meyer reports m.p. 188°), only when α-chlorocyclopentanone was condensed with ammonium dithiocarbamate at 100° (12 mm.) for 30 min. Recrystallization of the solid residue from ethanol gave the product in 24% yield. *Anal.* Calcd. for $C_6H_7NS_2$: N, 8.90. Found: N, 9.07.

SUMMIT, N. J.

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

Derivatives of Thiazolethiols

BY JOHN J. D'AMICO, MARION W. HARMAN AND R. H. COOPER

RECEIVED APRIL 10, 1957

The following compounds were prepared: (1) nine acetylenic derivatives of thiazolethiols; (2) three 2,2′-bis-(chloroalkenylthio)-6,6′-bibenzothiazoles; (3) six 2-mercaptobenzothiazole derivatives of esters of acetoacetic and levulinic acids; (4) four 5-substituted 4-methyl-2-thiazolyl diethyldithiocarbamates; (5) three 1,4-bis-[2-benzothiazolylthiomethyl)-*trans*-2,5-dimethylpiperazines; (6) 2,2′-(2-butenylenedithio)-bisbenzothiazole and 2-(4-chloro-2-butenylthio)-benzothiazole; (7) three 2-(2-carbamoylethylthio)-benzothiazoles; (8) N-(3-chloro-2-butenyl)-cyclohexylamine, N-isopropylallylamine, N-isopropyl-2-propynylamine, 2-chloro-N-isopropylallylamine, 2-chloro-N-(3-methoxypropyl)-allylamine; and (9) forty-four thiazolesulfenamides. The derivatives of thiazolethiols have been prepared for testing as accelerators for the vulcanization of rubber and their evaluation will be reported in another paper. Two thiazolesulfenamides, 5-carbethoxy-4-methyl-2-thiazolesulfenamide and 5-acetyl-4-methyl-2-thiazolesulfenamide were still stable after two years. All previous thiazolesulfenamides prepared by the oxidative condensation of thiazolethiols with ammonia are unstable.

The discovery that 2-mercaptobenzothiazoles are accelerators for the vulcanization of rubber with sulfur[1,2] has stimulated many workers[3-7] to prepare and extensively evaluate their derivatives. Among the many derivatives screened, the thiazolesulfenamides, in particular, N-cyclohexyl-2-benzothiazolesulfenamide[3] and N-*t*-butyl-2-benzothiazolesulfenamide, have shown merit because of their delayed action.

The purpose of this investigation was the preparation of new thiazolesulfenamides and derivatives of thiazolethiols. A second objective was to determine whether the structure modification enhanced the accelerator activity, in particular, the desired delayed action characteristic. This evaluation will be reported in another paper.

The acetylenic derivatives of thiazolethiols (I–IX) were prepared by the reaction of the sodium salt of the thiazolethiol in an aqueous solution with 3-bromo-1-propyne. An aqueous solution of the sodium salt of 2,2′-dimercapto-6,6′-bibenzothiazole reacted with 1,3-dichloro-2-butene, 2,3-dichloro-1-propene or 1,3-dichloropropene to form the 2,2′-bis-(chloroalkenylthio)-6,6′-bibenzothiazoles (X–XII). The 2-mercaptobenzothiazole derivatives of esters of acetoacetic and levulinic acids and 3-(2-benzothiazolylthio)-2,4-pentanedione (XIII–XVIII) were prepared by treating the potassium salt of 2-mercaptobenzothiazole in an acetone solution with the following halogen compounds: ethyl α-chloroacetoacetate, ethyl β-bromolevulinate, butyl α-chloroacetoacetate, ethyl γ-chloroacetoacetate, methyl α-chloroacetoacetate and 3-chloro-2,4-pentanedione.

The 5-substituted 4-methyl-2-thiazolyl diethyldithiocarbamates (XIX–XXII) were prepared by the reaction of the sodium salt of the thiazolethiol with N,N-diethylthiocarbamoyl chloride.

The reaction of 2-mercaptobenzothiazole, 5-chloro-2-mercaptobenzothiazole or 6-ethoxy-2-mercaptobenzothiazole with *trans*-2,5-dimethylpiperazine and formaldehyde gave 1,4-bis-(2-benzothiazolylthiomethyl)-*trans*-2,5-dimethylpiperazines (XXIII–XXV).

The reaction of the sodium salt of 2-mercaptobenzothiazole with 1,2-dichloro-3-butene gave both the 2,2′-(2-butenylenedithio)-bisbenzothiazole (XXVI) and 2-(4-chloro-2-butenylthio)-benzothiazole (XXVII) by allylic rearrangement. The same products were obtained by the reaction of the sodium salt of 2-mercaptobenzothiazole with 1,4-dichloro-2-butene.[8]

An aqueous solution of sodium 2-mercaptobenzothiazole, 6-ethoxy-2-mercaptobenzothiazole or 5-chloro-2-mercaptobenzothiazole reacted with acrylamide to give 2-(2-carbamoylethylthio)-benzothiazoles (XXVIII–XXX).

N-(3-Chloro-2-butenyl)-cyclohexylamine was prepared by the reaction of cyclohexylamine with 1,3-dichloro-2-butene. The reaction of allyl chloride, 3-bromo-1-propyne or 2,3-dichloro-1-propene with isopropylamine furnished N-isopropylallylamine, N-isopropyl-2-propynylamine and 2-chloro N-isopropylallylamine, respectively. 2-Chloro-N-(3-methoxypropyl)-allylamine was obtained by the reaction of 3-methoxypropylamine with 2,3-dichloro-1-propene.

The thiazolesulfenamides (XXXI–LXXIV) were prepared by the oxidative condensation of a primary, secondary amine or ammonia with thiazolethiol or by the reaction of the disulfide with the amine. Sodium hypochlorite or iodine was employed as the oxidizing agent. In some of the preparations a considerable excess of amine was used to ensure that the desired thiazolesulfenamide would be obtained. This excess probably would not be necessary if optimum conditions of temperature, concentration, *p*H and time of reaction

(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).

(3) M. W. Harman, *Ind. Eng. Chem.*, **29**, 205 (1937); U. S. Patent 2,191,656.

