The reaction of β,β'-thiodipropionic acid and *o*-aminothiophenol gave a quantitative yield of 2,2'-bis(2-benzothiazolyl)diethyl sulfide in polyphosphoric acid medium. 1,2,3-Propanetricarboxylic acid also condensed readily with *o*-aminothiophenol in a one:three molar ratio to give a quantitative yield of 1,2,3-tris(2-benzothiazolyl)propane in the polyphosphoric acid catalyzed reaction.

As polyphosphoric acid is a complex mixture, it does not lend itself to the cryoscopic methods which have been so successfully used in the study of mechanisms of the organic chemical reactions in pure sulfuric acid. Because polyphosphoric acid is highly viscous, and a poor medium for crystallization, it is not surprising that reaction intermediates have not been isolated by this means. At the present time only speculation may be made concerning the mechanisms by which it operates on organic compounds. The most obvious possibilities are that it functions as a protonic acid, as a Lewis acid, or as a phosphorylating agent. The intermolecular condensation of *o*-aminothiophenol and dibasic acids may be rationalized on the basis of an initial step which is either a protonation followed by elimination of water or conversion to mixed anhydride which cyclizes in the usual manner to give a benzothiazole nucleus.

EXPERIMENTAL[11]

The procedure for the preparation of bisbenzothiazole and the related compounds is described below. The data on the preparation, yields, melting points and analyses are summarized in Table I. All melting points reported here are uncorrected. Commercial polyphosphoric acid, obtained from Victor Chemical Works, was used in this investigation.

Preparation of bis(2-benzothiazolyl)alkanes. o-Aminothiophenol (0.2 mole) was mixed with the dicarboxylic acid, anhydride or nitrile (0.1 mole) and the mixture was poured into well stirred polyphosphoric acid (125 ml.) contained in a three neck flask at 70°. The reaction mixture was heated at 125–150° for 2 hr. with efficient stirring. It was then allowed to cool to room temperature and was then poured into ice cold water. The precipitate was removed by filtration, washed three times with dilute sodium bicarbonate solution, and dried in a vacuum desiccator. The crude product was crystallized preferentially from ethanol and in some cases from benzene until a constant melting point was obtained.

Preparation of 1,2- and 1,4-bis(2-benzothiazolyl)benzenes. A mixture of *o*-aminothiophenol (0.1 mole) and phthalic acid or terephthalic acid (0.05 mole) was added to polyphosphoric acid (100 ml.) at 100°. The reaction mixture was heated at 175° for 3 hr. for 1,2-bis(2-benzothiazolyl)benzene and 4 hr. for 1,4-bis(2-benzothiazolyl)benzene. The 1,2-bis(2-benzothiazolyl)benzene was isolated according to the procedure previously described.

Preparation of 2,2'-bis(2-benzothiazolyl)diethyl sulfide. This compound was prepared by treating *o*-aminothiophenol (0.2 mole) with β,β'-thiodipropionic acid (0.1 mole) in polyphosphoric acid (100 ml.) at 125°. The reaction was complete in 1 hr. and the product was worked up by the procedure described for bis(2-benzothiazolyl)alkanes.

Preparation of 1,2,3-trisbenzothiazolylpropane. 1,2,3-Propanetricarboxylic acid (0.1 mole) was mixed with *o*-aminothiophenol (0.3 mole) and added to well stirred warm polyphosphoric acid (125 ml.). The reaction mixture was heated for 2 hr. at 125°. 1,2,3-Trisbenzothiazolylpropane was obtained in 92% yield as shiny tan crystals following the normal isolation and crystallization method.

CRYSTAL LAKE, ILL.

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(11) Analyses were performed by the Analytical Research & Service Division of the Pure Oil Research Center.

[CONTRIBUTION FROM THE ORGANIC CHEMICALS DIVISION, NITRO RESEARCH DEPARTMENT, MONSANTO CHEMICAL CO.]

Derivatives of 2-Benzothiazolesulfenamides. I. Novel Method for Preparation of *N*-Substituted Benzothiazolesulfenamides

JOHN J. D'AMICO

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A novel method, the reduction of *N*-alkylidene- (or arylidene)-benzothiazolesulfenamides (I–XIII) with sodium borohydride, has been developed for the preparation of benzothiazolesulfenamides in 76–99% yields. This new method avoids the use of an amine as a reactant and also furnishes the benzothiazolesulfenamides with greater stability than those prepared by conventional known methods. During the course of this investigation the following interesting reactions were encountered: (1) The reaction of 2-benzothiazolesulfenamide with cyclohexanone or 2,4-pentanedione under basic conditions gave 2-(2-oxocyclohexylthio)benzothiazole (XIV) and 2-diacetylmethylthiobenzothiazole (XXXVIII), respectively; (2) the attempted reduction of *N*-isopropylidene-2-benzothiazolesulfenamide (XI) with (a) formic acid, (b) sulfur or hydrogen sulfide in isopropylamine-ethyl alcohol solvent, and (c) hydrogen sulfide in ethyl alcohol, gave 2,2'-dithiobis(benzothiazole) (XXXVI), the isopropylamine salt of 2-mercaptobenzothiazole (XXXVII), and 2-mercaptobenzothiazole (XXXV), respectively; (3) the reaction of *N*-cyclohexyl-2-benzothiazolesulfenamide (XXXII) with 4,4'-methylenebis(phenyl isocyanate) or toluene 2,4-diisocyanate furnished 1,1'-(*p*-methylenediphenylene)bis(3-cyclohexylurea) (XXXXI) and 1-cyclohexyl-3-(3-isocyanato-*p*-tolyl)urea (XXXXII), respectively. A possible mechanism for reaction (1) is discussed.

The discovery that 2-mercaptobenzothiazoles are accelerators for the vulcanization of rubber with sulfur[1,2] has stimulated many workers to prepare and extensively evaluate their derivatives. Among the many derivatives prepared and evaluated, the benzothiazolesulfenamide, in particular,

