl derivatives by one of the methods, namely, heating the corresponding disubstituted thio-urea with sulfur. To him, undoubtedly, belongs priority of publication of a description of these three derivatives by this one method. He did not describe the disulfides.

Historical

1-Mercapto-benzothiazole was first obtained by A. W. Hofmann[4] in an attempt to prepare the disulfhydryl derivative of thiocarbanilide by the action of carbon disulfide on *o*-aminophenol. He obtained the same substance by the action of sodium hydrosulfide on chlorophenyl mustard oil (1-chloro-benzothiazole) and also when carbon disulfide was caused to react with *o*-aminothiophenol disulfide. The product thus obtained, after recrystallization from alcohol, melted at 179° and was easily oxidized to a disulfide melting at 180°.

Jacobson and Frankenbacher[5] while studying the formation of benzothiazoles, heated azobenzene with carbon disulfide in a sealed tube at 250° for 5 hours. The product melted at 174° but was identical with Hofmann's 1-mercapto-benzothiazole. The disulfide obtained by the oxidation of this product with potassium dichromate in acetic acid solution after recrystallization from benzene melted at 186°.

In order to verify the assumption that phenyl mustard oil is an intermediate product in the formation of 1-mercapto-benzothiazole from azobenzene, these authors heated the former substance in a sealed tube with sulfur for 5 hours. The yield of mercapto-benzothiazole thus obtained was equal to 45% of the weight of mustard oil used. The constitution of the thiazole was further established by fusion with potassium hydroxide, thus regenerating *o*-aminothiophenol.

Azobenzene when heated with phenyl mustard oil was found to yield 1-anilido-benzothiazole although the same substance could not be obtained by the direct action of aniline on mercapto-benzothiazole.

Rassow, Dohle and Reim[8] have shown that 1-mercapto-benzothiazole is formed by the action of sulfur on dimethylaniline.

Bedford and Sebrell[7] as well as Bruni and Romani[8] have independently described the preparation of 1-mercapto-benzothiazole by the reaction of thiocarbanilide with sulfur when heated under pressure. More recently Romani[3b] has extended this method of preparation to the three monomethyl derivatives of 1-mercapto-benzothiazole. He recommends the use of an excess of sulfur and zinc oxide as a catalyst. Romani prepared the metallic salts of these methylated mercapto-benzothiazoles but not the disulfides.

Mechanism of the Reaction

Bruni and Romani,[8] apparently following the lead of Jacobson and Frankenbacher, have sought to explain the formation of 1-mercapto-benzothiazole from thiocarbanilide, monophenyl-thio-urea and methylene-aniline upon the assumption that these substances first decompose to give phenyl mustard oil. They mention an alkali-insoluble residue, which apparently was not further investigated. It is shown in the experimental part of this paper that this insoluble residue consists chiefly of 1-anilido-benzothiazole and that it is formed in largest amounts when thiocarbanilide is used as the starting material. Indeed, it is almost entirely absent when ammonium phenyl-dithiocarbamate or the free aniline and carbon

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

[5] Jacobson and Frankenbacher, *Ber.*, **24**, 1400 (1891).

[6] Rassow, Dohle and Reim, *J. prakt. Chem.*, **93**, 183 (1916).

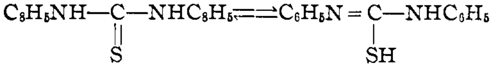
[7] Bedford and Sebrell, *J. Ind. Eng. Chem.*, **13**, 1034 (1921).

[8] Bruni and Romani, *Giorn. chim. ind. applicata*, **3**, 351 (1921).

disulfide are used. The insoluble residue obtained when the zinc salt is used consists almost wholly of zinc sulfide.

If the formation of 1-mercapto-benzothiazole from thiocarbanilide is assumed to take place through its decomposition products, such as aniline and carbon disulfide or phenyl mustard oil, by virtue of their reaction with sulfur, then little or no 1-anilido-benzothiazole should be expected since these latter reactions form only small amounts of the alkali-insoluble residue. These facts seem to indicate that direct sulfurization of the thiocarbanilide offers the most satisfactory explanation for the simultaneous formation of 1-mercapto-benzothiazole and 1-anilido-benzothiazole. The formation of these two products may be readily understood by use of the following mechanism.

