2-Substituted Thiobenzothiazole and Related Compounds. III.[1] The Rearrangement of 2,2'-Thiobis(benzothiazole) and Related Compounds

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The interconversion of 2,2'-thiobis(benzothiazole) (I) and 3-(2-benzothiazolyl)-2-benzothiazolinethione (II) has been shown to be an equilibrium reaction catalyzed by various catalysts, including 2-mercaptobenzothiazole. In studying this isomerization a by-product was obtained, identified as isosteric 3-(2-benzothiazolyl)-2-benzothiazolinone (III), and prepared by an alternate synthesis. The isomerization of 2-methylthiobenzothiazole (IV) to 3-methyl-2-benzothiazolinethione (V) was effectively *quenched* with 2-mercaptobenzothiazole. The reaction of IV with 2-chlorobenzothiazole gave I, II, and V as products. The various reactions are discussed and possible mechanisms are offered. Pertinent infrared data are presented.

In previous work[1] the synthesis of 2,2'-thiobis(benzothiazole) (I) by a new method was reported. Continued interest in the chemistry of I led us to a study of the rearrangement of this compound and related compounds. Teppema[2] prepared two "bis(benzothiazyl) sulfides," one melting at 98–99° (I)[1] and the other at 145°, by the reaction of 2-mercaptobenzothiazole (or its metal salt) with 2-chlorobenzothiazole. Teppema obtained the higher melting isomer at higher reaction temperatures (above 200°) and, in fact, stated that I is converted to its isomeric form by heating to 150° or above. We have reinvestigated the reaction of 2-mercaptobenzothiazole (or its sodium salt) with 2-chlorobenzothiazole at temperatures of 190–230° (Table I). A mixture of I and the higher melting isomer was the product, with the latter isomer generally in greater yield. The infrared spectrum of the higher melting product is consistent with the structure for the rearranged isomer, 3-(2-benzothiazolyl)-2-benzothiazolinethione (II). When 5-chloro-2-mercaptobenzothiazole and 2,5-dichlorobenzothiazole were the reactants, 2,2'-thiobis(5-chlorobenzothiazole) (Ia)[1] and 3-[2-(5-chlorobenzothiazolyl)]-5-chloro-2-benzothiazolinethione (IIa) were the products.

The analyses of the crude products in Table I were determined by vapor phase chromatography. In the course of this work, it was discovered that 2-mercaptobenzothiazole was catalyzing the isomerization of I to II, or II to I, during the chromatographic analysis. It was impossible to analyze by v.p.c. either I or II in the presence of 2-mercaptobenzothiazole, without limited conversion to the other isomer (II or I, respectively) during the brief time of the analysis. This important fact made it necessary to eliminate 2-mercaptobenzothiazole, by extraction with base, from all samples for v.p.c. analysis. In fact, it was desirable to exclude 2-mercaptobenzothiazole from the v.p.c. system altogether, since some of this material tended to remain on the column for some time and caused undesirable isomerization during later analyses.

As a result of the discovery that 2-mercaptobenzothiazole catalyzes the interconversion of I and II, a systematic study of the isomerization of I and II was made using various catalysts and reaction temperatures and a reaction time of 5 hr. The effect of temperature on the uncatalyzed isomerization was also studied. The results are summarized in Table II. It may be noted in Table II that the uncatalyzed rearrangement was almost negligible below 200°; at 225°, 11.5% of I was converted to II in 5 hr. Using a 1:10 mole ratio of catalyst to I, the catalytic effect of 2-mercaptobenzothiazole is readily seen by comparing the uncatalyzed and catalyzed reactions. The uncatalyzed rearrangement at 175° in 5 hr. gave only 0.6% of II whereas the catalyzed rearrangement gave 41.8% of II at the same temperature and reaction time. Other catalysts equivalent to 2-mercaptobenzothiazole were the sodium salt of 2-mercaptobenzothiazole, *p*-bromothiophenol, and trifluoroacetic acid. Iodine and 2-chlorobenzothiazole, although active as catalysts, were not so effective as 2-mercaptobenzothiazole.

The rearrangement of II to I was carried out in the presence of 2-mercaptobenzothiazole at 225° for 5 hr. and gave essentially the same equilibrium product ratio of I to II as the comparable rearrangement of I. Increase in the ratio of 2-mercaptobenzothiazole to I increased the rate of isomerization (Table II). The reaction is believed to be a first-order reversible equilibrium reaction and a detailed study of the kinetics is anticipated for a future publication.

In view of the knowledge that 2-mercaptobenzothiazole, and also 2-chlorobenzothiazole to a lesser extent, is a catalyst for interconversion of I and II, the results in Table I should be reviewed. The reactants, 2-mercaptobenzothiazole and 2-chlorobenzothiazole, catalyze the isomerization at the temperatures used. The use of excess 2-mercaptobenzothiazole should be noted since this ensured the presence of catalyst after all 2-chlorobenzothiazole had reacted, and thereby gave in the 5-hr. reaction period either a higher conversion to II or a faster attainment of equilibrium.