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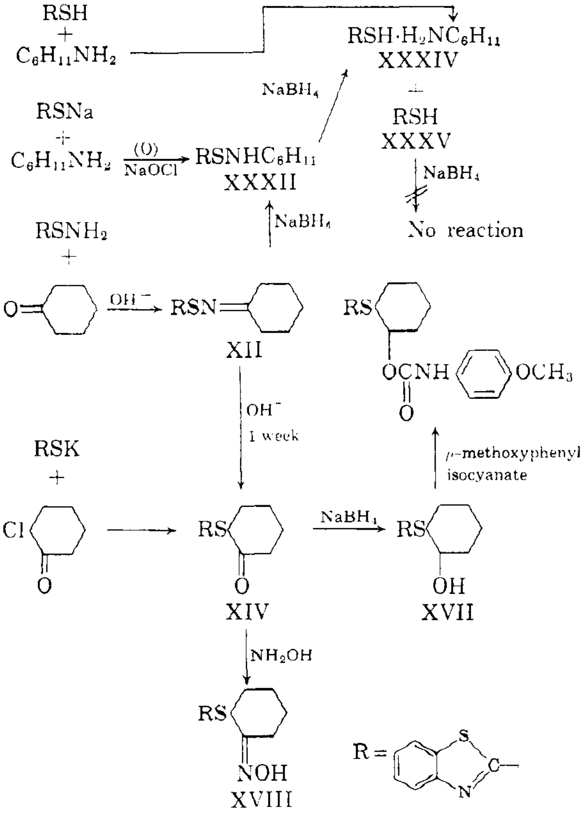
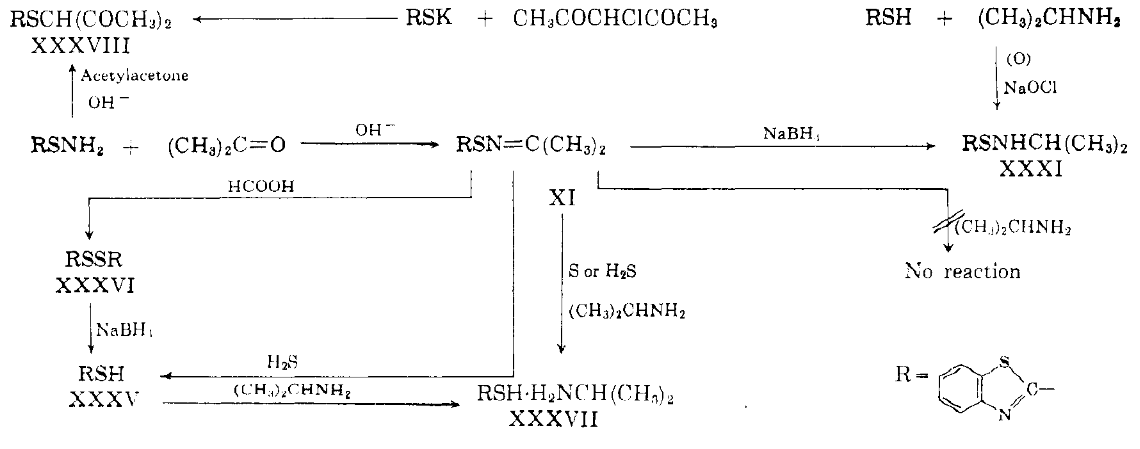
(1) C. W. Bedford and L. B. Sebrell, *Ind. Eng. Chem.*, **13**, 1034 (1921).

(2) G. Bruni and B. Romani, *Giorn. chim. ind. applicata*, **3**, 196 (1921).

2-(2,6-dimethylmorpholinothio)benzothiazole,[3] *N*-cyclohexyl-2-benzothiazolesulfenamide,[4] and *N*-*tert*-butyl-2-benzothiazolesulfenamide[5] have shown merit because of their delayed action properties. Thiazolesulfenamides have been prepared by the following methods: (1) Oxidative condensation of an amine with thiazolethiol; (2) reaction of chloroamine with thiazolethiol; (3) reaction of sulfenyl chloride with an amine; and (4) reaction of disulfide with an amine. The above methods possess the following inherent disadvantages: (1) an excess of amine must be employed and this necessitates that it be recovered in order to have an economical commercial process and (2) the thiazolesulfenamide in most cases contains impurities which accelerate their decomposition. Accordingly, it was desirable to discover a novel method to prepare thiazolesulfenamides with enhanced storage stability which avoids the use of amines.





J. A. Barltrop[6] reported the preparation of *N*-alkylidene- (or arylidene)benzothiazolesulfenamides by the reaction of 2-benzothiazolesulfenamide with an aldehyde or ketone under basic conditions. A further study of this reaction revealed that the yields of these compounds (I–XIII) were dependent upon the time of the heating period. Based on our study the following maximum yields were obtained: For *N*-(3,4-dimethoxybenzylidene)-2-benzothiazolesulfenamide (X), a poor yield (22.1%) was obtained and could not be improved by increasing or decreasing the ninety minute heating period.

Compounds	Heating Period, Minutes	Maximum, % Yield
I, II, III, XI	15	88.5–91.2
IV, VI, XII, XIII	30	69.0–87.3
V	60	84.4
VII, VIII, IX	150	96.0–97.0

If the reaction heating time of 2-benzothiazolesulfenamide, cyclohexanone and ethyl alcohol containing 2*N* sodium hydroxide was extended to one hour, followed by the addition of water and allowing the reaction mixture to stand for one week, the desired *N*-cyclohexylidene-2-benzothiazolesulfenamide (XII) was not obtained. The elemental analysis of the product isolated indicated an

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[3] J. J. D'Amico, M. W. Harman, and R. H. Cooper, *J. Am. Chem. Soc.*, **79**, 5270 (1957); U. S. Patent **2,871,239**. Commercially available under Monsanto trademark Santocure 26.

[4] M. W. Harman, *Ind. Eng. Chem.*, **29**, 205 (1937). U. S. Patent **2,191,656**. Commerically available under Monsanto tradename Santocure.

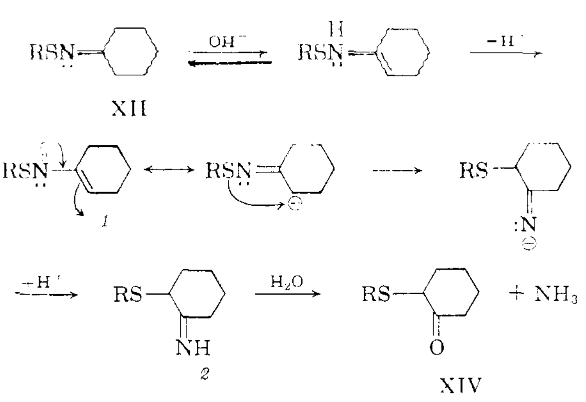
[5] R. H. Cooper and J. J. D'Amico, U. S. Patent **2,807,-620**. Commercially available under Monsanto trademark Santocure NS.

[6] J. A. Barltrop and K. J. Morgan, *J. Chem. Soc.*, 3072 (1957).

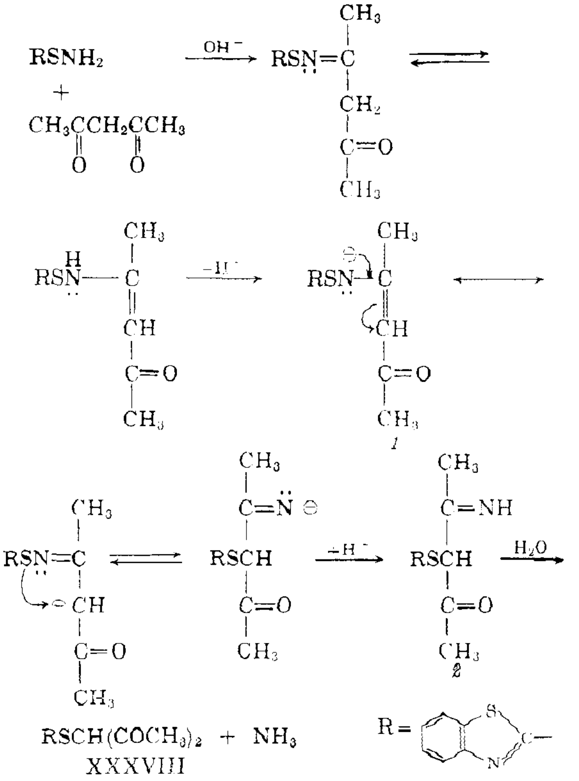
empirical formula of $C_{13}H_{13}NOS_2$ and the infrared spectra revealed the presence of benzothiazolylthio and carbonyl radicals and the absence of the $\text{—N=C}<$ group. It was also noted that the reaction mixture, upon standing, gave off ammonia. From this data, it was conceived that the product isolated could be 2-(2-oxocyclohexylthio)benzothiazole (XIV). Our postulate was substantiated by the fact that the reaction of the potassium salt of 2-mercaptobenzothiazole with 2-chlorocyclohexanone gave XIV. The mixture melting point of XIV derived from the two methods gave no depression and the infrared spectra of the two were superimposable. Additional proof of the structure was obtained by treating XIV, derived from either method, with sodium borohydride and hydroxylamine to give 2-(2-hydroxycyclohexylthio)-benzothiazole (XVII) and 2-(2-hydroxyiminocyclohexylthio)benzothiazole (XVIII), respectively. The presence of the hydroxyl radical in XVII was confirmed by the reaction of XVII with *p*-methoxyphenyl isocyanate to give 2-(benzothiazol-2-ylthio)-cyclohexyl *p*-methoxycarbanilate.