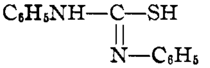
1. Thiocarbanilide may be assumed to be in equilibrium with its tautomeric form.



$$C_6H_5NH{-}\underset{\underset{S}{\|}}{C}{-}NHC_6H_5 \rightleftharpoons C_6H_5N{=}\underset{\underset{SH}{|}}{C}{-}NHC_6H_5$$

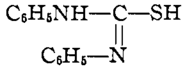
2. This tautomeric form should occur as two geometric isomers, *A* and *B*.

A



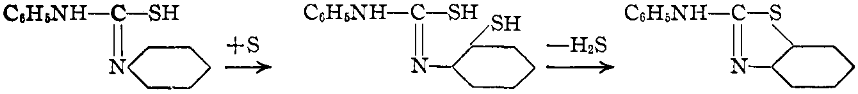
$$C_6H_5NH{-}\underset{\underset{N-C_6H_5}{\|}}{C}{-}SH$$

B

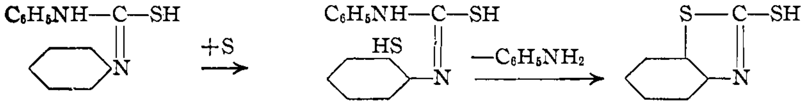


$$C_6H_5NH{-}\underset{\underset{C_6H_5-N}{\|}}{C}{-}SH$$

3. When *A* is sulfurized and hydrogen sulfide eliminated 1-anilido-benzothiazole is formed.



4. When *B* is sulfurized and aniline eliminated 1-mercapto-benzothiazole is formed.



In the experimental part of this paper it is shown that the combined yield of these two products will account for between 90 and 96% of the thiocarbanilide used. These facts are of especial significance since Jacobson and Frankenbacher have shown that 1-anilido-benzothiazole is not formed by the action of aniline on 1-mercapto-benzothiazole.

The formation of 1-mercapto-benzothiazole from phenyl-dithiocarbamic acid and its salts is not so easily traced. It may be explained in one of three ways.

1. The dithiocarbamic acid derivative may decompose with the formation of phenyl mustard oil, which in turn reacts with the sulfur to form the mercapto-benzothiazole. This explanation would correspond to that offered by Jacobson and Frankenbacher[5] and by Bruni and Romani[8] to

account for the formation of the mercapto-thiazoles in other cases. The former workers obtained a 45% yield of 1-mercapto-benzothiazole by heating phenyl mustard oil with sulfur. In this Laboratory as high as 60% yields have been obtained by the same method. By reference to Table I it will be seen that phenyl-dithiocarbamic acid and its salts yield 75 to 80% of the same thiazole. It seems doubtful, therefore, whether phenyl mustard oil is an intermediate product in the formation of mercapto-benzothiazoles from phenyl-dithiocarbamic acid and its salts.

2. Phenyl-dithiocarbamic acid and its salts not only yield phenyl mustard oil but also undergo a second type of splitting with the formation of aniline and carbon disulfide. This is especially true of the ammonium salt, since thiocarbanilide is found among its decomposition products. Thiocarbanilide should be expected to react with sulfur yielding the mercapto-thiazole according to the scheme given above. Such a reaction would produce a large amount of an alkali-insoluble residue which experiment shows is not the case.

3. There is no *a priori* reason why phenyl-dithiocarbamic acid and its salts should not undergo direct sulfurization as readily as its anilide. The present authors believe this to be a more logical explanation and that the mercapto-benzothiazole is produced by the loss of the appropriate hydrosulfide from the addition product thus formed.

Experimental Part

Preparation of Materials.—The ammonium salts of the aryl dithiocarbamic acids were prepared by the method of Losanitch,[9] by the reaction of the arylamine and carbon disulfide in the presence of ammonium hydroxide or ammonium sulfide in alcoholic solution. The rapid decomposition characteristic of these ammonium salts has caused many investigators to doubt their actual existence.