(4) E. W. Carr, U. S. Patents 2,381,384 and 2,393,507.

(5) G. E. P. Smith, U. S. Patent 2,560,021.

(6) W. J. S. Naunton, W. Baird and H. M. J. Bunbury, *J. Soc. Chem. Ind. (London)*, **53**, 127 (1934).

(7) L. B. Sebrell and C. E. Boord, *Ind. Eng. Chem.*, **15**, 1009 (1923).

(8) J. J. D'Amico, THIS JOURNAL, **75**, 681 (1953).

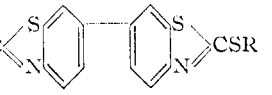
TABLE I

ACETYLENIC DERIVATIVES OF THIAZOLETHIOL, $RCH_2C{\equiv}CH$

No.	R	Yield, % crude	M.p., °C.	Empirical formula	Nitrogen, % Calcd.	Nitrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found
I	5-Chloro-2-benzothiazolylthio-	86.5	70–71[a]	$C_{10}H_6ClNS_2$	5.84	5.97	26.75	26.71
II	6-Ethoxy-2-benzothiazolylthio-	98.8	85–86	$C_{12}H_{11}NOS_2$	5.62	5.66	25.72	25.75
III	2,2′-Bibenzothiazolylthio-	95.8	184–186[b]	$C_{20}H_{12}N_2S_4$	6.86	6.86	31.39	31.10
IV	5-Ethoxycarbonyl-4-methyl-2-thiazolylthio-	98.0	50–51[a]	$C_{10}H_{11}NO_2S_2$	5.80	6.12	26.57	26.69
V	5-Methoxycarbonyl-4-methyl-2-thiazolylthio-	83.7	79–80[a]	$C_9H_9NO_2S_2$	6.16	6.44	28.21	28.40
VI	5-Acetyl-4-methyl-2-thiazolylthio-	91.0	65–66[a]	$C_9H_9NOS_2$	6.63	6.62	30.35	30.29
VII	2-Benzothiazolylthio-	89.7	Oil	$C_{10}H_7NS_2$	6.82	6.89	31.24	31.38
VIII	4-Methyl-2-benzothiazolylthio-	94.7	Oil	$C_{11}H_9NS_2$	6.39	6.37	...	...
IX	4-Methyl-2-thiazolylthio-	91.4	Oil	$C_7H_7NS_2$	8.27	8.36	37.88	38.09

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

TABLE II

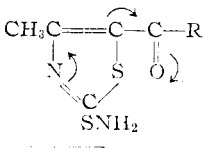
2,2′-BIS-(CHLOROALKENYLTHIO)-6,6′-BIBENZOTHIAZOLE RSC  CSR

No.	R	Yield, % crude	M.p., °C.	Empirical formula	Nitrogen, % Calcd.	Nitrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found	Chlorine, % Calcd.	Chlorine, % Found
X	$CH_2CH{=}CClCH_3$	94.5	148–149[a]	$C_{22}H_{18}Cl_2N_2S_4$	5.50	5.59	25.17	25.13	13.92	13.60
XI	$CH_2CCl{=}CH_2$	89.7	113–114[a]	$C_{20}H_{14}Cl_2N_2S_4$	5.82	5.88	26.64	26.23	...	...
XII	$CH_2CH{=}CHCl$	96.7	109–110[a]	$C_{20}H_{14}Cl_2N_2S_4$	5.82	6.12	26.64	26.61	14.73	14.19

[a] Recrystallization from ethyl acetate.

were determined. The oxidative condensation of *trans*-2,5-dimethylpiperazine with 2-mercaptobenzothiazole gave the expected 1,4-bis-(2-benzothiazolylthio)-*trans*-2,5-dimethylpiperazine (XXXI). However, substitution of 5-chloro-2-mercaptobenzothiazole for 2-mercaptobenzothiazole gave 1-(5-chloro-2-benzothiazolylthio)-*trans*-2,5-dimethylpiperazine (XXXV). The reaction of 1,8-diaminomenthane with 2-mercaptobenzothiazole or 5-chloro-2-mercaptobenzothiazole did not give the expected bis derivatives. The sulfur and chlorine analyses obtained were in good agreement for the mono derivatives. The reaction could occur in the 1- or 8-position of the amine, the former position being favored because of less steric hindrance.

A literature search revealed that no stable thiazolesulfenamide has been prepared from a thiazolethiol and ammonia. This is very desirable from an economic standpoint. The use of inexpensive 4,5-dimethylthiazolesulfenamide[9] as an accelerator has been limited because of its instability. It decomposes upon standing under ordinary conditions over a one-week period. However, the 5-carbethoxy-4-methyl-2-thiazolesulfenamide (LXXIII) and 5-acetyl-4-methyl-2-thiazolesulfenamide (LXXIV) were still stable after two years. This increased stability probably can be explained by the presence of electron-withdrawing groups on the 5-position of the thiazolethiol ring which would stabilize the sulfur–nitrogen bond.



R = CH_3 or OC_2H_5

(9) E. L. Carr, *et al.*, U. S. Patent 2,445,722.

Experimental[10]

Acetylenic Derivatives of Thiazolethiol (I–IX).—To a stirred solution containing 1.0 mole of either 5-chloro-2-mercaptobenzothiazole, 6-ethoxy-2-mercaptobenzothiazole, 2,2′-dimercapto-6,6′-bibenzothiazole (0.5 mole), alkyl 2-mercapto-4-methyl-5-thiazolecarboxylate,[11] 2-mercapto-4-methyl-5-thiazolyl methyl ketone,[11] 2-mercaptobenzothiazole, 4-methyl-2-mercaptobenzothiazole or 4-methyl-2-thiazolethiol,[12] 160 g. (1.0 mole) of 25% sodium hydroxide and 1000 ml. of water was added 119 g. (1.0 mole) of 3-bromo-1-propyne.[13] The reaction mixture was stirred for 5 hr. For I–VI, the solid was filtered, washed with water until the washings were neutral to litmus and air-dried at 35°.