The reaction of 2-benzothiazolesulfenamide with 2,4-pentanedione in ethyl alcohol containing sodium hydroxide did not yield the *N*-alkylidenebenzothiazolesulfenamide but instead 2-diacetylmethylthiobenzothiazole (XXXVIII) was obtained in 46% yield. It has previously been reported[7] that the reaction of the potassium salt of 2-mercaptobenzothiazole with 3-chloro-2,4-pentanedione gave XXXVIII. The mixture melting point of XXXVIII derived from the two methods gave no depression and the infrared spectra of the two were superimposable.

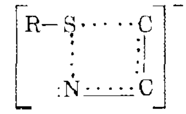
The following mechanisms are offered for these rearrangement reactions:



The initial prototropic shift is supported by the fact that the rearrangement occurs even more readily in the case:



Ammonia and amines normally give enamines rather than imines with β-diketones and in this case the enamine is analogous to 1. The rearrangement of 1 to 2 should occur with ease since sulfur is large and also has an empty *d*-orbital to attack the far end of the double bond. The proposed transition state appears reasonable. It should



be pseudoaromatic as there are six π electrons involved in the system of the dotted bonds and five atomic orbitals (four *p*-atomic orbitals and one *d*-atomic orbital of sulfur). In fact this proposed transition state is isoconjugated with the relatively stable cyclopentadienide anion which also has six π electrons.

The reduction of I–XIII with sodium borohydride in ethyl alcohol gave the benzothiazolesulfenamides (XXVI–XXXIII) in 76 to 99% yields. The mixture melting points of XXVI, XXXI, and XXXII with authentic samples gave no depression and the infrared spectra were in agreement with the proposed structures. The crude benzothiazolesulfenamides prepared by the oxidative condensation of the primary or secondary amine with the thiazolethiol are often contaminated with unreacted 2-mercaptobenzothiazole (XXXV), 2,2′-dithiobis-(benzothiazole) (XXXVI) and the amine salt of XXXV which accelerates their decomposition upon standing under ordinary conditions. The benzo-

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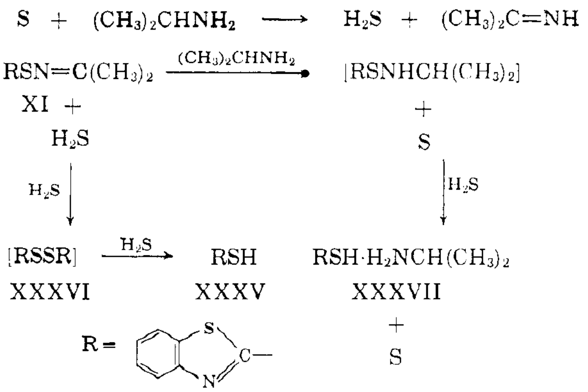
(7) J. J. D'Amico, U. S. Patent 2,772,277, Nov. 27, 1956.

thiazolesulfenamides prepared by this novel method were found to be stable up to three years at room temperature in shelf aging tests. This enhanced stability can be explained by the fact that the benzothiazolesulfenamides prepared by this new method are free of impurities. Under the basic conditions of the reduction reaction, the presence of XXXV, XXXVI, and amine salt of XXXV would be converted to sodium salt of XXXV which is water soluble and thus removed.

The reduction of *N*-cyclohexyl-2-benzothiazolesulfenamide (XXXII) with sodium borohydride gave cyclohexylamine salt of 2-mercaptobenzothiazole (XXXIV) and XXXV in 37.7% and 56.7% yields, respectively. The mixture melting point of XXXIV and XXXV with authentic samples gave no depression. In order to ascertain that sodium borohydride did not reduce XXXV, an experiment was conducted under the same condition as employed for XXXII. As expected, XXXV was recovered in theoretical yield upon acidification of the aqueous solution.

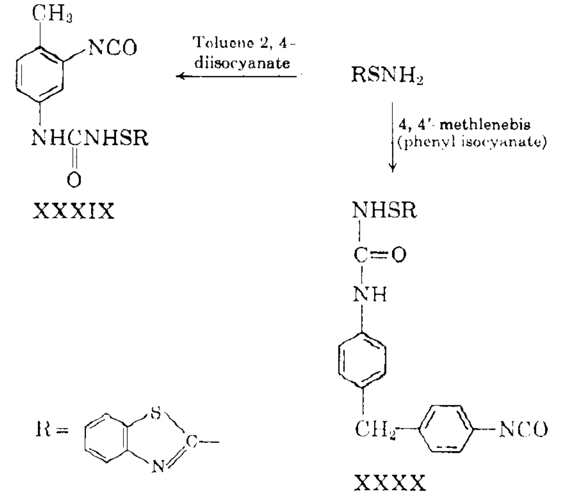
The attempted reduction of *N*-isopropylidene-2-benzothiazolesulfenamide (XI) with formic acid did not yield *N*-isopropyl-2-benzothiazolesulfenamide (XXXI) but instead XXXVI was isolated in 99.5% yield. Proof of structure was elucidated by reducing XXXVI to XXXV with sodium borohydride and the mixture melting point of XXXV and XXXVI with authentic samples gave no depression. It was not surprising that XXXVI was obtained in this reaction as it is an established fact that *N*-alkylidene-(or arylidene)benzothiazolesulfenamides[6] and sulfenamides[8,9] are known to be decomposed by acids into disulfide.

A. F. Hardman[10] reported the preparation of 2-(morpholinodithio)benzothiazole by the reaction of 2-(morpholinothio)benzothiazole with sulfur in a morpholine-ethyl alcohol media. It was anticipated that the reaction of XI with sulfur in an isopropylamine–ethyl alcohol solvent would yield 2-(isopropylideneaminodithio)benzothiazole but instead the isopropylamine salt of 2-mercaptobenzothiazole (XXXVII) was obtained in 79.6% yield. If hydrogen sulfide were substituted for sulfur in the above reaction the same product (XXXVII) was obtained in 62% yield. Proof of structure was elucidated by preparing XXXVII by reaction of isopropylamine with XXXV. A mixture melting point of XXXVII obtained by the three methods gave no depression and the infrared spectra of the three were superimposable. However, it was surprising to discover that the reaction of XI with only hydrogen sulfide in an ethyl alcohol solution furnished XXXV in 84% yield. A plausible explanation for these reduction reactions may be represented as follows:



In order to ascertain that XXXVII was not formed by the reaction of XI with isopropylamine an experiment was conducted employing these reactants and, as expected, XI was recovered in theoretical yield.