The rearrangement of Ia in the presence of 5-chloro-2-mercaptobenzothiazole at 225° gave essentially a quantitative yield of the rearranged isomer (IIa). In this reaction no solvent was used and the reaction mixture soon became impossible to stir because of the separation of IIa. The anticipated equilibrium mixture of Ia and IIa was not obtained and no unreacted Ia was recovered. Presumably, the equilibrium was driven to completion by the separation of IIa from the reaction medium. It should be noted in Table I that a mixture of Ia and IIa resulted from the reaction of 2,5-dichlorobenzothiazole with excess 5-chloro-2-mercaptobenzothiazole in decalin. The products remained in solution in the latter reaction.

(1) (a) Paper I: J. J. D'Amico, S. T. Webster, R. H. Campbell, and C. E. Twine, *J. Org. Chem.*, **30**, 3618 (1965); (b) paper II: J. J. D'Amico, R. H. Campbell, S. T. Webster, and C. E. Twine, *ibid.*, **30**, 3625 (1965).

(2) J. Teppema, U. S. Patent 2,028,082 (1936).

TABLE I

REACTION OF 2-MERCAPTOBENZOTHIAZOLES WITH 2-CHLOROBENZOTHIAZOLES

Compd.	X	M	Mole ratio A:B	Solvent	Temp., °C.	% Yield crude	M.p., °C. (crude)	V.p.c. analysis of crude product: Wt. % I or Ia	Wt. % II or IIa	% yield I or Ia	% yield II or IIa	Recrystallized product (II or IIa): M.p., °C.	Formula	% N: Calcd.	% N: Found	% S: Calcd.	% S: Found
I, II	H	H	1.25:1	None	225–230	99.0	121–123	23.6	76.4	23.4	75.6	146–147[a]	$C_{14}H_8N_2S_3$	9.33	9.34	32.03	32.06
I, II	H	H	1.35:1	Decalin	190–200	98.0	115–120	41.3	58.7	40.5	57.5	146–147[b]	$C_{14}H_8N_2S_3$	9.33	9.31	32.03	32.14
I, II	H	Na	1.35:1	Decalin	190–200	99.0	105–116	50.5	49.5	50.0	49.0	146–147[c]	$C_{14}H_8N_2S_3$	9.33	9.25	32.03	31.98
Ia, IIa	Cl	H	1.35:1	Decalin	190–200	97.0	240–245	23.0	77.0	22.3	74.7	287[d]	$C_{14}H_6Cl_2N_2S_3$	7.59	7.29	26.05	25.96
I, II	H	H	1.35:1	1,2-Bis(2-methoxyethoxy)ethane	225–230	100.0	110–115	26.6	73.4	26.6	73.4	146–147[a]	$C_{14}H_8N_2S_3$	9.33	9.12	32.03	32.04

[a] First recrystallization from ethyl alcohol. Second recrystallization from ethyl acetate. [b] Two recrystallizations from ethyl alcohol. [c] Three recrystallizations from ethyl alcohol. [d] Recrystallization from dimethylformamide. *Anal.* Calcd.: Cl, 19.20. Found: Cl, 19.01.

In the course of studying the isomerization of I to II with various catalysts, a small amount of by-product [subsequently identified as 3-(2-benzothiazolyl)-2-benzothiazolinone (III)] was observed upon v.p.c. analysis of the products. The elution time of III was slightly less than that of I. Very small amounts of III were detected in reactions catalyzed by trifluoroacetic acid or sodium 2-mercaptobenzothiazole, or in 2-mercaptobenzothiazole-catalyzed reactions which had extended reaction times (Table II). In the latter case, where samples of the reaction mixture were analyzed at various time intervals, the appearance of III seemed to coincide with attainment of equilibrium. Also in Table II it may be noted that catalytic amounts of concentrated sulfuric acid or *p*-toluenesulfonic acid gave considerably larger yields (32.6 and 39.7%, respectively) of III. These observations were considered together with an additional experiment in which equimolar amounts of I and concentrated sulfuric acid were heated to 135° for 1.5 hr. to yield 2-hydroxybenzothiazole as the major product (63% yield). II and III were also products of the latter reaction, and a quantity of III sufficient for an infrared spectrum was collected at the exit port of the chromatograph. The infrared spectrum of III indicated the presence of a carbonyl group and an *ortho*-substituted phenyl group. From the infrared spectrum of III and a knowledge of the reactants and products of the latter reaction, it was postulated that III might be 3-(2-benzothiazolyl)-2-benzothiazolinone, an isostere of II. The latter compound, previously unreported in the literature, was prepared in good yield by the reaction of anhydrous sodium 2-hydroxybenzothiazole with 2-chlorobenzothiazole in dimethylformamide or dimethyl sulfoxide. Elemental analysis, molecular weight, and the infrared spectrum of the product were in agreement with 3-(2-benzothiazolyl)-2-benzothiazolinone. Moreover, the infrared spectra of the latter product and by-product III were superimposable.

An attempt to prepare III by air oxidation of isosteric II at 225° gave only 0.7% of III in 24 hr., along with 14.6% of I and recovered II.