Ammonium phenyl-dithiocarbamate prepared in the presence of strong ammonium hydroxide is quite stable and after careful drying shows little tendency to decompose. By recrystallization from strong ammonium hydroxide it is obtained as long hexagonal crystals, which when carefully washed and dried have been kept for more than a year without evidence of decomposition. In the presence of moisture however it is slowly converted into thiocarbanilide, carbon disulfide and ammonia, as reported by Losanitch.

These ammonium salts may also be prepared by passing ammonia gas into a solution of aryl amine and carbon disulfide in benzene, but the method has no advantages over the one previously described.

The zinc salts of the aryl dithiocarbamic acids were prepared by adding a solution of zinc acetate in water or ammonium hydroxide to an aqueous solution of the corresponding ammonium salt. They may also be prepared by the method of Krulla[10] who added the metallic oxide to a mixture of the aniline and carbon disulfide. The first method gives the purer product.

Thiocarbanilide and its substituted derivatives were prepared by the action of the aryl amine with carbon disulfide in the usual manner. These products were purified un-

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[9] Losanitch, *Ber.*, **24**, 3022 (1891); *Ann.*, **166**, 142 (1873).

[10] Krulla, *Ber.*, **46**, 2669 (1913).

til the melting points varied not more than 3° or 4° from the highest recorded values in any case.

Apparatus.—The apparatus used in this work consisted of a steel autoclave mounted in an electric resistance oven. The autoclave, which had a capacity of 2 liters, was turned from tool steel and was capable of withstanding a pressure of 2000 pounds. The oven consisted of 3 heating elements specially wound from Chromel wire and mounted on a reinforced frame built up from Alundum cement. The heating unit was effectually insulated by packing in a mixture of asbestos and magnesite. Temperature control, secured by an external hot wire rheostat, was sufficiently exact to make it possible to reproduce any given set of temperature conditions. Temperatures up to 600° were easily obtained.

Procedure.—The substance used to prepare the thiazole was mixed intimately with one molar equivalent of sulfur and placed in the autoclave. Practically all runs were made by bringing the oven to a temperature of 390–400°, then lowering the autoclave to position and allowing the temperature of the reaction mixture to rise until the pressure reached a maximum. The pressure would rise gradually with the temperature to about 170–180° where the increase became much more rapid reaching a maximum at about 225–250°. The pressure generated varied with the substance used to produce the thiazole, being greatest with the ammonium salts and least with the disubstituted thio-ureas. Reproducing the heating conditions did not always give the same yield of product. Usually the autoclave was withdrawn from the oven immediately after the pressure reached the maximum to secure more rapid cooling, and when it was quite cold the accumulation of hydrogen sulfide was blown off and the autoclave opened.

Method of Purification.—The crude reaction product was removed from the autoclave by solution in warm dil. sodium hydroxide solution. This alkaline solution was submitted to steam distillation to remove any free aryl amine. The solution was then filtered from a residue of insoluble material and fractionally precipitated by the addition of small portions of hydrochloric acid. The first precipitates were very dark and carried down most of the coloring matter. The last fractions precipitated consisted of the 1-mercapto-benzothiazole in an almost pure form. The product was redissolved in sodium carbonate solution and reprecipitated further purification varied depending upon the nature of the product and will be described for each individual substance together with its physical and chemical characteristics.

Discussion of the Experimental Results

The data collected in the preparation of 1-mercapto-benzothiazole and 6 of its substituted derivatives are set forth in Table I. Not all of the runs made are listed, but those selected are typical. Failure to prepare all the thiazoles by each of the four methods was due to a lack of sufficient quantity of the aryl amines from which to prepare the necessary starting materials. In such cases that method was selected which promised to yield the largest amount of easily purified product.