The reaction of 2-benzothiazolesulfenamide with toluene 2,4-diisocyanate or 4,4′-methylenebis-(phenyl isocyanate) furnished *N*-(3-isocyanato-*p*-tolylcarbamoyl) - 2 - benzothiazolesulfenamide (XXXIX) and *N*-[*p*-(*p*-isocyanatobenzyl)phenylcarbamoyl]-2-benzothiazolesulfenamide (XXXX), respectively. These reactions may be represented as:



However, when XXXII was substituted for 2-benzothiazolesulfenamide in the above reactions, the products isolated were 1-cyclohexyl-3-(3-isocyanoto-*p*-tolyl)urea (XXXXII) and 1,1′-(*p*-methylenediphenylene)bis(3 - cyclohexylurea) (XXXXI), respectively. Proof of structure was elucidated by treating cyclohexylamine with 4,4′-methylenebis(phenylisocyanate) to give XXXXI. This abnormal reaction can be explained on the basis that XXXII used in this experiment contained a very small amount of XXXV which catalyzed the

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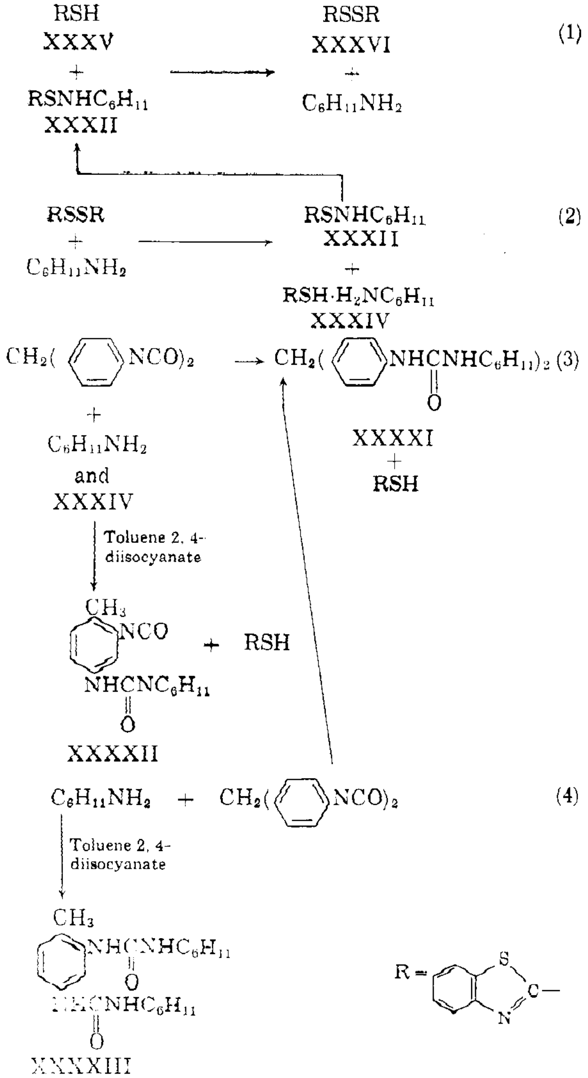
(8) M. L. Moore and T. B. Johnson, *J. Am. Chem. Soc.*, 57, 1517 (1935).

(9) M. L. Moore and T. B. Johnson, *J. Am. Chem. Soc.*, 58, 1091 (1936).

(10) A. F. Hardman, U. S. Patent 2,837,519.

formation of cyclohexylamine and XXXIV as illustrated by the following reactions:



The reaction of one or two moles of cyclohexylamine with one mole of toluene 2,4-diisocyanate did not yield XXXXII but instead 3,3′-(4-methyl-*m*-phenylene)bis(1-cyclohexylurea) (XXXXIII) was the product isolated.

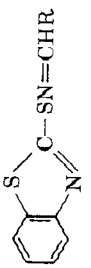
Ten benzothiazolesulfenamides (XXXXIV–LIII) were prepared by the oxidative condensation of XXXIV with the appropriate amine.

EXPERIMENTAL[11]

N-(Substituted benzylidene)-2-benzothiazolesulfenamide (I–X). A stirred slurry containing 100 g. (0.55 mole) of 2-benzothiazolesulfenamide, 72 g. (0.52 mole) of potassium carbonate, 500 ml. of ethyl alcohol and 0.55 mole of the appropriate aldehyde was heated to 70° over a 10-min. period. The stirred reaction mixture was maintained at 70–79° for the time period specified in Table I. After cooling to 25°, 1500 g. of ice water was added and stirring continued at 0–10° for 1 hr. The solid was collected by filtration, washed with water until the washings were neutral to litmus and air-dried at 25–30°. The data are summarized in Table I.

TABLE I

N-(SUBSTITUTED BENZYLIDENE)-2-BENZOTHIAZOLESULFENAMIDE



Compound	R	Time, Mins.	% Yield, Crude	M.P. Obtained	M.P. Reported	Empirical Formula	Nitrogen, % Calcd.	Nitrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found	Chlorine, % Calcd.	Chlorine, % Found
I	*m*-Nitrophenyl	15	91.2	184–185[a]	178–181[6]	$C_{14}H_9N_3O_2S_2$	—	—	20.34	20.35	—	—
II	2,4-Dichlorophenyl	15	89.5	147–148[b]	—	$C_{14}H_8Cl_2N_2S_2$	8.26	8.21	18.90	18.84	20.90	20.12
III	*p*-Chlorophenyl	15	88.5	157–158[b]	—	$C_{14}H_9ClN_2S_2$	9.19	9.25	21.04	21.01	11.63	11.52
IV	*o*-Chlorophenyl	30	83.5	108–109[c]	—	$C_{14}H_9ClN_2S_2$	9.19	9.20	21.04	21.05	11.63	11.65
V	3,4-Dichlorophenyl	60	84.4	178–180[a]	—	$C_{14}H_8Cl_2N_2S_2$	8.26	8.29	18.90	19.00	20.90	20.90
VI	Phenyl	30	69.0	116–118[c]	112[6]	$C_{14}H_{10}N_2S_2$	—	—	—	—	—	—
VII	4-Ethoxy-3-methoxyphenyl	150	96.5	118–119[c]	—	$C_{17}H_{16}N_2O_2S_2$	8.13	8.09	18.82	18.77	—	—
VIII	2,3-Dimethoxyphenyl	150	96.0	127–129[c]	—	$C_{15}H_{14}N_2O_2S_2$	8.48	8.50	19.41	19.45	—	—
IX	1,3-Benzodioxol-5-yl	150	97.0	165–166[d]	—	$C_{15}H_{10}N_2O_2S_2$	8.91	8.78	20.40	20.61	—	—
X	3,4-Dimethoxyphenyl	90	22.1	134–135[c]	—	$C_{16}H_{14}N_2O_2S_2$	8.48	8.36	—	—	—	—

[a] Recrystallization from benzene. [b] Recrystallization from ethyl alcohol and benzene. [c] Recrystallization from ethyl alcohol. [d] Recrystallization from ethyl acetate.

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[11] All melting points were taken upon a Fisher-Johns block and are uncorrected.

TABLE II

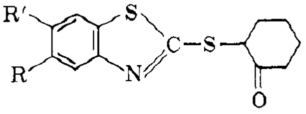
N-(ISOPROPYLIDENE, CYCLOHEXYLIDENE, OR CYCLOPENTYLIDENE)-2-BENZOTHIAZOLESULFENAMIDE

Compound	R	Reaction Conditions Temp.	Reaction Conditions Time, mins.	% Yield, Crude	M.P. Obtained	M.P. Reported	Empirical Formula	Nitrogen, % Calcd.	Nitrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found
XI	—C(CH$_3$)$_2$	60–70	15	89.1	133–134[a]	131[6]	$C_{10}H_{10}N_2S_2$	12.60	12.65	28.85	29.11
XII	—C$_6$H$_{10}$	70–72	30	71.9	106–107[a]	106–107[6]	$C_{13}H_{14}N_2S_2$	10.68	10.67	24.44	24.42
XIII	—C$_5$H$_8$	60–70	30	87.3	131–132[a]	131[6]	$C_{12}H_{12}N_2S_2$	—	—	—	—

[a] Recrystallization from ethyl alcohol.