Since 2-mercaptobenzothiazole proved to be such an effective catalyst for the isomerization of I (and II), it was desirable to know if this catalytic effect was general for other 2-substituted thiobenzothiazoles. Table III summarizes the results of a study of the isomerization of 2-methylthiobenzothiazole (IV) with various catalysts at 150 and 225° for a 5-hr. reaction time. As other workers[3] have found, very little isomerization occurred while simply heating IV alone at 150°. However, the heating of IV at 225° gave 78.5% 3-methyl-2-benzothiazolinethione (V). Iodine was the only substance employed which gave isomerization to V greater than that obtained by simply heating IV alone. Moreover, 2-mercaptobenzothiazole effectively *quenched* the isomerization. Using a 1:10 molar ratio of 2-mercaptobenzothiazole to IV, only 7.5% of V was obtained at 225°. Small amounts of I and II were found in the latter product, but 88% of unreacted IV was recovered (Table III).

(3) J. M. Sprague and A. H. Land, "Heterocyclic Compounds," Vol. 5, R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1957. p.567.

TABLE II

ISOMERIZATION OF 2,2'-THIOBIS(BENZOTHIAZOLE)

$$I \rightleftharpoons II$$

Catalyst	Mole ratio, catalyst:I	Temp., ±5°	Time, hr.	Crude product,[a] v.p.c. analysis, wt. %[b] I	Crude product,[a] v.p.c. analysis, wt. %[b] II	Recrystallized product,[c,d] m.p., °C.
None		150	5	99.3	0.7	102–103[e,f]
2-Mercaptobenzothiazole	0.1	150	5	86.7	13.3	101-102.5[e]
None		175	5	99.4	0.6	102–103[e,f]
2-Mercaptobenzothiazole	0.1	175	5	58.2	41.8	149–151[g]
2-Mercaptobenzothiazole	0.1	175[h]	24	35.6	64.4	146–150[g]
			48	26.7	73.3	
			120	19.1	79.4[i]	
None		200	5	98.1	1.9	101–102[e,f]
2-Mercaptobenzothiazole	0.1	200	5	41.5	58.5	148–149.5[g]
None		225	2.5	92.6	7.4	101–102[e]
None		225	5	88.5	11.5	100–103[e]
2-Mercaptobenzothiazole	0.1	225	5	24.4	75.6	144.5–146.5[g]
2-Mercaptobenzothiazole	0.1	225[h]	0.17[j]	66.8	33.2	145–149[g]
			0.5	43.9	56.1	
			1.17	32.8	67.2	
			3.17	25.6	74.4	
			5.0	24.9	74.2[k]	
			24.0	23.3	72.1[l]	
2-Mercaptobenzothiazole	1.0	225	0.4	24.7	75.3	*m*
2-Mercaptobenzothiazole	1.0	225	5	20.9	79.1	144.5–148.5[g]
Sodium salt of 2-mercaptobenzothiazole	0.1	225	5	21.0	78.0[n]	147–148[g]
None		250	5	73.9	26.1	101–103[e]
2-Mercaptobenzothiazole	0.1	250	5	28.4	71.6	147–148[g]
Iodine	0.04	225	5	72.6	27.4	101–102[e]
2-Chlorobenzothiazole	0.1	225	5	72.8	27.2	101–102[e]
p-Bromothiophenol	0.1	225	5	20.1	73.6[o]	148.5–149.5[g]
CF_3COOH	0.1	225	5	21.1	69.8[p]	147–148[g]
Concd. H_2SO_4	0.1	225	5	22.9	44.5[q]	*m*
p-Toluenesulfonic acid	0.1	225	5	16.2	44.1[r]	*m*

[a] Essentially quantitative yields of crude product were obtained. [b] All samples for v.p.c. analysis were routinely dissolved in chloroform and extracted two times with 3 *N* sodium hydroxide solution. This procedure ensured the removal of 2-mercaptobenzothiazole, which catalyzed the interconversion of I and II to a small extent in the v.p.c. system under the conditions of analysis. [c] A part of the crude product was recrystallized to obtain either II or I in the pure state. I was isolated in those reactions which gave limited isomerization to II. Ethanol, ethyl acetate, and ethanol–ethyl acetate were used for recrystallization. [d] *Anal.* Calcd. for $C_{14}H_8N_2S_3$: N, 9.33; S, 32.03. Found: N, 8.96–9.38; S, 31.68–32.24. [e] A mixture melting point with an authentic sample of I was not depressed, and the infrared spectra of the two were superimposable. [f] The crude product was not recrystallized. [g] A mixture melting point with an authentic sample of II was not depressed, and the infrared spectra of the two were superimposable. [h] These results are from a single experiment during which samples were removed for analysis. Only a final sample was recrystallized. [i] Contained 1.6% of III. [j] 13 min. was required for the reaction to reach 225°. [k] Contained 1.0% of III. [l] Contained 4.7% of III. [m] Crude product was not purified. [n] Contained 1.0% of III. [o] Contained 6.3% of unidentified product. [p] Contained 9.1% of III. [q] Contained 32.6% of III. [r] Contained 39.7% of III.