TABLE I

DATA ON THE PREPARATION OF 1-MERCAPTO-BENZOTHIAZOLES

	Substances used	Used G.	Time Hrs.	Max. temp. °C.	Max. press. Lbs.	NaOH insol. G.	Yield G.	Yield %	Product
1	Thiocarbanilide	456	4.00	265	300	105.0	245.0	74.0	1-Mercapto-benzothiazole
2	Ammonium phenyl-dithiocarbamate	263	1.50	224	1000	7.3	174.5	74.0	
3	Zinc phenyl-dithiocarbamate	350	1.83	247	575	101.0	225.2	77.5	
4	Aniline and carbon disulfide	93							
		76	2.00	271	571	9.0	128.0	76.6	
5	Di-*o*-tolyl-thio-urea	512	4.00	293	520	194.0	177.0	49.0	1-Mercapto-3-methyl-benzothiazole
6	Ammonium *o*-tolyl-dithiocarbamate	170	1.42	253	1050	18.5	103.0	67.0	
7	Zinc *o*-tolyl-dithiocarbamate	214	1.25	266	625	137.5	65.7	37.0	
8	*o*-Toluidine and carbon disulfide	105							
		76	1.58	255	675	34.7	80.4	45.5	
9	Ammonium *m*-tolyl-dithiocarbamate	186	1.00	242	625	15.5	116.6	69.5	1-Mercapto-4-methyl-benzothiazole
10	Di-*p*-tolyl-thio-urea	384	1.50	295	475	104.0	185.0	68.0	1-Mercapto-5-methyl-benzothiazole
11	Ammonium *p*-tolyl-dithiocarbamate	308	1.25	227	1050	22.8	199.2	71.5	
12	*p*-Toluidine and carbon disulfide	105							
		76	1.50	240	738	44.0	102 0	57.9	
13	2,4,2',4' - Tetramethyl-diphenyl-thio-urea	260	1.25	228	450	178.6	30.7	17.2	1-Mercapto-3,5-dimethyl-benzothiazole
14	Ammonium *o,p*-xylyl-dithiocarbamate	198	1.70	220	1000	37.1	62.1	34.5	
15	Zinc *o,p*-xylyl-dithiocarbamate	239	1.00	239	775	114.5	66.2	32.4	
16	*m*-Xylidine and carbon disulfide	121							
		76	1.58	247	725	84.0	59.3	30.4	
17	Di-*p*-phenetyl-thio-urea	269	1.83	244	325	109.0	104.5	58.4	1-Mercapto-5-ethoxy-benzothiazole
18	Ammonium *p* - phenetyl - dithiocarbamate	339	1.10	206	1275	8.5	227.5	73.0	
19	Zinc *p*-phenetyl-dithiocarbamate	288	1.58	246	550	125.0	147.7	59.3	
20	*p*-Phenetidine and carbon disulfide	137							
		76	1.30	249	455	49.0	117.4	55.6	
21	*p*-Anisidine and carbon disulfide	62							1-Mercapto-5-methoxy-benzothiazole
		38	1.20	237	365	36.5	61.5	62.0	

Runs 1 and 5 were made first, and without preheating the oven, thus accounting for the longer reaction time. In later runs the reaction time was shortened to avoid heat decomposition. The ammonium aryl-dithiocarbamates gave in general the best yields, but the products from the zinc salts contained less tarry material and were therefore more readily purified.

The more highly substituted the arylamine, the lower the yield of the thiazole so that only a 34.5% yield of the dimethyl derivative was obtained even from the ammonium salt of xylyl-dithiocarbamic acid.

The disubstituted thio-ureas always yielded large amounts of an alkali-insoluble by-product. The yield of this substance is markedly lower when the ammonium salt of the aryl-dithiocarbamic acid or the aryl amine and carbon disulfide were used. In the case of the zinc salts the alkali-insoluble product consisted almost wholly of zinc sulfide.

Nature of the Alkali-Insoluble Material

In the case of thiocarbanilide the alkali-insoluble part of the reaction product was found to consist largely of 1-anilido-benzothiazole. The purification of this anilido derivative proved to be so tedious that the separation of a similar derivative was not successfully completed in any of the other cases.