For VII–IX, the reaction mixture was extracted with 500 ml. of ethyl ether. The ether solution was washed with 400 ml. of 2% aqueous sodium hydroxide solution, then with water until the washings were neutral to litmus. The ether solution was dried over sodium sulfate and the ether was removed *in vacuo*. The data are summarized in Table I.

2,2′-Bis-(chloroalkenylthio)-6,6′-bibenzothiazole (X–XII).—A solution containing 0.1 mole of 2,2′-dimercapto-6,6′-bibenzothiazole was prepared by dissolving 33.2 g. of the mercaptobenzothiazole in 32 g. (0.2 mole) of 25% aqueous sodium hydroxide and 250 ml. of water. To this stirred solution 0.2 mole of either 1,3-dichloro-2-butene,[14] 2,3-dichloro-1-propene[15] or 1,3-dichloropropene[15] was added. The reaction mixture was stirred for 20 hr. The solid was collected by filtration, washed with water until the wash water was neutral to litmus and dried at 50°. The data are summarized in Table II.

2-Mercaptobenzothiazole Derivatives of Esters of Acetoacetic and Levulinic Acids and 3-(2-Benzothiazolylthio)-2,4-pentanedione (XIII–XVIII).—A solution of potassium 2-mercaptobenzothiazole was prepared by mixing 86.2 g. (0.5 mole) of 97% 2-mercaptobenzothiazole, 28.1 g. (0.5 mole) of potassium hydroxide, 1500 ml. of acetone and 22 g. of

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

(11) J. J. D'Amico, THIS JOURNAL, **75**, 102 (1953).

(12) R. A. Mathes, U. S. Patent 2,186,421.

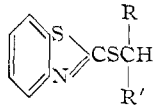
(13) Kindly furnished by General Aniline and Film Corporation, New York, N. Y.

(14) Kindly furnished by E. I. du Pont de Nemours and Co., Wilmington, Del.

(15) Kindly supplied by Shell Chemical Corp., Emeryville, Calif.

TABLE III

2-MERCAPTOBENZOTHIAZOLE DERIVATIVES OF ESTERS OF ACETOACETIC AND LEVULINIC ACIDS AND 3-(2-BENZOTHIAZOLYLTHIO)-2,4-PENTANEDIONE

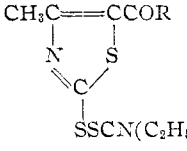


No.	R	R′	Yield, % crude	M.p., °C.	Empirical formula	Nitrogen, % Calcd.	Nitrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found
XIII	$COCH_3$	$COOC_2H_5$	90.0	Oil	$C_{13}H_{13}NO_3S_2$	4.74	4.77	21.70	21.95
XIV	$COCH_3$	$CH_2COOC_2H_5$	93.0	Oil	$C_{14}H_{15}NO_3S_2$	4.53	4.47	20.73	20.50
XV	$COCH_3$	$COOC_4H_9$	80.0	Oil	$C_{15}H_{17}NO_3S_2$	4.33	4.46	19.83	20.18
XVI	H	$COCH_2COOC_2H_5$	80.2	Oil	$C_{13}H_{13}NO_3S_2$	4.74	4.73	21.70	22.00
XVII	$COCH_3$	$COOCH_3$	98.0	108–109[a]	$C_{12}H_{11}NO_3S_2$	4.98	5.00	22.79	22.92
XVIII	$COCH_3$	$COCH_3$	95.9	104–105[a]	$C_{12}H_{11}NO_2S_2$	5.28	5.49	24.17	23.98

[a] Recrystallization from ethyl alcohol.

TABLE IV

5-SUBSTITUTED-4-METHYL-2-THIAZOLYL DIETHYLDITHIOCARBAMATE



No.	R	Yield, % crude	M.p., °C.	Empirical formula	Nitrogen, % Calcd.	Nitrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found
XIX	OCH_3	75.5	78–79[a]	$C_{11}H_{16}N_2O_2S_3$	9.20	9.47	31.59	31.97
XX	OC_2H_5	88.5	75–76[a]	$C_{12}H_{18}N_2O_2S_3$	8.80	8.91	30.20	30.60
XXI	OC_4H_9	78.3	Oil	$C_{14}H_{22}N_2O_2S_3$	8.08	8.30	27.76	27.79
XXII	CH_3	89.0	71–72[b]	$C_{11}H_{16}N_2OS_3$	9.71	9.90	33.35	33.40

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

water. To this stirred solution 0.5 mole of either ethyl α-chloroacetoacetate,[16] ethyl β-bromolevulinate,[17] butyl α-chloroacetoacetate, ethyl γ-chloroacetoacetate,[18] methyl α-chloroacetoacetoacetate[16] or 3-chloro-2,4-pentanedione[19] was added. An exothermic reaction set in, the temperature rising from 30° to 50° over a period of 5 minutes. The reaction mixture was stirred for 8 hr. The potassium chloride was collected by filtration and the acetone removed *in vacuo*. For XIII–XVI, the residue was dissolved in 500 ml. of ethyl ether. The ether solution was washed with water until the washings were neutral to litmus, dried over sodium sulfate and ether was removed *in vacuo*.

For XVII and XVIII, after the removal of acetone, 500 ml. of water was added to the residue. The solid was filtered, washed with water until the wash water was neutral to litmus and dried at 50°. The data are summarized in Table III.

5-Substituted-4-methyl-2-thiazolyl Diethyldithiocarbamate. Procedure A (XIX–XXI).—To a stirred solution containing 0.25 mole of alkyl 2-mercapto-4-methyl-5-thiazolecarboxylate, 40 g. (0.25 mole) of 25% aqueous sodium hydroxide and 500 ml. of water was added 37.9 (0.25 mole) of N,N-diethylthiocarbamoyl chloride[20] over a 15-minute period at 25–30°. The reaction mixture was stirred for 2 hr. For XIX and XX, the product was collected by filtration, washed with water until the washings were neutral to litmus and air-dried at room temperature. For XXI, the reaction mixture was extracted with 400 ml. of ethyl ether. The ether extract was washed with water until the wash water was neutral to litmus, dried over sodium sulfate and ether removed *in vacuo*.