TABLE III

ISOMERIZATION OF 2-METHYLTHIOBENZOTHIAZOLE

$$IV \longrightarrow V$$

Catalyst	Mole ratio, catalyst:III	Temp., ±5°	Crude product,[a,b] v.p.c. analysis, wt. % IV	V	I	II	Recrystallized product,[c,d] m.p., °C.
None		150	98.0	2.0			45–46[e,f]
2-Mercaptobenzothiazole	1:10	150	98.6	1.0	0.4		44–45[e,f]
None		225	21.5	78.5			89–91[g,h]
2-Mercaptobenzothiazole	1:10	225	88.0	7.5	2.7	1.9	43–45.5[e,i]
2-Mercaptobenzothiazole	1:1	225	81.4	12.6	2.9	3.0	42–44[e,i]
CF_3COOH	1:10	225	22.7	77.3			92–93[g,h]
Iodine	1:75	225	7.6	92.4			92–93[g,h]

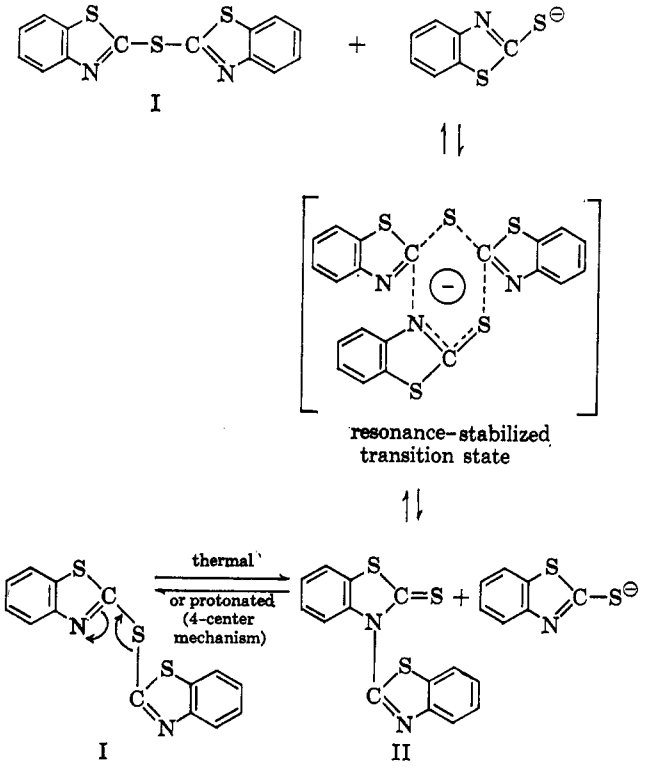
[a] Essentially quantitative yields of crude product were obtained. [b] All samples for v.p.c. analysis were dissolved in chloroform and extracted twice with 3 *N* sodium hydroxide solution. [c] A portion of the crude product was recrystallized to obtain either V or IV in pure state. IV was isolated in those reactions which gave limited isomerization to V. [d] *Anal.* Calcd. for $C_8H_7NS_2$: N, 7.73; S, 35.38. Found: N, 7.51–8.07; S, 35.19–35.55. [e] A mixture melting point with an authentic sample of IV was not depressed, and the infrared spectra of the two were superimposable. [f] Recrystallized from heptane. [g] A mixture melting point with an authentic sample of V was not depressed, and the infrared spectra of the two were superimposable. [h] Crude product was stirred with concentrated hydrochloric acid according to the method of W. H. Davies and W. A. Sexton [*J. Chem. Soc.*, 304 (1942)] to remove IV. The insoluble solid (V) was collected, washed neutral with water, and recrystallized from ethanol. [i] Crude product was dissolved in ether and extracted with 3 *N* sodium hydroxide solution. The ether extract was evaporated *in vacuo* and the resulting solid was recrystallized from heptane.

Attempts to rearrange I or IV to II or V, respectively, by heating the compound with a catalytic amount of dicumyl peroxide at 150° gave a quantitative recovery of starting material in each case.

The reaction of IV with 2-chlorobenzothiazole gave I as the major product (48.4% yield) along with lesser amounts of II (10.5% yield) and V (35.7% yield).

The mechanisms offered for the interconversion of I and II are illustrated in Chart I. The thermal (uncatalyzed) rearrangement of I is relatively slow when compared to the rearrangement of I catalyzed by *p*-bromothiophenol or trifluoroacetic acid. A four-center mechanism for the acid-catalyzed rearrangement of I is feasible, and a protonated intermediate might facilitate the breaking of old bonds and the formation of new bonds in the transition state. Four-center reactions should not require acid catalysis, but may be subject to such catalysis.[4]

CHART I



Fully aware that the mechanism proposed for the acid-catalyzed rearrangement of I might suffice for the 2-mercaptobenzothiazole-catalyzed interconversion of I and II, we have nevertheless chosen to consider this catalyst as a special case. The uniqueness of the 2-mercaptobenzothiazole moiety is supported by the fact that sodium 2-mercaptobenzothiazole is equally effective as a catalyst. A mechanism for the interconversion of I and II, catalyzed by the thiobenzothiazolyl anion, is shown in Chart I. A resonance-stabilized transition state involving a planar six-membered ring is postulated. The transition state, after the appropriate shifting of electrons, will yield either I or II, along with regeneration of the catalyst. The regenerated thiobenzothiazolyl anion, as shown in Chart I, is not necessarily the same anion moiety used initially to catalyze the interconversion. This postulate is supported by an experiment in which I was heated at 225° with an equimolar amount of 5-chloro-2-mercaptobenzothiazole; Ia, II, and IIa were among the products. Also, the reaction of I and 5-chloro-2-mercaptobenzothiazole at 110–120° in dimethylformamide was reported previously[1] to give a mixture of the three unrearranged thioethers, I, Ia, and 2-(5-chlorobenzothiazolyl)thiobenzothiazole.