1-Anilidobenzothiazole.[4]—The alkali-insoluble residue from the thiocarbanilide-sulfur reaction mixture was dissolved in alcohol and the solution poured into dil. hydrochloric acid. A small amount of acid-insoluble substance was removed by filtration and the anilido derivative precipitated by the addition of sodium hydroxide. Fifty g. of the original residue gave 36 g. of the purified anilido derivative and 5 g. of the acid-insoluble substance, which proved to be mostly 1-mercapto-benzothiazole. After recrystallization from benzene the 1-anilido-benzothiazole was obtained as light yellow crystals melting at 154°. A mixture of this product with 1-anilido-benzothiazole prepared by the action of phenyl mustard oil on azobenzene gave the same melting point.

Analyses. Subs., 0.5470: 46.9 cc. 0.1 *N* H_2SO_4. Subs., 0.5102: $BaSO_4$, 0.5293. Calc. for $C_{13}H_{10}N_2S$: N, 12.38; S, 14.16. Found: N, 12.00; S, 14.25.

Using the above data the calculated yield of pure 1-anilido-benzothiazole available from the 105 g. of alkali-insoluble residue from the thiocarbanilide in Table I is 75.6 g. or 16.5%. By combining this yield with the 73.3% of 1-mercapto-benzothiazole obtained, approximately 90.0% of the thiocarbanilide is accounted for. When one considers the losses incident to purification it is easy to conceive that the actual yield of the two derivatives is much higher, being about 96% on the basis of the crude products.

Disulfides

The disulfides of each of the mercapto-thiazoles described were prepared by the method of Hofmann.[5] An alcoholic or alkaline solution of the mercapto-thiazole was oxidized by the gradual addition of an alcoholic solution of iodine. The resulting disulfide, insoluble in alcohol or alkalies, precipitated immediately, and after it was filtered, washed and dried was purified by recrystallization from the solvent indicated in each case.

Zinc and Lead Salts

The zinc salts of the mercapto-benzothiazoles may be prepared by either of two methods. A solution of the ammonium salt may be precipitated by the addition of a solution of ammonium zincate, or an alcoholic solution of the thiazole may be precipitated by adding an aqueous solution of any zinc salt. The first method gives the purer product.

Both the normal and the basic lead salts may be prepared, depending upon the method used. The normal lead salts were obtained by precipitating an alcoholic solution of the free thiazole or an aqueous solution of its sodium salt by an aqueous solution of any soluble lead salt. The basic lead salts were obtained by precipitating an alkaline solution of the mercapto-benzothiazole by a solution of lead hydroxide in an excess of sodium hydroxide. These salts were thoroughly washed, dried and subjected to analysis without further purification.

The zinc and lead salts of each of the several mercapto-benzothiazoles were prepared, but in only three cases were they actually analyzed and tested for their accelerating power as indicated in the following pages.

1-Mercapto-benzothiazole[5] is soluble in alcohol, benzene and acetic acid. By recrystallization from dil. alcohol it was obtained as light yellow needles, melting at 177°.

Analyses. Subs., 0.7502: 44.8 cc. of 0.1 N H_2SO_4. Subs., 0.1016: $BaSO_4$, 0.2840. Calc. for $C_7H_5NS_2$: N, 8.38; S, 38.32. Found: N, 8.37; S, 38.38.

THE DISULFIDE[5]; an amorphous slightly yellow powder, melting at 176°; yield, 87%.

THE ZINC SALT; a white, amorphous powder.

Analysis. Calc. for $C_{14}H_8N_2S_4Zn$: N, 7.05; Zn, 16.45. Found: N, 7.21; Zn, 16.05.

THE NORMAL LEAD SALT; a bright yellow powder.

Analysis. Calc. for $C_{14}H_8N_2S_4Pb$: Pb, 38.40. Found: 38.49.

THE BASIC LEAD SALT; an amorphous white powder.

Analysis. Calc. for $C_7H_5NS_2OPb$: Pb, 53.05. Found: 52.35.

1-Mercapto-3-mtehyl-benzothiazole[3b] after repeated recrystallizations from dil. alcohol and finally from 50% acetic acid was obtained as white needles melting at 186°.