TABLE III

2-(2-Oxocyclohexylthio)benzothiazole



Compound	R	R′	% Yield, Crude	M.P.	Empirical Formula	Nitrogen, % Calcd.	Nitrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found
XIV	H	H	89.5	92–93[a]	$C_{13}H_{13}NOS_2$	5.32	5.24	24.35	24.43
XV	Cl	H	90.0	92–93[b]	$C_{13}H_{12}ClNOS_2$	4.70	4.67	21.53	21.51
XVI	H	OC$_2$H$_5$	89.5	oil	$C_{15}H_{17}NO_2S_2$	4.56	4.54	20.86	20.22

[a] Recrystallization from ethyl alcohol. [b] Recrystallization from heptane.

N-(Isoproplyidene)-2-benzothiazolesulfenamide (XI) (*N-cyclohexylidene)-2-benzothiazolesulfenamide* (XII) *and N-(cyclopentylidene)-2-benzothiazolesulfenamide* (XIII). A stirred slurry containing 100 g. (0.55 mole) of 2-benzothiazolesulfenamide, 100 ml. of ethyl alcohol containing 30 ml. of 2*N* sodium hydroxide and 1 mole of acetone, cyclohexanone, or cyclopentanone was heated to 60° over a 10-min. period. The stirred reaction mixture was maintained at 60–72° for the time period specified in Table II. The stirred reaction mixture was cooled to 5° and the resulting solid was collected by filtration. The solid was washed with 100 ml. of cold ethyl alcohol and air-dried at 25–30°. The data are summarized in Table II.

2-(2-Oxocyclohexylthio)benzothiazole (XIV). A stirred mixture containing 100 g. (0.55 mole) of 2-benzothiazolesulfenamide, 58.8 g. (0.6 mole) of cyclohexanone and 400 ml. of ethyl alcohol containing 30 ml. of 2*N* sodium hydroxide was heated at 75–80° for 1 hr. After cooling to 5°, 400 ml. of cold water was added and stirring continued for 30 min. The reaction mixture was allowed to stand for 1 week. The resulting semisolid was filtered, washed with 200 ml. of heptane and air-dried on a porous plate at 25–30°. The product, m.p. 85–90°, was obtained in 79.1% yield. It melted at 92–93° after recrystallization from ethyl alcohol.

Anal. Calcd. for $C_{13}H_{13}NOS_2$: N, 5.32; S, 24.35. Found: N, 5.40; S, 24.27.

2-(2-Oxocyclohexylthio)benzothiazole (XIV), *2-(2-oxocyclohexylthio)-5-chlorobenzothiazole* (XV) *and 2-(2-oxocyclohexylthio-6-ethoxybenzothiazole* (XVI). To a stirred solution containing 0.5 mole of 97% 2-mercaptobenzothiazole, 5-chloro-2-mercaptobenzothiazole, or 6-ethoxy-2-mercaptobenzothiazole, 500 ml. of acetone, 10 ml. of water, and 33 g. (0.5 mole) of 85% potassium hydroxide was added 66.8 g. (0.5 mole) of 2-chlorocyclohexanone. The stirred reaction mixture was heated at 50–56° for 4 hr. For XIV and XV the cooled reaction mixture was added to 1000 g. of stirred ice water. After stirring for 1 hr. at 0–10°, the resulting solid was collected by filtration, washed with water until the washings were neutral to litmus, and air-dried at 25–30°. For XVI, to the cooled stirred reaction mixture 500 ml. of water and 400 ml. of ethyl ether were added. The ether layer was separated, washed with water until the washings were neutral to litmus, and dried over sodium sulfate. The ether was removed *in vacuo* at a maximum temperature of 90° at 1–2 mm. A mixture melting point of XIV derived from the rearrangement of XII and by the reaction of potassium 2-mercaptobenzothiazole with 2-chlorocyclohexanone gave no depression and the infrared spectra of the two were superimposable. The data are summarized in Table III.

2-(2-Hydroxycyclohexylthio)benzothiazole (XVII). *Method* I. To a stirred solution containing 10 g. (0.038 mole) of XIV (derived from the rearrangement of XII) in 100 ml. of ethyl alcohol was added dropwise at 65–70° a solution containing 1.45 g. (0.038 mole) of sodium borohydride in 100 ml. of ethyl alcohol over a 15-min. period. The stirred solution was heated at 70–78° for 1 hr. After cooling to 25°, the solution was added to 500 g. of ice water and stirred at 0–10° for 2 hr. The resulting solid was collected by filtration, washed with water until the washings were neutral to litmus and air-dried at 25–30°. The product, m.p. 78–81°, was obtained in 90.4% yield. After successive recrystallization from ethyl alcohol and heptane it melted at 88–90°.

Anal. Calcd. for $C_{13}H_{15}NOS_2$: N, 5.28; S, 24.17. Found: N, 5.35; S, 24.14.

Method II. This reaction was carried out in the same manner as described in Method I except 10 g. of XIV derived by the reaction of potassium 2-mercaptobenzothiazole and 2-chlorocyclohexanone was employed. The product m.p. 78–81°, was obtained in 89.3% yield. After successive recrystallization from ethyl alcohol and heptane it melted at 88–90°. A mixture melting point with the product obtained from Method I was not depressed and the infrared spectra of the two were superimposable.

Anal. Calcd. for $C_{13}H_{15}NOS_2$: N, 5.28; S, 24.17. Found: N, 5.26; S, 24.18.

2-(Benzothiazol-2-ylthio)cyclohexyl p-methoxycarbanilate. To a stirred mixture containing 26.5 g. (0.1 mole) of XVII in 300 ml. of heptane was added 14.9 g. (0.1 mole) of *p*-methoxyphenyl isocyanate. The stirred reaction mixture was heated at 80–90° for 6 hr. After cooling to 5°, the solid was collected by filtration and air-dried on a porous plate at 25–30°. The product, m.p. 122–128°, was obtained in 67.5% yield. After recrystallization from acetone ethyl alcohol it melted at 141–143°.

Anal. Calcd. for $C_{21}H_{22}N_2O_3S_2$: N, 6.76; S, 15.47. Found: N, 6.52; S, 15.50.

TABLE IV

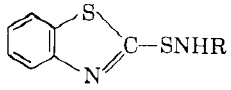
2-(2-HYDROXYIMINOCYCLOHEXYLTHIO)BENZOTHIAZOLE

Compound	R	R′	% Yield, Crude	M.P.	Empirical Formula	Nitrogen, % Calcd.	Nitrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found
XVIII	H	H	73.3	146–148[a]	$C_{13}H_{14}N_2OS_2$	10.06	9.64	23.04	22.96
XIX	Cl	H	76.9	186–187[a]	$C_{13}H_{13}ClN_2OS_2$	8.96	8.83	20.50	20.67
XX	H	OC_2H_5	80.5	139–141[a]	$C_{15}H_{18}N_2O_2S_2$	8.69	8.51	19.89	19.57

[a] Recrystallization from ethyl alcohol.