Only limited work was done to elucidate the mechanism for the formation of by-product III during the isomerization of I with various catalysts. Previous workers[5] converted V to its isostere, 3-methyl-2-benzothiazolinone, with either mercuric oxide or bromine water. However, the reaction of II with these reagents did not furnish III. Surveys[6,7] of the literature on thiones indicate that thio ketones (such as thiobenzophenone) are quite easily converted to ketones by air oxidation, or by hydrolysis when boiled in aqueous acid or base. With the assumption that thione II, which is isosteric with III, might be an intermediate in the formation of III from I, an attempt to convert II to III by air oxidation at 225° was carried out, but gave only 0.7% of III. Thus II is not readily oxidized to III under these conditions, and air oxidation of II can explain only those reactions (Table II) in which very low yields of III were observed. A plausible explanation for the formation of III from II would be the addition of the acid (sulfuric acid, trifluoroacetic acid, and *p*-toluenesulfonic acid) to the thiocarbonyl group of II followed by the loss of the thio acid derivative ($H_2S_2O_3$, F_3CCOSH, p-$CH_3C_6H_4SO_2SH$). Similar oxythiol-type compounds have been considered previously[8] as intermediates in the hydrolysis of thiones. Determination of the fate of the isomerization catalysts should afford further insight into the mechanism of this reaction.

The isomerization of IV to V has been studied rather extensively.[9–15] Various mechanisms have been suggested and these involve (1) the formation of 2-alkylthio-3-alkylbenzothiazolium halide salts as intermediates[9,11]; (2) heterolytic fission of the C–S bond to give the thiobenzothiazolyl anion and methyl carbonium ion[10]; and (3) decomposition of an initially formed sulfonium salt.[14,15] Although Wheatley's[16] work on the molecular structure of IV would allow a four-center type mechanism to be operable in the isomerization of IV, a preponderance of evidence supports a benzothiazolium salt intermediate for the isomerization. This type of mechanism, although originally applied to the isomerization of IV by means of alkyl halides, seems quite applicable when the isomerization is effected thermally or with iodine (Chart II). The benzothiazolium cation may exist as an ion pair along

(4) J. Hine, "Physical Organic Chemistry," 2nd Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 505.

(5) W. Mills, L. Clark, and J. Aeschlimann, *J. Chem. Soc.*, **123**, 2362 (1923).

(6) E. Campaigne, *Chem. Rev.*, **39**, 1 (1946).

(7) E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. III, Chemical Publishing Co., Inc., New York, N. Y., 1960, p. 148.

(8) E. Campaigne, "Organic Sulfur Compounds," Vol. 1, N. Kharasch, Ed., Pergamon Press Inc., New York, N. Y., 1961, p. 134.

(9) K. J. Morgan, *J. Chem. Soc.*, 854 (1958).

(10) C. G. Moore and E. S. Waight, *ibid.*, 4237 (1952).

(11) D. J. Fry and J. D. Kendall, *ibid.*, 1716 (1951).

(12) W. A. Sexton, *ibid.*, 471 (1939).

(13) F. P. Reed, A. Robertson, and W. A. Sexton, *ibid.*, 473 (1939).