Procedure B (XXII).—To a stirred solution containing 52.g. (0.3 mole) of 2-mercapto-4-methyl-5-thiazolyl methyl ketone, 12 g. (0.3 mole) of sodium hydroxide, 600 ml. of acetone and 20 g. of water was added dropwise 45.5 g. (0.3 mole) of N,N-diethylthiocarbamoyl chloride dissolved in 200 ml. of acetone. The reaction mixture was stirred at 25–30° for 4 hr. and the sodium chloride was removed by filtration. The acetone was removed *in vacuo* and to the residue was added 500 ml. of water. The slurry was stirred thoroughly and the precipitate was filtered, washed with water until the wash water was neutral to litmus and air-dried at room temperature.

The data are summarized in Table IV.

1,4-Bis-(2-benzothiazolylthiomethyl)-*trans*-2,5-dimethylpiperazines (XIII–XV).—To a stirred solution containing 28.6 g. (0.25 mole) of *trans*-2,5-dimethylpiperazine[21] in 100 ml. of water was added dropwise 40 g. (0.5 mole) of 37% aqueous formaldehyde solution at 0–5°. To this stirred solution at 5° was added in one portion 0.5 mole of 2-mercaptobenzothiazole, 5-chloro-2-mercaptobenzothiazole or 6-ethoxy-2-mercaptobenzothiazole dissolved in 800 ml. of acetone. A precipitate formed immediately and the reaction mixture was stirred for 2 hr. at room temperature. The solid was collected by filtration and air-dried at 50°. The data are summarized in Table V.

2,2′-(2-Butenylenedithio)-bisbenzothiazole (XXVI) and 2-(4-Chloro-2-butenylthio)-benzothiazole (XXVII).—A solution of sodium 2-mercaptobenzothiazole was prepared by stirring 172 g. (1.0 mole) of 97% 2-mercaptobenzothiazole, 160 g. (1.0 mole) of 25% aqueous sodium hydroxide and 1100 mg. of water. The solution was filtered, and to the stirred filtrate was added 63 g. (0.5 mole) of 1,2-dichloro-3-butene.[21] The reaction mixture was stirred at room temperature for 24 hr. The aqueous layer was decanted and the semi-solid residue diluted with 400 g. of acetone. The acetone mixture was stirred thoroughly; the white solid was filtered and air-dried at 50°. The product, m.p. 147–150°, was obtained in 39.0% yield. After recrystallization from benzene, it melted at 153–155°. A mixed melting point with authentic 2,2′-(2-butenylenedithio)-bis-benzothiazole[8] showed no depression

The acetone was removed from the filtrate under reduced pressure and the residue was dried over anhydrous sodium sulfate. The product, an amber colored oil, was obtained in 58.9% yield. Analysis confirmed it to be 2-(4-chloro-2-butenylthio)-benzothiazole.

Anal. Calcd. for $C_{18}H_{14}N_2S_4$: N, 7.25; S, 33.18. Found: N, 7.19; S, 32.90. Calcd. for $C_{11}H_{10}ClNS_2$: N, 5.48; S, 25.07; Cl, 13.86. Found: N, 5.49; S, 25.10; Cl, 13.60.

(16) E. R. Buchman and E. M. Richardson, THIS JOURNAL, **61**, 891 (1939).

(17) D. Price and F. D. Pickel, U. S. Patent 2,209,092.

(18) J. F. Hamel, *Bull. soc. chim. France*, [4] **29**, 390 (1921).

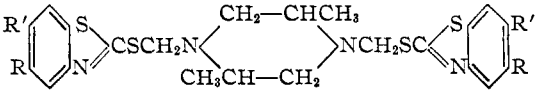
(19) E. R. Buchman and E. M. Richardson, THIS JOURNAL, **67**, 395 (1945).

(20) Kindly supplied by Sharples Chemicals, Inc., Philadelphia, Pa.

(21) Kindly furnished by Carbide and Carbon Chemical Co., New York, N. Y.

TABLE V

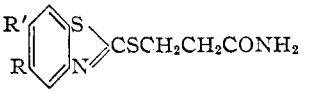
1,4-BIS-(2-BENZOTHIAZOLYLTHIOMETHYL)-*trans*-2,5-DIMETHYLPIPERAZINES



No.	R	R′	Yield, % crude	M.p., °C.	Empirical formula	Nitrogen, % Calcd.	Nitrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found	Chlorine, % Calcd.	Chlorine, % Found
XXIII	H	H	93.9	169–171	$C_{22}H_{24}N_4S_4$	11.85	12.02	27.13	27.23	...	...
XXIV	H	OC_2H_5	84.3	165–167	$C_{26}H_{32}N_4O_2S_4$	9.99	9.72	22.87	22.85	...	...
XXV	Cl	H	98.3	153–154	$C_{22}H_{22}Cl_2N_4S_4$	10.35	9.98	23.68	23.47	13.09	12.93

TABLE VI

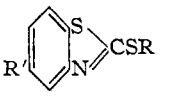
2-(2-CARBAMOYLETHYLTHIO)-BENZOTHIAZOLES



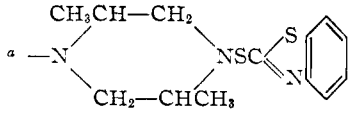
No.	R	R′	Yield, % crude	M.p., °C.	Empirical formula	Nitrogen, % Calcd.	Nitrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found
XXVIII	H	H	24.3	224–225	$C_{10}H_{10}N_2OS_2$	11.76	11.83	26.91	27.23
XXIX	H	OC_2H_5	21.2	234–236	$C_{12}H_{14}N_2O_2S_2$	9.92	9.97	22.71	22.77
XXX	Cl	H	24.4	224–225	$C_{10}H_9ClN_2OS_2$	10.27	10.26	23.51	23.37

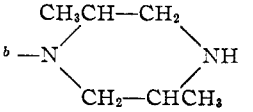
TABLE VII

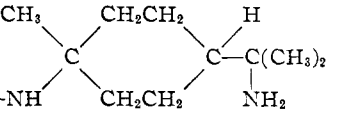
THIAZOLESULFENAMIDES (PROCEDURE A)