TABLE V

BENZOTHIAZOLESULFENAMIDES



Compound	R	% Yield, Crude	M.P.	Empirical Formula	Nitrogen, % Calcd.	Nitrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found	Chlorine, % Calcd.	Chlorine, % Found
XXI	*m*-Nitrobenzyl	96.0	86–88	$C_{14}H_{11}N_3O_2S_2$	13.24	13.21	—	—	—	—
XXII	2,4-Dichlorobenzyl	82.0	80–82[a]	$C_{14}H_{10}Cl_2N_2S_2$	8.21	8.27	18.79	18.92	—	—
XXIII	*p*-Chlorobenzyl	79.4	114–115[b]	$C_{14}H_{11}ClN_2S_2$	9.13	9.13	—	—	—	—
XXIV	*o*-Chlorobenzyl	85.0	62–63[a]	$C_{14}H_{11}ClN_2S_2$	9.13	9.08	—	—	—	—
XXV	3,4-Dichlorobenzyl	76.2	133–134	$C_{14}H_{10}Cl_2N_2S_2$	8.21	8.08	18.79	18.78	20.78	20.80
XXVI	Benzyl	90.2	119–120	$C_{14}H_{12}N_2S_2$	10.29	10.23	23.54	23.72	—	—
XXVII	4-Ethoxy-3-methoxybenzyl	83.7	80–82[b]	$C_{17}H_{18}N_2O_2S_2$	8.09	7.88	18.51	18.95	—	—
XXVIII	2,3-Dimethoxybenzyl	93.1	129–130[b]	$C_{16}H_{16}N_2O_2S_2$	8.43	8.42	19.29	19.54	—	—
XXIX	1,3-Benzodioxol-5-yl methyl	89.5	77–78[b]	$C_{15}H_{12}N_2O_2S_2$	8.85	8.78	20.27	20.16	—	—
XXX	3,4-Dimethoxybenzyl	82.0	126–127[b]	$C_{16}H_{16}N_2O_2S_2$	8.42	8.28	—	—	—	—
XXXI	Isopropyl	87.0	94–95	$C_{10}H_{12}N_2S_2$	12.49	12.26	28.59	28.55	—	—
XXXII	Cyclohexyl	99.0	102–103[b]	$C_{13}H_{16}N_2S_2$	10.60	10.65	24.26	24.15	—	—
XXXIII	Cyclopentyl	87.6	67–69[c]	$C_{12}H_{14}N_2S_2$	11.19	10.76	25.61	25.70	—	—

[a] Recrystallization from benzene. [b] Recrystallization from ethyl alcohol. [c] Recrystallization from heptane.

2-(2-Hydroxyiminocyclohexylthio)benzothiazole (XVIII), 5-chloro - 2 - (2 - hydroxyiminocyclohexylthio)benzothiazole (XIX), 6-Ethoxy-2-(2-hydroxyiminocyclohexylthio)benzothiazole (XX). A stirred slurry containing 0.2 mole of XIV, XV, or XVI and 400 ml. of ethyl alcohol was heated to 60°. To the cooled stirred solution was added in one portion a solution containing 16.4 g. (0.25 mole) of hydroxylamine hydrochloride in 50 ml. of water. A solution containing 13.3 g. (0.125 mole) of sodium carbonate in 60 ml. of water was added dropwise at 25-30° over a 15-min. period. The stirred reaction mixture was heated at 75-80° for 2 hr. and then cooled to 5°. For XVIII and XIX, the resulting solid was collected by filtration, washed with water until the wash water was neutral to litmus and air-dried at 25–30°. For XX, the ethyl alcohol was removed *in vacuo* and the cooled resulting residue was extracted with 400 ml. of ethyl ether. The ether solution was washed with water until the washings were neutral to litmus and dried over sodium sulfate. Upon removal of ether *in vacuo* a solid resulted which was air-dried at 25-30°. The data are summarized in Table IV.

Benzothiazolesulfenamides (XXI–XXXIII). *New method.* To a stirred slurry containing 0.2 mole of the appropriate *N*-alkylidene-(or arylidene)benzothiazolesulfenamides in 300 ml. of ethyl alcohol was added dropwise at 65–70° a solution containing 7.6 g. (0.2 mole) of sodium borohydride in 400 ml. of ethyl alcohol over a 30-min. period. The stirred solution was heated at 75-80° for 1 hr. After cooling to 25°, the reaction mixture was added to 1500 g. of stirred ice water. The reaction mixture was stirred at 0–10° for 1 hr. The solid was collected by filtration, washed with water until the washings were neutral to litmus and air-dried at 25–30°. Mixture melting points of XXVI, XXXI, and XXXII with authentic recrystallized samples were not depressed and infrared spectra were in agreement for the proposed structures. The data are summarized in Table V.

N-Cyclopentyl-2-benzothiazoleulfenamide (XXXIII). *Conventional method.* To a stirred solution containing 33.6 g. (0.2 mole) of 97% 2-mercaptobenzothiazole, 60 ml. of water, and 32 g. (0.2 mole) of 25% sodium hydroxide was added dropwise 68 g. (0.8 mole) of cyclopentylamine. After stirring for a period of 15 min., 33.6 ml. of 25% sulfuric acid solution was added dropwise over a period of 15 min. and stirring continued for another 15 min. Then 140 ml. (0.24 mole) of an aqueous solution of sodium hypochlorite (12.7 per 100 ml.) was added dropwise at 30–35° over a period of 1.5 hr. The stirred reaction mixture was maintained at these temperatures for an additional hour and then 2 g. of sodium sulfite was added to destroy the excess oxidizing agent. After cooling to 5°, 200 ml. of water and 300 ml. of ether were added and stirring continued for a period of 15 min. The ether solution was separated, washed successively with 200 ml. of 2% acetic acid, and finally with water until the wash water was neutral to litmus. The ether solution was dried over sodium sulfate and the ether removed *in vacuo* at a maximum temperature of 30°. The *N*-cyclopentyl-2-benzothiazolesulfenamide, m.p. 66–68°, was obtained in 99% yield. After recrystallization from dilute methyl alcohol it melted at 67–69° and a mixture melting point with a recrystallized sample obtained by the reduction of XIII was not depressed.

Anal. Calcd. for $C_{12}H_{14}N_2S_2$: S, 25.61. Found: S, 25.72.

Cyclohexylamine salt of 2-mercaptobenzothiazole (XXXIV) *and 2-mercaptobenzothiazole* (XXXV). To a stirred slurry containing 52.8 g. (0.2 mole) of XXXII in 300 ml. of ethyl alcohol was added dropwise at 65–70° a solution containing 7.6 g. (0.2 mole) of sodium borohydride in 250 ml. of ethyl alcohol over a 30-min. period. The stirred resulting solution was heated at 70–75° for 1 hr. After cooling to 25°, the solution was added dropwise to 1500 g. of ice water and stirred at 0–10° for 1 hr. The resulting solid was collected by filtration, washed with 100 ml. of water and air-dried at 25–30°. The product (XXXIV), m.p. 154–155° after recrystallization from ethyl acetate–ethyl alcohol, was obtained in 37.7% yield. A mixture melting point with an authentic sample obtained from the reaction of 2-mercaptobenzothiazole with cyclohexylamine gave no depression. To the stirred filtrate, concd. hydrochloric acid was added dropwise until a *p*H 4 was obtained. The resulting solid was collected by filtration, washed with water until the washings were neutral to litmus and air-dried at 25–30°. The product (XXXV), m.p. 180–181°, was obtained in 56.7% yield. A mixture melting point with an authentic recrystallized sample gave no depression.

Anal. XXXIV—Calcd. for $C_{13}H_{18}N_2S_2$: N, 10.52; S, 24.07. Found: N, 10.41; S, 24.28. XXXV—Calcd. for $C_7H_5NS_2$: N, 8.38; S, 38.34. Found: N, 8.27; S, 38.12.

Attempted reduction of XXXV. To a stirred solution containing 33.5 g. (0.2 mole) of XXXV in 300 ml. of ethyl alcohol was added at 65–70° a solution containing 7.6 g. (0.2 mole) of sodium borohydride in 250 ml. of ethyl alcohol over a 30 min. period. After heating the stirred solution at 75–80° for 1 hr., the cooled solution was added to 1500 g. of ice water. To the stirred, cooled solution, concentrated hydrochloric acid was added dropwise until a *p*H 3 was obtained. The resulting solid was collected by filtration, washed with water until the washings were neutral to litmus and air-dried at 25–30°. XXXV, m.p. 180–181°, was recovered in theoretical yield. A mixture melting point with an authentic sample gave no depression.