Analyses. Subs., 0.7205: 41.2 cc. of 0.1 N H_2SO_4. Subs., 0.1060, 0.1143: $BaSO_4$, 0.2720; 0.2929. Calc. for $C_8H_7NS_2$: N, 7.73; S, 35.36. Found: N, 8.00; S, 35.26, 35.21.

THE DISULFIDE; white needles from chloroform; m. p., 162°.

Analysis. Calc. for $C_{16}H_{12}N_2S_4$: S, 35.55. Found: 35.63, 35.48.

THE ZINC SALT; a white amorphous powder.

Analysis. Calc. for $C_{16}H_{12}N_2S_4Zn$: Zn, 15.37. Found: 15.35.

THE NORMAL LEAD SALT; an amorphous yellow powder.

Analysis. Calc. for $C_{16}H_{12}N_2S_4Pb$: Pb, 36.50. Found: 36.78.

THE BASIC LEAD SALT; an amorphous white powder.

Analysis. Calc. for $C_8H_7NS_2OPb$: Pb, 51.24. Found: 51.50.

1-Mercapto-4-methyl-benzothiazole[3b] was prepared only through the ammonium salt of *m*-tolyl-dithiocarbamic acid. After successive recrystallizations from 75% alcohol, 50% acetic acid and benzene, it was obtained as light yellow plates melting at 163°.

Analyses. Subs., 0.1585, 0.2270: $BaSO_4$, 0.4075, 0.5878. Calc. for $C_8H_7NS_2$: S, 35.36. Found: 35.30, 35.52.

THE DISULFIDE; white plates from benzene; m. p., 195°.

Analysis. Calc. for $C_{16}H_{12}N_2S_4$: S, 35.55. Found: 35.57; 35.65.

1-Mercapto-5-methyl-benzothiazole[3b] was recrystallized twice from 50% acetic acid and finally from benzene. It forms fine, very light yellow crystals melting at 181°.

Analyses. Subs., 0.7234: 38.37 cc. of 0.1 N H_2SO_4. Subs., 0.1860, 0.1985: $BaSO_4$, 0.4784, 0.5109. Calc. for $C_8H_7NS_2$: N, 7.73; S, 35.36. Found: N, 7.44; S, 35.39, 35.34.

THE DISULFIDE; This was insoluble in alcohol but soluble in benzene and chloroform, white needles from chloroform melting at 201–202°.

Analysis. Calc. for $C_{16}H_{12}N_2S_4$: S, 35.55. Found: 35.59.

THE ZINC SALT; a white amorphous powder.

Analysis. Calc. for $C_{16}H_{12}N_2S_4Zn$: Zn, 15.37. Found: 15.40.

1-Mercapto-3,5-dimethyl-benzothiazole was recrystallized several times from alcohol from which it separates in light yellow crystals melting at 250.5°. It is only very slightly soluble in acetic acid or benzene.

Analyses. Subs., 0.2050, 0.1888: $BaSO_4$, 0.4904, 0.4523. Calc. for $C_9H_9NS_2$: S, 32.82. Found: 32.85, 32.90.

THE DISULFIDE; fine white needles, m. p. 193°, obtained by repeated precipitation from chloroform with the gradual addition of alcohol.

Analyses. Calc. for $C_{18}H_{16}N_2S_4$: S, 32.99. Found: 33.02, 33.13.

1-Mercapto-5-ethoxy-benzothiazole was prepared by each of the four methods but only the ammonium *p*-phenetyl-dithiocarbamate yielded an easily purified product. Recrystallized from 75% alcohol and twice from benzene it was obtained as well-formed, long, cream-colored needles melting at 198°. It is only slightly soluble in benzene and other organic solvents.

Analyses. Subs., 0.1950, 0.1852: $BaSO_4$, 0.4303, 0.4044. Calc. for $C_9H_9NOS_2$: S, 30.33. Found: 30.31, 29.99.

Attempts to prepare the disulfide were unsuccessful.