No.	R	R′	Amine	Yield, % crude	Mole ratio amine to thiazole	M.p., °C.	Empirical formula	Nitrogen, % Calcd. Found	Sulfur, % Calcd. Found	Chlorine, % Calcd. Found
XXXI	$C_{13}H_{16}N_3S_2$[a]	H	*trans*-2,5-Dimethylpiperazine	79.1	8:1	151–153	$C_{20}H_{20}N_4S_4$	12.60 12.56	... ...	... ...
XXXII	C_4H_3NO[d]	Cl	Morpholine	58.5	10:1	95–96	$C_{11}H_{11}ClN_2OS_2$	9.77 9.81	22.36 22.11	12.36 12.39
XXXIII	$NHC(CH_3)_3$	Cl	*t*-Butylamine	64.5	10:1	134–135	$C_{11}H_{13}ClN_2S_2$	10.27 10.33	23.51 23.48	13.00 12.92
XXXIV	$NHCH(CH_3)_2$	Cl	Isopropylamine	92.6	10:1	65–66	$C_{10}H_{11}ClN_2S_2$	10.83 10.85	24.78 24.43	13.70 13.74
XXXV	$C_6H_{13}N_2$[b]	Cl	*trans*-2,5-Dimethylpiperazine	53.6	10:1	200–202	$C_{13}H_{16}ClN_3S_2$	... ...	20.43 20.81	11.30 11.27
XXXVI	$NHC(CH_3)_2$ CH_2OH	H	2-Amino-2-methyl-1-propanol[f]	36.8	10:1	117–118	$C_{11}H_{14}N_2OS_2$	11.01 10.78	25.21 25.18	... ...
XXXVII	$NHCCH_3$ $(CH_2OH)_2$	H	2-Amino-2-methyl-1,3-propanediol[f]	22.2	10:1	154–155	$C_{11}H_{14}N_2O_2S_2$	... ...	23.72 23.42	... ...
XXXVIII	$C_{10}H_{21}N_2$[c]	H	1,8-Diaminomethane[e]	68.9	5:1	79–80	$C_{17}H_{25}N_3S_2$	... ...	19.11 19.06	... ...
XXXIX	$C_{10}H_{21}N_2$[c]	Cl	1,8-Diaminomenthane	60.6	5:1	65–67	$C_{17}H_{24}ClN_3S_2$	... ...	17.33 17.50	9.58 9.54

[a] 

[b] 

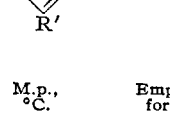
[c] 

[d] Morpholinyl.

[e] Kindly furnished by Rohm and Haas Company, Philadelphia, Penna. [f] Kindly supplied by Commercial Solvents Corporation, New York, N. Y.

TABLE VIII

THIAZOLESULFENAMIDES (PROCEDURE B)

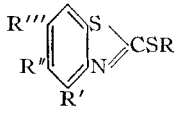


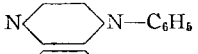
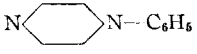
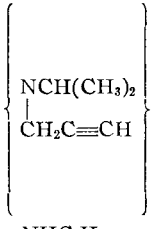
No.	R	R	R″	Amine	Yield, % crude	M.p., °C.	Empirical formula	Nitrogen, % Calcd. Found	Sulfur, % Calcd. Found	Chlorine, % Calcd. Found
XL	$N[CH(CH_3)_2]_2$	H	Cl	Diisopropylamine	64.1	61	$C_{13}H_{17}ClN_2S_2$	9.31 9.41	21.32 21.42	11.78 11.96
XLI	$NHC(CH_3)_2$ CH_2OH	H	Cl	2-Amino-2-methyl-1-propanol	58.5	153–154[a]	$C_{11}H_{13}ClN_2OS_2$	9.70 9.50	22.20 21.90	... ...

[a] Recrystallization from heptane.

TABLE IX

THIAZOLESULFENAMIDES (PROCEDURE C)