2,2'-Dithiobis(benzothiazole) (XXXVI). A stirred charge containing 43 g. (0.194 mole) of XI, 200 ml. of methyl alcohol and 45.5 g. (0.97 mole) of 98% formic acid was heated at reflux temperature for 3 hr. After cooling to 5°, 500 g. of ice water were added and stirring continued at 0–5° for 30 min. The solid was collected by filtration, washed with water until the washings were neutral to litmus, and air-dried at 25–30°. The product, m.p. 179–180° after recrystallization from benzene, was obtained in 99.5% yield. A mixture melting point with an authentic sample was not depressed.

Anal. Calcd. for $C_{14}H_8N_2S_4$: N, 8.43; S, 38.58. Found: N, 8.62; S, 38.50.

2-Mercaptobenzothiazole (XXXV). *Method* I. To a stirred slurry of 33.2 g. (0.1 mole) of XXXVI in 300 ml. of ethyl alcohol was added dropwise at 65–70° a solution containing 3.8 g. (0.1 mole) of sodium borohydride in 200 ml. of ethyl alcohol. The stirred reaction mixture was heated at 75–80° for 1 hr. After cooling to 25°, the solution was added to 1000 g. of ice water. To this stirred solution concentrated hydrochloric acid was added dropwise at 0–10° until a *p*H 3 was obtained. The solid was collected by filtration, washed with water until neutral to litmus and air-dried at 25–30°. The product, m.p. 180–181°, after recrystallization from ethyl alcohol, was obtained in 96% yield. A mixture melting point with an authentic sample gave no depression.

Anal. Calcd. for $C_7H_5NS_2$: N, 8.38; S, 38.34. Found: N, 8.82; S, 38.42.

Method II. Hydrogen sulfide was bubbled through a stirred mixture containing 44.5 g. (0.2 mole) of XI and 150 ml. of ethyl alcohol at 70–75° over a 1-hr. period. The resulting solution was heated at 75–80° for 1 hr. After cooling to −5°, the resulting solid was collected by filtration and air-dried at 25–30°. The product, m.p. 172–176°, was obtained in 84% yield. After recrystallization from ethyl alcohol it melted at 180–181°. A mixture melting point with product obtained from Method I or with an authentic sample gave no depression and infrared spectra of the two were superimposable.

Anal. Calcd. for $C_7H_5NS_2$: N, 8.38; S, 38.334. Found: N, 8.29; S, 38.29.

Isopropylamine salt of 2-mercaptobenzothiazole (XXXVII). *Method* I. A stirred slurry containing 44.5 g. (0.2 mole) of XI, 3.2 g. of sulfur, 70 g. of isopropylamine and 150 ml. of ethyl alcohol was heated at 70–75° for 2 hr. After cooling the stirred resulting solution to −5°, 300 ml. of heptane was added. The stirred reaction mixture was maintained at −5° for 2 hr. The resulting solid was collected by filtration, washed with 200 ml. of heptane, and air-dried at 25–30°. The product, m.p. 180–182°, was obtained in 79.6% yield. After recrystallization from ethyl alcohol it melted at 181–182°.

Anal. Calcd. for $C_{10}H_{14}N_2S_2$: S, 28.33. Found: S, 28.66.

Method II. To a stirred slurry at 5° containing 43 g. (0.25 mole) of 97% 2-mercaptobenzothiazole in 500 ml. of ethyl ether was added in one portion 17.7 g. (0.3 mole) of isopropylamine. The reaction mixture was stirred at 25–30° for 2 hr. The solid was collected by filtration and air-dried at 25–30°. The product, m.p. 179–181°, was obtained in 88.2% yield. After recrystallization from ethyl alcohol it melted at 181–182°. A mixture melting point with the product obtained by Method I gave no depression and the infrared spectra of the two were superimposable.

Anal. Calcd. for $C_{10}H_{14}N_2S_2$: N, 12.38; S, 28.33. Found: 11.98; S, 28.81.

Method III. Hydrogen sulfide was bubbled through a stirred mixture containing 44.5 g. (0.2 mole) of XI, 70 g. of isopropylamine and 150 ml. of ethyl alcohol at 50–70° over a 2-hr. period. After cooling the resulting stirred solution to −5°, 300 ml. of heptane were added. The stirred reaction mixture was held at −5° for 2 hr. The resulting solid was collected by filtration and air-dried at 25–30°. The product, m.p. 179–181°, was obtained in 62% yield. After recrystallization from ethyl alcohol it meted at 181–182°. A mixture melting point with product obtained by Method I or II gave no depression.

Anal. Calcd. for $C_{10}H_{14}N_2S_2$: N, 12.38. Found: N, 12.00.

2-Diacetylmethylthiobenzothiazole (XXXVIII). *Method* I. A stirred mixture containing 18.2 g. (0.1 mole) of 2-benzothiazolesulfenamide, 10 g. (0.1 mole) of 2,4-pentanedione, 150 ml. of ethyl alcohol and 10 drops of 25% sodium hydroxide was heated at 75–80° for 2 hr. During the first hour heating period, ammonia was being evolved. The reaction mixture was filtered at 75° in order to remove a small amount of impurities. The filtrate was poured into an evaporating dish and allowed to stand overnight. The residue was transferred to a porous plant and air-dried at 25–30°. The brown oily crystals (19.5 g.) were recrystallized from 50 ml. of ethyl alcohol. The product, m.p. 110–111°, was obtained in 46% yield.

Anal. Calcd for $C_{12}H_{11}NO_2S_2$: N, 5.28; S, 24.17. Found: N, 5.34; S, 24.41.

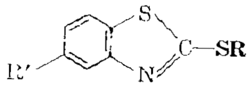
Method II. The product was obtained by the reaction of potassium 2-mercaptobenzothiazole with 3-chloro-2,4-pentanedione.[7] A mixture melting point with the product obtained from Method I was not depressed and the infrared spectra of the two were superimposable.

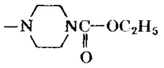
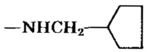
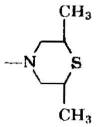
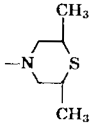
N-(3-Isocyanato-p-tolylcarbamoyl)-2-benzothiazolesulfenamide (XXXIX) *and N-[p-(p-isocyanatobenzyl)phenylcarbamoyl]-2-benzothiazolesulfenamide* (XXXX). To a stirred slurry containing 54.7 g. (0.3 mole) of 2-benzothiazolesulfenamide in 300 ml. of dry benzene was added in one portion 0.15 mole of toluene 2,4-diisocyanate or 4,4'-methylenebis(phenyl isocyanate). The stirred reaction mixture was heated at 40–45° for 7 hr. After cooling to 25°, the solid was collected by filtration, washed with 300 ml. of ethyl ether, and air-dried at 25–30°.