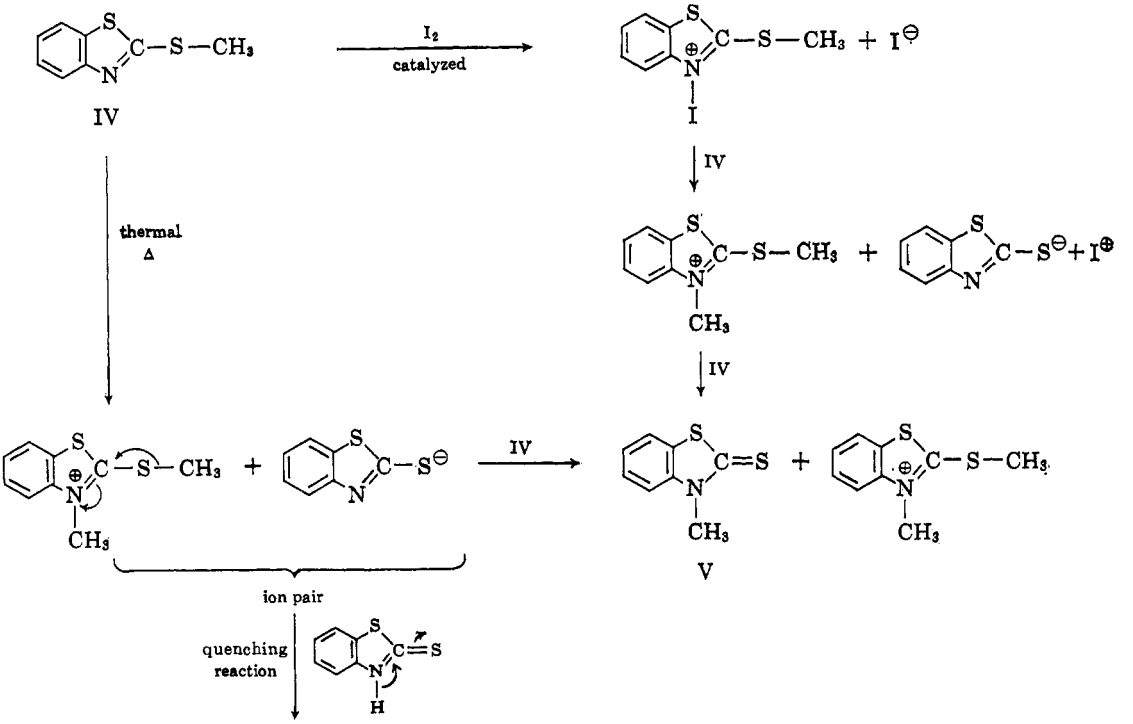
(14) W. H. Davies and W. A. Sexton, *ibid.*, 304 (1942).

(15) F. G. Mann and J. Watson, *J. Org. Chem.*, **13**, 502 (1948).

(16) P. J. Wheatley, *J. Chem. Soc.*, 3636 (1962).

CHART II

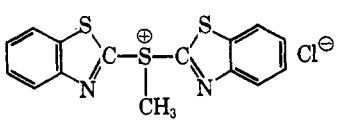
REARRANGEMENT OF 2-METHYLTHIOBENZOTHIAZOLE AND QUENCHING EFFECT OF 2-MERCAPTOBENZOTHIAZOLE



2-mercaptobenzothiazole, IV and V

with the resonance-stabilized thiobenzothiazolyl anion. Assuming then that the 2-methylthio-3-methylbenzothiazolium ion is the effective catalyst and chain-carrying alkylating agent, destruction of this intermediate would stop the rearrangement. The quenching effect of 2-mercaptobenzothiazole upon the isomerization of IV may be conveniently explained by the reaction of the benzothiazolium catalyst (ion pair) with 2-mercaptobenzothiazole to give IV and V with regeneration of 2-mercaptobenzothiazole (Chart II). It may be noted that a small amount of V was found in the reaction quenched with 2-mercaptobenzothiazole.

Since rearrangement conditions prevailed in the reaction of IV with 2-chlorobenzothiazole, V would be expected as a major product. A quite plausible explanation for the formation of I and II is shown in Chart III. 2-Chlorobenzothiazole reacts with either IV or V in a manner similar to alkyl halides to give 2-substituted thio-3-benzothiazolium salts, which can react with either IV or V to give II and I, respectively. Formation of a sulfonium salt intermediate would



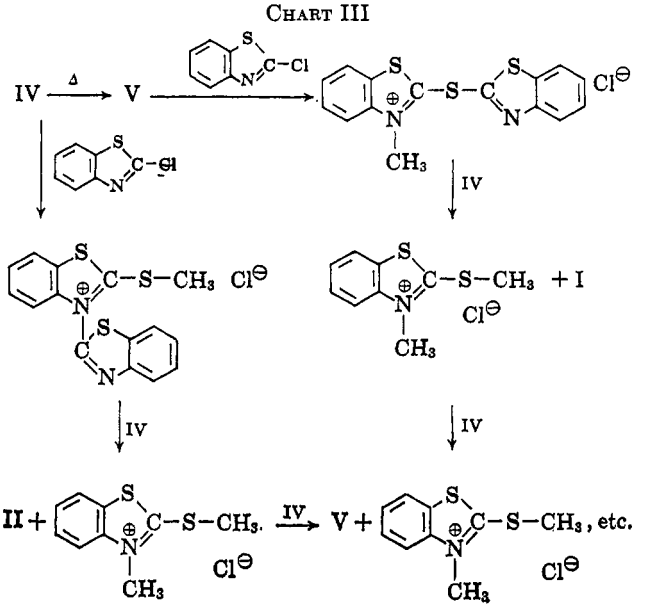
explain product II, but recent work[9] with dialkyl salts of IV favors 2-alkyl-3-alkylthiobenzothiazolium structures and transalkylation mechanisms.

Experimental Section[17]

Analytical Methods.—Vapor phase chromatographic analyses of I–V were done with an F & M Model 720 dual-column pro-

(17) All melting points were taken upon a Fisher-Johns block and are uncorrected.