No.	R	R′	R″	R‴	Amine	Mole ratio amine to thiazole	25% H_2SO_4, ml.	Reaction temp., °C.	Yield, % crude	M.p., °C.	Empirical formula	Nitrogen Calcd.	Nitrogen Found	Sulfur Calcd.	Sulfur Found	Chlorine Calcd.	Chlorine Found
XLII	$NHC(CH_3)_3$	H	H	H	*t*-Butylamine	1.5:1	60	45–50	95.0	112–113	$C_{11}H_{14}N_2S_2$	11.75	11.65	26.90	26.98	...	...
XLIII	$NHC(CH_3)_3$	H	H	OC_2H_5	*t*-Butylamine	4:1	60	45–50	92.3	128–129	$C_{13}H_{18}N_2OS_2$	9.92	9.86	22.71	22.74	...	...
XLIV	$NHC(CH_3)_3$	CH_3	H	H	*t*-Butylamine	5:1	50	45–50	82.5	Semi-sol.	$C_{12}H_{16}N_2S_2$	11.10	10.84	25.41	25.69	...	...
XLV	NHC_8H_{17}	H	H	H	2,4,4-Trimethyl-2-aminopentane[e]	1.5:1	50	45–50	99.0	99–100	$C_{15}H_{22}N_2S_2$	9.51	9.46	21.78	21.83	...	...
XLVI	NHC_8H_{17}	H	H	OC_2H_5	2,4,4-Trimethyl-2-aminopentane	1.5:1	50	25–30	63.9	92–93[a]	$C_{17}H_{26}N_2OS_2$	8.28	8.09	18.94	19.00	...	...
XLVII		H	H	H	1-Phenylpiperazine	1.5:1	50	45–50	99.0	163–165[b]	$C_{17}H_{17}N_3S_2$	12.83	12.46	19.58	19.43	...	...
XLVIII		H	Cl	H	1-Phenylpiperazine	1.5:1	50	45–50	97.5	184–185[c]	$C_{17}H_{16}ClN_3S_2$	11.61	11.57	17.72	17.72	...	...
XLIX	$NHCH_2C_7H_{11}$	H	H	H	2-Norcamphanylmethylamine[f]	4:1	50	25–30	71.5	63–65	$C_{15}H_{18}N_2S_2$	9.65	9.48	...	...	...	...
L	$NHCH_2C_7H_{11}$	H	H	OC_2H_5	2-Norcamphanylmethylamine	4:1	50	25–30	83.6	69–71[d]	$C_{17}H_{22}N_2OS_2$	8.38	8.38	19.17	18.95	...	...
LI	$NHCH_2C_7H_{11}$	H	Cl	H	2-Norcamphanylmethylamine	4:1	50	25–30	88.5	113–114	$C_{15}H_{17}ClN_2S_2$	8.62	8.58	...	...	10.91	11.00
LII		H	H	H	N-Isopropyl-2-propynylamine	4:1	50	25–30	54.8	Semi-sol.	$C_{13}H_{14}N_2S_2$	10.67	10.41	...	...	...	...
LIII		H	Cl	H	N-Isopropyl-2-propynylamine	4:1	50	25–30	54.0	43–45	$C_{13}H_{13}ClN_2S_2$	9.44	9.80	...	...	11.94	12.41
LIV		H	H	OC_2H_5	N-Isopropyl-2-propynylamine	5:1	42	45–50	62.6	90–91[a]	$C_{15}H_{18}N_2OS_2$	9.14	9.17	20.93	20.70	...	...
LV		CH_3	H	H	N-Isopropyl-2-propynylamine	5:1	42	25–30	69.5	Oil	$C_{14}H_{16}N_2S_2$	10.15	9.91	...	...	...	...
LVI	NHC_6H_{11}	H	Cl	H	Cyclohexylamine	4:1	42	35–40	92.5	93–94	$C_{13}H_{15}ClN_2S_2$	9.37	9.40	21.46	21.57	11.86	11.89
LVII	NHC_6H_{11}	CH_3	H	H	Cyclohexylamine	5:1	50	45–50	57.6	85–86	$C_{14}H_{18}N_2S_2$	10.06	9.81	23.03	22.93	...	...
LVIII	$NHCH_2C_6H_{11}$	H	H	H	Cyclohexylmethylamine	4:1	42	20–25	73.1	47–48	$C_{14}H_{18}N_2S_2$	10.06	10.26	23.03	22.81	...	...
LIX	$NCH(CH_3)_2$ | $CH_2CH{=}CH_2$	H	H	H	N-Isopropylallylamine	4:1	50	25–30	77.2	Oil	$C_{13}H_{16}N_2S_2$	10.60	10.62	24.25	24.33	...	...
LX	NC_6H_{11} | $CH_2CH{=}CClCH_3$	H	H	H	N-(3-Chloro-2-butenyl)-cyclohexylamine	4:1	50	25–30	74.0	Oil	$C_{17}H_{21}ClN_2S_2$	7.94	7.93	18.17	18.31	...	...
LXI	NC_6H_{11} | $CH_2CH{=}CClCH_3$	H	H	OC_2H_5	N-(3-Chloro-2-butenyl)-cyclohexylamine	4:1	50	25–30	90.0	Oil	$C_{19}H_{25}ClN_2OS_2$	7.06	6.79	...	...	...	...
LXII	$N(CH_2)_3OCH_3$ | $CH_2CCl{=}CH_2$	H	Cl	H	2-Chloro N-(3-methoxypropyl)-allylamine	5:1	50	45–50	43.0	Oil	$C_{14}H_{16}Cl_2N_2OS_2$	7.71	7.53	...	...	19.52	19.62

LXIII	$NCH(CH_3)_2$ $CH_2CCl=CH_2$	H	Cl	H	2-Chloro-N-isopropyl-allylamine	5:1	50	45–50	38.3	Oil	$C_{13}H_{14}Cl_2N_2S_2$	8.41	8.25	...	...	...	...	...
LXIV	$NHC(CH_3)_2$ CH_2OH	CH_3	H	H	2-Amino-2-methyl-1-propanol	5:1	50	45–50	47.8	82–84[a]	$C_{12}H_{16}N_2OS_2$	10.44	10.13	23.89	23.75	...	...	...
LXV	NC_8H_{16}	H	H	H	5-Ethyl-2-methyl-piperidine[f]	1.5:1	42	25–30	79.3	Oil	$C_{15}H_{20}N_2S_2$	...	...	21.93	21.56	...	...	...
LXVI	NC_8H_{16}	H	Cl	H	5-Ethyl-2-methyl-piperidine	1.5:1	42	25–30	53.9	Semi-sol.	$C_{15}H_{19}ClN_2S_2$	8.57	8.18	19.62	19.42	10.85	11.03	
LXVII	$NHCH_2C_7H_{13}$	H	H	H	1,4-Dimethylcyclopent-1-ylmethylamine[f]	1.5:1	42	25–30	87.6	Oil	$C_{15}H_{20}N_2S_2$	9.58	9.30	...	...	...	...	...
LXVIII	$NHCH_2C_7H_{13}$	H	Cl	H	1,4-Dimethylcyclopent-1-ylmethylamine	1.5:1	42	25–30	85.0	73–75	$C_{15}H_{19}ClN_2S_2$	8.57	8.74	...	...	10.85	11.16	
LXIX	$NHCH_2C_7H_{13}$	H	H	OC_2H_5	1,4-Dimethylcyclopent-1-ylmethylamine	2:1	42	45–50	81.2	Oil	$C_{17}H_{24}N_2OS_2$	8.33	8.00	...	...	...	...	...
LXX	$NC_6H_{12}O$	H	H	H	2,6-Dimethylmorpholine[f]	4:1	42	25–33	94.0	96–98	$C_{13}H_{16}N_2OS_2$	...	...	22.87	22.90	...	...	
LXXI	$NC_6H_{12}O$	CH_3	H	H	2,6-Dimethylmorpholine	4:1	50	25–30	77.5	87–88[a]	$C_{14}H_{18}N_2OS_2$	9.52	9.79	21.78	22.11	...	...	
LXXII	$NC_6H_{12}O$	H	Cl	H	2,6-Dimethylmorpholine	8:1	50	30–40	99.0	97–99	$C_{13}H_{15}ClN_2OS_2$	...	...	20.37	20.37	11.26	11.59	

[a] Recrystallization from ethyl alcohol. [b] Recrystallization from ethyl acetate. [c] Recrystallization from benzene. [d] Recrystallization from heptane. [e] Kindly supplied by Rohm and Haas Company, Philadelphia, Penna. [f] Kindly furnished by Carbide and Carbon Chemical Co., New York, N. Y.