1,1'-(p-Methylenediphenylene)-bis(3-cyclohexylurea) (XXXXI). *Method* I. To a stirred slurry containing 43 g. (0.167 mole) of N-cyclohexyl-2-benzothiazolesulfenamide in 200 ml. of dry benzene was added in one portion 20.9 g. (0.084 mole) of 4,4'-methylenebis(phenyl isocyanate). The stirred reaction mixture was heated at 40–45° for 7 hr. The temperature of the stirred reaction mixture was raised to 75° in order to dissolve a small amount of disulfide. The

TABLE VI

BENZOTHIAZOLESULFENAMIDES (CONVENTIONAL METHOD)

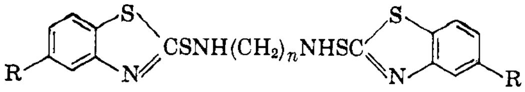


No.	R	R′	Amine	Mole Ratio Amine to Thiazole	Yield % Crude	M.P.	Empirical Formula	Nitrogen, % Calcd.	Nitrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found
XXXXIV		H	*N*-Carboethoxypiperazine	4:1	87.8	82–83[a]	$C_{14}H_{17}N_3O_2S_2$	12.99	13.00	—	—
XXXXV		H	Cyclopentylmethyl	1.4:1	88.5	44–46[a]	$C_{13}H_{16}N_2S_2$	10.59	10.52	24.26	24.04
XXXXVI		H	2,6-Dimethyl-1,4-thiazane	4:1	39.0	Semi solid	$C_{13}H_{16}N_2S_3$	9.45	9.05	32.45	32.45
XXXXVII		Cl	2,6-Dimethyl-1,4-thiazane	5:1	55.7	133–134[b]	$C_{13}H_{15}ClN_2S_3$	8.47	8.15	29.07	29.26

[a] Recrystallization from dilute ethyl alcohol. [b] Recrystallization from benzene.

TABLE VII

TRI-, TETRA-, AND HEXAMETHYLENEBIS(2-BENZOTHIAZOLESULFENAMIDES) (CONVENTIONAL METHOD)



No.	R	n	Amine	Mole Ratio Amine to Thiazole	% Yield, Crude	M.P.	Empirical Formula	Nitrogen, % Calcd.	Nitrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found
XXXXVIII	H	3	1,3-Propanediamine	5:1	77.5	106–107[a]	$C_{17}H_{16}N_4S_4$	13.85	13.43	31.70	31.67
XXXXIX	Cl	3	1,3-Propanediamine	6:1	84.5	170–172	$C_{17}H_{14}Cl_2N_4S_4$	11.83	11.92	—	—
L	H	4	1,4-Butanediamine	5:1	93.5	117–118[a]	$C_{18}H_{18}N_4S_4$	13.38	13.05	30.64	30.03
LI	Cl	4	1,4-Butanediamine	5:1	98.0	168–170	$C_{18}H_{16}Cl_2N_4S_4$	11.49	11.56	—	—
LII	H	6	1,6-Hexanediamine	5:1	45.0	66–68	$C_{20}H_{22}N_4S_4$	12.54	12.12	—	—
LIII	Cl	6	1,6-Hexanediamine	5:1	92.5	145–150[b]	$C_{20}H_{20}Cl_2N_4S_4$	10.87	11.40	—	—

[a] Recrystallization from ethyl alcohol. [b] Decomposed when attempted to recrystallize.

product was collected by a hot filtration and air-dried at 25–30°. The product, m.p. 330–332°, was obtained in 76.8% yield.

Compound	M.P.	Yield, %	Empirical Formula	Nitrogen, % Calcd.	Nitrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found
XXXIX	178–180	80.5	$C_{16}H_{12}N_4O_2S_2$	15.72	15.76	17.99	17.92
XXXX	225–227	69.5	$C_{22}H_{16}N_4O_2S_2$	12.96	12.97	14.83	14.73

Anal. Calcd. for $C_{27}H_{36}N_4O_2$: N, 12.49. Found: N, 12.18.

Method II. To a stirred solution containing 25 g. (0.1 mole) of 4,4′-methylenebis(phenyl isocyanate) in 300 ml. of dry benzene was added in one portion 19.9 g. (0.2 mole) of cyclohexylamine. The stirred reaction mixture was heated at 78–80° for 1 hr. After cooling to 25°, the solid was collected by filtration and air-dried at 25–30°. The product, m.p. 330–332, was obtained in 94% yield. A mixture melting point with the product obtained by Method I was not depressed.

Anal. Calcd. for $C_{27}H_{36}N_4O_2$: N, 12.49. Found: N, 12.40.

1-Cyclohexyl-3-(3-isocyanato-p-tolyl)urea (XXXXII). To a stirred cooled solution containing 51 g. (0.193 mole) of N-cyclohexyl-2-benzothiazolesulfenamide in 600 ml. of ethyl ether was added in one portion 16.8 g. (0.097 mole) of toluene 2,4-diisocyanate. The stirred reaction mixture was maintained at 25–30° for 24 hr. The resulting solid was collected by filtration, washed with 200 ml. of ethyl ether, and air-dried at 25–30°. The product, m.p. 167–169°, was obtained in 91% yield. After recrystallization from chloroform-acetate it melted at 168–169°.

Anal. Calcd. for $C_{15}H_{19}N_3O_2$: N, 15.37. Found: N, 15.16.

3,3′-(4-Methyl-m-phenylene)bis(1-cyclohexylurea) (XXXXIII). *Method* I. To a stirred solution containing 19.8 g. (0.2 mole) of cyclohexylamine in 150 ml. of heptane was added dropwise 17.4 g. (0.1 mole) of toluene 2,4-diisocyanate. The stirred reaction mixture was heated at 70–80° for 5 hr. After cooling to 25°, the solid was collected by filtration, washed with 100 ml. of benzene and air-dried at 25–30°. The product, m.p. 248–250°, was obtained in 96.8% yield.

Anal. Calcd. for $C_{21}H_{32}N_4O_2$: N, 15.04. Found: N, 14.85.

Method II. To a stirred cooled solution containing 17.4 g. (0.1 mole) of toluene 2,4-diisocyanate in 200 ml. of benzene 9.9 g. (0.1 mole) of cyclohexylamine was added dropwise at 10–20° over a 10-min. period. External cooling was removed and the reaction mixture was stirred at 25–30° for 1 hr. The solid was collected by filtration, washed with 100 ml. of benzene and air-dried at 25–30°. The product, m.p. 248–250°, was obtained in 96% yield. A mixture melting point with the product obtained by Method I was not depressed.

Anal. Calcd. for $C_{21}H_{32}N_4O_2$: N, 15.04. Found: N, 14.85.

Benzothiazolesulfenamide (XXXXIV–LIII). *Conventional method.* To a stirred aqueous slurry containing 0.25 mole of 2-mercaptobenzothiazole or 5-chloro-2-benzothiazole, 40 g. (0.25 mole) of 25% aqueous sodium hydroxide, and 50 ml. of water was added in one portion 0.35 to 1.5 mole of the appropriate amine. After stirring for 15 min., 42 ml. of 25% sulfuric acid was added dropwise. To the stirred reaction mixture was added drop by drop at 45–50° in 1.5 hr., 151 ml. (14.9 g./100 ml.) (0.30 mole) of aqueous sodium hypochlorite. The stirred reaction mixture was held at these temperatures for 1 hr. longer. The excess oxidizing agent was destroyed by the addition of 4 g. of sodium sulfite. For all compounds except XXXXIV, XXXXV and XXXXVI, 400 ml. of water was added and the stirred reaction mixture was cooled to 5°. The solid was collected by filtration, washed with water until the washings were neutral to litmus, and air-dried at 25–30°. For XXXXIV, XXXXV and XXXXVI, the cooled reaction mixture was extracted with 500 ml. of ethyl ether and was filtered to remove any disulfide. The ether extract was washed with water until the wash water was neutral to litmus and dried over sodium sulfate. The ether was removed *in vacuo* at a maximum temperature of 30°. The data are summarized in Tables VI and VII.

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