1-Mercapto-5-methoxy-benzothiazole was prepared by each of the four methods but the product in all cases proved very difficult to purify. It was found that by rapidly heating the reaction mixture and rapidly cooling the autoclave a more easily purified product was obtained. Recrystallized from 70% alcohol and twice from benzene it forms light yellow needles melting at 201°.

Analysis. Subs., 0.1505: $BaSO_4$, 0.3546. Calc. for $C_8H_7NOS_2$: S, 32.48. Found: 32.37.

Attempts to prepare substituted mercapto-benzothiazoles from *o*-anisidine, the *o*- and *p*-chloro- and bromo-anilines and *p*-aminophenol were unsuccessful. Benzidine and carbon disulfide yielded an alkali-soluble product melting above 250°, which was not further investigated.

Acknowledgment

The authors wish to acknowledge the coöperation of the Goodyear Tire and Rubber Company as expressed through Dr. E. B. Spear, former Research Director, for the loan of apparatus and the testing of samples. Further acknowledgment is due Mr. C. W. Bedford for helpful advice during the early part of the work, to Dr. W. J. Kelly for valued suggestions and to Mr. C. M. Carson for assistance rendered.

Summary and Conclusions

1. The chemistry of the zinc and ammonium salts of phenyl-dithiocarbamic acid has been extended and the work of Losanitch verified.
2. Three new methods for the preparation of 1-mercapto-benzothiazole and its substituted derivatives have been described.
3. A fourth method previously described by one of us and independently announced about the same time by Bruni of Italy, has been extended to these derivatives.

4. The mechanism of the reaction involved in the formation of 1-mercapto-benzothiazoles by the action of sulfur on disubstituted thioureas is fully discussed. Experimental evidence is offered in support of the view that this reaction takes place by virtue of direct sulfurization of the *cis*-mercapto form of thiocarbanilide and subsequent loss of the aryl amine to form the mercapto-benzothiazole. It is also pointed out that sulfurization of the *trans*-mercapto form of thiocarbanilide and loss of hydrogen sulfide explains the simultaneous formation of anilido-benzothiazole.

5. Direct sulfurization and subsequent elimination of the corresponding hydrosulfide is offered as the best explanation of the formation of mercapto-benzothiazoles by the action of sulfur on the aryl dithiocarbamic acids and their salts.

6. Six substituted mercapto-benzothiazoles are described together with four of the corresponding disulfides.

7. Methods are given for the preparation of the zinc, normal lead and basic lead salts of the 1-mercapto-benzothiazoles and in three cases such salts are described.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

THE INFLUENCE OF SULFUR ON THE COLOR OF AZO DYES

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The purpose of the present investigation was to study the effect of the sulfur atom and of the sulfone group, in various positions, on the color of azo dyes.

Brand[2] and coworkers found the —SCH_3 group to be strongly bathochromic as compared with —OCH_3 when introduced into azobenzene or into triphenyl carbinol, but they did not prepare any real dyes except to tetrazotize the dimethylether of *o,o'*-dimercapto-benzidine and couple it with salicylic acid, which gave a direct yellow on cotton, and with H-acid which gave a blue shade.

Several workers[3] have mentioned that various amines containing sulfur give red dyes when diazotized and coupled with β-naphthol. The importance of thio-indigo and other dyes containing sulfur appeared to warrant a thorough investigation of the influence of sulfur in azo dyes.

Two classes of dyes have been considered. (1) Those derived from mono-amines, particularly those from *p*-thio-anisidine, $CH_3SC_6H_4NH_2$, and its sulfone, $CH_3SO_2C_6H_4NH_2$, which have been contrasted with the corresponding dyes from *p*-toluidine and *p*-anisidine, thus showing the

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[1] From a dissertation by W. R. Waldron, 1922.

[2] Brand, (a) *Ber.*, **42**, 3463 (1909). Brand and Wirsing, (b) *Ber.*, **45**, 1757 (1912); (c) **46**, 820 (1913). Brand and Stallmann, (d) *Ber.*, **54**, 1578 (1921).

[3] Nietzki and Bothof, (a) *Ber.*, **27**, 3262 (1894). Claasz, (b) *Ber.*, **45**, 1027 (1912).