2-(2-Carbamoylethylthio)-benzothiazoles (XXVIII–XXX).—To a stirred solution containing one mole of a 14% aqueous solution of sodium 2-mercaptobenzothiazole, 6-ethoxy-2-mercaptobenzothiazole or 5-chloro-2-mercaptobenzothiazole was added in one portion 71.1 g. (1.0 mole) of acrylamide.[22] The stirred reaction mixture was heated at 50–55° for 24 hr. After cooling to 25°, the solid was filtered, washed with water until the washings were neutral to litmus and air-dried at 50°. The data are summarized in Table VI.

N-(3-Chloro-2-butenyl)-cyclohexylamine.—To 1063 g. (10.7 moles) of cyclohexylamine at 100° was added dropwise 625 g. (5.0 moles) of 1,3-dichloro-2-butene over a 2-hr. period. The stirred reaction mixture was heated at 128–130° for 2 hr. After cooling to 90°, 800 g. (5.0 moles) of 25% aqueous sodium hydroxide was added in one portion and stirring was continued for 1 hr. longer. The sodium chloride was removed by filtration. The top layer of the filtrate was dried over caustic and the excess cyclohexylamine was removed by distillation. Vacuum distillation of the residue through a 4-foot Vigreux-type column yielded a colorless liquid (75%), b.p. 110–112° (5 mm.), $n^{25}D$ 1.4880.

Anal. Calcd. for $C_{10}H_{18}ClN$: N, 7.46; Cl, 18.89. Found: N, 7.82; Cl, 18.61.

N-Isopropylallylamine, N-Isopropyl-2-propynylamine and 2-Chloro-N-isopropylallylamine.—To a stirred solution containing 591 g. (10.0 moles) of isopropylamine and 400 ml. of water, 5 moles of allyl chloride, 3-bromo-1-propyne or 2,3-dichloro-1-propene was added dropwise at 47–65° over a 3-hr. period. The stirred reaction mixture was heated at 60–70° for 4 hr. After cooling to 10°, 500 g. of 50% aqueous sodium hydroxide was added over a 10-minute period. The reaction mixture was stirred for one additional hour and the sodium halide was removed by filtration. The top organic layer was dried over caustic and excess isopropylamine was removed by distillation. The distillation of the residues through a 4-foot Vigreux-type column gave N-isopropylallylamine, b.p. 96–97°, $n^{25}D$ 1.4140, N-isopropyl-2-propynylamine, b.p. 110–111°, $n^{25}D$ 1.4230, and 2-chloro-N-isopropylallylamine, b.p. 138–140°, $n^{25}D$ 1.4430, in yields of 67, 69 and 77.5%, respectively.

Anal. Calcd. for $C_6H_{13}N$: N, 14.12. Found: N, 14.00. Calcd. for $C_6H_{11}N$: N, 14.42. Found: N, 14.54. Calcd. for $C_6H_{12}ClN$: N, 10.48; Cl, 26.54. Found: N, 10.10; Cl, 26.70.

2-Chloro-N-(3-methoxypropyl)-allylamine.—To 393 g. (4.4 moles) of 3-methoxypropylamine at 80° was added dropwise 222 g. (2.0 moles) of 2,3-dichloro-1-propene over a 2-hr. period. During this addition an exothermic reaction set in causing a temperature rise from 80 to 103°. The stirred reaction mixture was heated at 145–150° for 2 hr. After cooling to 50°, 200 g. of 50% aqueous sodium hydroxide was added and stirring continued for 30 minutes. After removal of sodium chloride by filtration, the top organic layer was dried over caustic and the excess 3-methoxypropylamine removed by distillation. Vacuum distillation of the residue yielded a colorless liquid (65.9%), b.p. 118–120° (50 mm.), $n^{25}D$ 1.4568.

Anal. Calcd. for $C_7H_{14}ClNO$: N, 8.56; Cl, 21.67. Found: N, 8.42; Cl, 21.20.

Thiazolesulfenamides. Procedure A (XXXI–XXXIX).—To an aqueous solution containing 0.25 mole of 2-mercaptobenzothiazole or 5-chloro-2-mercaptobenzothiazole, 80 g. (0.5 mole) of 25% aqueous sodium hydroxide solution, 1.25 to 2.50 moles of the amine and 200 ml. of water at 25–30° was added, drop by drop with stirring over a 1.5-hr. period, 64 g. of iodine dissolved in 800 ml. of water containing 69 g. of potassium iodide. For all thiazolesulfenamides except XXXIV, XXXVIII and XXXIX, after the addition of the oxidizing solution the stirred reaction mixture was heated at 45–50° for 1 hr. For XXXIV, XXXVIII and XXXIX the temperature was maintained at 25–30°. The reaction mixture was cooled to 15–20°, the precipitate was filtered, washed with water until free from alkali and air-dried at room temperature. The data are summarized in Table VII.

Procedure B (XL–XLI).—A suspension containing (0.16 mole) of 2,2′-dithiobis-(5-chlorobenzothiazole), 32 g. (0.2 mole) of 25% aqueous sodium hydroxide, 200 ml. of water and 1 mole of the amine was stirred at 35–40° for 3 hr. After cooling to 15° the product was filtered, washed with

(22) Kindly supplied by American Cyanamid Co., New York, N. Y.

water until the washings were neutral to litmus and air-dried at room temperature. The data are summarized in Table VIII.