CHART III



grammed-temperature gas chromatograph. A 0.25 × 24 in. stainless steel column packed with 15% SE-30 silicone rubber on Gas Chrom CL, 45–60 mesh (flow rate of helium, 100 cc./min.), was operated isothermally at 180, 260, and 300° and programmed from 140 to 300° at 20°/min. All samples containing 2-mercaptobenzothiazole and 5-chloro-2-mercaptobenzothiazole were dissolved in chloroform and extracted three times with dilute sodium hydroxide solution before chromatographic analysis. Chloroform was suitable for the preparation of chromatographic samples for all compounds except IIa, for which dimethylformamide was used. The data were rendered quantitative by the use of *p*-terphenyl as an internal standard.

The infrared spectra of II and III were obtained from solutions in chloroform (5000 to 830 cm.$^{-1}$) and dimethylformamide (830 to 650 cm.$^{-1}$). Because of insolubility, the infrared spectrum of IIa was obtained from Nujol and halocarbon mulls. A Perkin-Elmer Model 21 spectrophotometer with a sodium chloride prism was used.

2,2′-Thiobis(benzothiazole) (I) and 3-(2-Benzothiazolyl)-2-benzothiazolinethione (II). Method I.—A stirred mixture containing 42.5 g. (0.25 mole) of 99% 2-mercaptobenzothiazole and 34 g. (0.2 mole) of 2-chlorobenzothiazole was heated at 225–230° for 5 hr. At the end of this heating period the hot liquid was poured into a glass dish and allowed to stand overnight. The resulting solid was added to 500 ml. of water containing 40 g. (0.25 mole) of 25% aqueous sodium hydroxide and stirred for 1 hr. The solid was collected by filtration, washed with water until neutral to litmus, and air dried at 45°. The infrared spectrum of II contained bands at 1460, 1328, 1308, and 767 cm.$^{-1}$. The data are summarized in Table I.

I and II or 2,2′-Thiobis(5-chlorobenzothiazole) (Ia) and 3-[2-(5-Chlorobenzothiazolyl)]-2-(5-chlorobenzothiazolinethione) (IIa). Method II.—A stirred mixture containing 0.27 mole of either 2-mercaptobenzothiazole (or its sodium salt) or 5-chloro-2-mercaptobenzothiazole, 0.2 mole of 2-chlorobenzothiazole or 2,5-dichlorobenzothiazole, and 300 ml. of decalin or 1,2-bis(2-methoxyethoxy)ethane was heated for 5 hr. at the temperatures specified in Table I. After cooling to 60°, 500 ml. of water containing 48 g. (0.3 mole) of 25% aqueous sodium hydroxide was added in one portion. After stirring at 25–30° for 1 hr., the solid was collected by filtration, washed with water until the washings were neutral to litmus, and air dried at 45°. A mixture melting point of II derived from the two methods was not depressed, and the infrared spectra of the two were superimposable. The infrared spectrum of IIa contained bands at 1492, 1415, 1312, 870, and 846 cm.$^{-1}$. The data are summarized in Table I.

II *via* Isomerization of I.—A stirred solution containing 30.0 g. (0.10 mole) of I and the quantity of catalyst specified in Table II was heated at a constant (±5°) temperature as specified in Table II. In most cases the reaction time was 5 hr. [However, in two of the runs samples for v.p.c. analysis were removed during the course of the reaction at other time intervals (see Table II) and the reaction time was also extended.] At the end of the reaction the hot liquid was poured into a Pyrex dish and allowed to stand overnight. The resulting solid was stirred with dilute sodium hydroxide solution for 1 hr. in order to remove catalyst. The insoluble material was collected by filtration, washed with water until neutral, and air dried at room temperature. The crude product was analyzed by v.p.c. and purified by recrystallization as summarized by the data in Table II.

Ia, II, and IIa *via* Isomerization of I with 5-Chloro-2-mercaptobenzothiazole.—A stirred mixture containing 0.1 mole of I and 0.1 mole of 5-chloro-2-mercaptobenzothiazole was heated at 225 ± 5° for 5 hr. The hot liquid was poured into a Pyrex dish and allowed to stand overnight. The treatment of this crude product with dilute sodium hydroxide for 1 hr. removed 2-mercaptobenzothiazole and its 5-chloro homolog. The insoluble material was collected by filtration, washed with water until neutral, and air dried at 25–30°. The crude product was analyzed by v.p.c. and found to contain 6.7, 46.9, 40.1, and 6.4 wt. % of I (recovered), Ia, II, and IIa, respectively.

I *via* Isomerization of II.—A stirred solution containing 30.0 g. (0.1 mole) of II and 1.67 g. (0.01 mole) of 2-mercaptobenzothiazole was heated at 225 ± 1° for 6 hr. Samples for v.p.c. analysis were removed at various intervals of time during the course of the reaction. After 3-hr. reaction time the reaction mixture was essentially equilibrated and the composition did not change appreciably thereafter. Chromatographic analysis of the final product showed it to be 20.2% I, 79.1% II, and 0.7% 3-(2-benzothiazolyl)-2-benzothiazolineone (III). III began to appear as equilibrium was reached. Fractional recrystallization of the crude product from ethyl acetate–ethanol, removing II by successive evaporation of the mother liquor, gave I, m.p. 101–102°. A mixture melting point with an authentic sample of I was not depressed, and the infrared spectra of the two were superimposable.