Procedure C (XLII–LXXII).—To an aqueous slurry containing 0.25 mole of 2-mercaptobenzothiazole, 5-chloro-2-mercaptobenzothiazole, 6-ethoxy-2-mercaptobenzothiazole or 4-methyl-2-mercaptobenzothiazole, 40 g. (0.25 mole) of 25% aqueous sodium hydroxide and 50 ml. of water was added dropwise, with agitation, 0.38 to 2.0 moles of amine. After stirring for 15 minutes, 42 to 60 ml. of 25% sulfuric acid was added dropwise. To the resulting slurry was added, drop by drop at temperatures specified in Table IX 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 XLII, XLIII, XLV, XLVI, XLVII, XLVIII, LI, LVI, LXX, LXXI and LXXII, the reaction mixture was cooled to 15°, the solid collected by filtration, washed with water until the washings were neutral to litmus and air-dried at room temperature.

For the remaining compounds, the 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 Table IX.

Procedure D (LXXIII and LXXIV).—A solution was prepared by dissolving either 0.25 mole of ethyl 2-mercapto-4-methyl-5-thiazolecarboxylate or 2-mercapto-4-methyl-5-thiazolyl methyl ketone in 140 g. (0.25 mole) of 7.15% aqueous sodium hydroxide solution. This solution and 148 ml. (15.1 g./100 ml.) of aqueous sodium hypochlorite solution were added dropwise at equal rates by volume in 750 ml. of concentrated ammonium hydroxide (d. 0.9) at 0–5° in 1.5 hr. The reaction mixture was stirred for 1 hr. at 25–28°, and 4 g. of sodium sulfite was added to destroy the excess oxidizing agent. The product was collected by filtration, washed with water until free of chloride and air-dried at room temperature. 5-Carbethoxy-4-methyl-2-thiazolesulfenamide, m.p. 124–125°, and 5-acetyl-4-methyl-2-thiazolesulfenamide, m.p. 83–85°, were obtained in yields of 73.5 and 59.5%, respectively.

Anal. Calcd. for $C_7H_{10}N_2O_2S_2$: N, 12.83; S, 29.38. Found: N, 13.06; S, 29.14. Calcd. for $C_6H_8N_2OS_2$: N, 14.88; S, 34.06. Found: N, 14.63; S, 34.22.

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Nitro, West Virginia

[Contribution from the L. G. Ryan Research Laboratories of Monsanto Canada Ltd.]

A New Molecular Rearrangement. III.[1] Aminolysis of 1-(β-Chloroethyl)-2-imidazolidone

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1-(β-Chloroethyl)-2-imidazolidone on ammonolysis gives a mixture of 1-(β-aminoethyl)-2-imidazolidone and 1-(β-hydroxyethyl)-2-iminoimidazolidine. Aminolysis with methylamine and benzylamine gives 1-(β-methylaminoethyl)-2-imidazolidone and 1-(β-benzylaminoethyl)-2-imidazolidone, respectively. The mechanism of these reactions is discussed. Δ^7-1-Oxa-4,7-diazabicyclo[3.3.0]octene, which is described as one of the intermediates in the ammonolysis of 1-(β-chloroethyl)-2-imidazolidone, was prepared by heating 1-(β-chloroethyl)-2-imidazolidone with methanolic potassium hydroxide solution. 1-(β-Nitroxyethyl)-2-nitrimino-3-nitroimidazolidine has been prepared directly from 1-(β-hydroxyethyl)-2-iminoimidazolidine by nitration in an acetic anhydride–nitric acid medium.

An attempt to prepare 1-(β-aminoethyl)-2-imidazolidone (III) by the ammonolysis of 1-(β-chloroethyl)-2-imidazolidone (I) gave a rearrangement product, 1-(β-hydroxyethyl)-2-iminoimidazolidine (V),[2] as well as the expected compound. Since this rearrangement is similar to that observed[1] in the aminolysis of 1-(β-chloroethyl)-2-nitriminoimidazolidine, it was investigated further.

The reaction of 1-(β-chloroethyl)-2-imidazolidone (I) with ammonia is shown as a stepwise reaction for convenience. It is realized that the steps involved may occur concurrently, but this difference is one of degree rather than kind. An electrophilic state is established in the vicinity of the β-carbon atom of the side chain which is satisfied by formation of the bicyclic intermediate IV or addition of ammonia to give 1-(β-aminoethyl)-2-imidazolidone (III). The bicyclic intermediate, Δ^7-1-oxa-4,7-diazabicyclo[3.3.0]octene (IV), combined with ammonia to give 1-(β-hydroxyethyl)-2-iminoimidazolidine (V).

The reaction of ammonia with 1-(β-chloroethyl)-2-imidazolidone to give 1-(β-hydroxyethyl)-2-iminoimidazolidine (V) may be considered to occur by the over-all concerted mechanism[3] in the Chart. This over-all concerted mechanism considers that the reaction is initiated by the approach of the amine reagent or ammonia to carbon atom 2 of the heterocyclic structure. It has been shown that ammonia combines with 1-(β-chloroethyl)-2-imidazolidone to give a mixture of 1-(β-aminoethyl)-2-imidazolidone (III) and 1-(β-hydroxyethyl)-2-iminoimidazolidine (V).

The following facts have been ascertained from the study of this reaction. 1. Ammonia combines with 1-(β-chloroethyl)-2-imidazolidone at 100° under atmospheric pressure to give a mixture of 1-(β-aminoethyl)-2-imidazolidone (III) and 1-(β-hydroxyethyl)-2-iminoimidazolidine (V), whereas the same reaction at 100° under pressure gives exclusively or mainly 1-(β-aminoethyl)-2-imidazolidone (III). 2. The more nucleophilic reagents, for example, methylamine and benzylamine, on refluxing with 1-(β-chloroethyl)-2-imidazolidone at atmospheric pressure give exclusively or mainly 1-(β-substituted aminoethyl)-2-imidazolidones. 3. The bicyclic compound, Δ^7-1-oxa-4,7-diazabicyclo-

(1) Previous paper in this series, A. F. McKay, W. G. Hatton and R. O. Braun, This Journal, **78**, 6144 (1956).

(2) This compound may exist in the tautomeric form as 1-(β-hydroxyethyl)-2-amino-2-imidazoline.

(3) This mechanism was suggested by one of the Referees as being a better one for the reaction[1] of benzylamine with 1-(β-chloroethyl)-2-nitriminoimidazolidine than the mechanism proposed by the authors.