IIa. Isomerization of Ia.—A stirred mixture of 24.5 g. (0.066 mole) of Ia and 1.34 g. (0.0066 mole) of 5-chloro-2-mercaptobenzothiazole was heated at 225 ± 5° for 5 hr. The product solidified during the reaction. A quantitative yield of crude product was obtained; v.p.c. analysis showed it to be entirely IIa with no recovered Ia present. Two recrystallizations of the crude product from dimethylformamide gave white crystals, m.p. 286–287°. A mixture melting point with a sample of IIa, prepared as in Table I, was not depressed, and the infrared spectra of the two were superimposable.

Anal. Calcd. for $C_{14}H_6Cl_2N_2S_3$: Cl, 19.20; N, 7.59; S, 26.05. Found: Cl, 19.47; N, 7.54; S, 25.95.

3-(2-Benzothiazolyl)-2-benzothiazolinone (III).—To a stirred solution of 69.3 g. (0.4 mole) of anhydrous sodium 2-hydroxybenzothiazole in 300 ml. of dimethylformamide, 66 g. (0.39 mole) of 2-chlorobenzothiazole was added in one portion. The stirred solution was heated at 150–160° for 5 hr. After cooling to 40°, the resulting precipitate was added to 1000 g. of ice–water containing 64 g. (0.4 mole) of 25% aqueous sodium hydroxide. After stirring at 25–30° for 1 hr., the precipitate was collected, washed with water until the washings were neutral to litmus, and air dried at 45°. The crude product, m.p. 149–152°, was obtained in 86.5% yield. Recrystallization from ethyl acetate raised the melting point to 159–160°, and the vapor phase chromatogram of the recrystallized sample had only one peak. The infrared spectrum of III contained bands at 1723, 1675, 1510, 1335, 1308, and 763 cm.$^{-1}$.

Anal. Calcd. for $C_{14}H_8N_2OS_2$: N, 9.85; S, 22.55; mol. wt., 284.4. Found: N, 9.71; S, 22.71; mol. wt., 290.

With the use of the same procedure as above and the same charge except for the substitution of 300 ml. of dimethyl sulfoxide for dimethylformamide, the crude product, m.p. 145–148°, was obtained in 84.5% yield. Recrystallization from ethyl acetate raised the melting point to 159–160°.

Anal. Found: N, 9.72; S, 22.45.

Reaction of I and Concentrated Sulfuric Acid. Identification of By-product III.—A stirred mixture of 30.04 g. (0.1 mole) of I and 10.3 g. (0.1 mole) of 95.5% sulfuric acid was heated to 135° during 18 min. The stirred solution was maintained at 135 ± 5° for 1.5 hr. and then poured (hot) into a Pyrex dish. The reaction mixture, on cooling, crystallized to a cream-yellow solid (35 g.). A portion of the product was dissolved in chloroform and exhaustively extracted with 1.0 *N* sodium hydroxide solution. Acidification of the caustic extract gave a white precipitate, the infrared spectrum of which was superimposable with that of 2-hydroxybenzothiazole. The crude product contained 63 wt. % of 2-hydroxybenzothiazole. The chloroform solution was concentrated and subjected to v.p.c. analysis, which indicated the presence of I, II, and III. An amount of III sufficient for an infrared spectrum was collected at the exit port of the v.p.c. instrument. The infrared spectra of by-product III and 2-(2-benzothiazolyl)-2-benzothiazolinone prepared from anhydrous sodium 2-hydroxybenzothiazole and 2-chlorobenzothiazole by the above method were superimposable.

3-Methyl-2-benzothiazolinethione (V). Isomerization of 2-Methylthiobenzothiazole (IV).—A stirred solution containing 36.3 g. (0.20 mole) of IV and the quantity of catalyst specified in Table III was heated at either 150 ± 5 or 225 ± 5° for 5 hr. At the end of the heating period the hot liquid was poured into a Pyrex dish and allowed to stand overnight. The resulting solid, or semisolid, was analyzed by v.p.c. and purified by recrystallization as summarized by the data in Table III.

Reaction of IV with 2-Chlorobenzothiazole.—A stirred solution of 54.3 g. (0.30 mole) of IV and 52.5 g. (0.31 mole) of 2-chlorobenzothiazole was heated at 225–230° for 5 hr. The hot reaction mixture was poured into a Pyrex dish and allowed to stand overnight. The crude product, 84 g. of low-melting solid (paste), was analyzed by v.p.c. and was found to contain 51.9 wt. % of I (48.4% yield), 11.2 wt. % of II (10.5% yield), 23.1 wt. % V (35.7% yield), 6.6 wt. % of recovered IV (10.2% recovery), and 7.2 wt. % of recovered 2-chlorobenzothiazole (13.2% recovery). The pasty product was recrystallized twice from ethanol, m.p. 101–102°. A mixture melting point with an authentic sample of I was not depressed and the infrared spectra of the two were superimposable.

Anal. Calcd. for $C_{14}H_8N_2S_3$: N, 9.33; S, 32.03. Found: N, 9.13; S, 31.94.

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