

John J. D'Amico*, Lydia Suba and Peter G. Ruminski

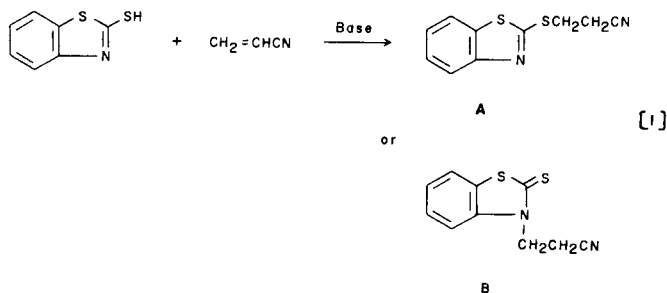
Monsanto Agricultural Products Company, Research Department, 800 N. Lindbergh Boulevard, St. Louis, Missouri 63167

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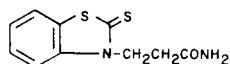
The reaction of 2-mercaptobenzothiazole, 2-mercaptobenzoxazole or 5-chloro-2-mercaptobenzothiazole with either acrylonitrile or acrylamide under basic conditions afforded the *N*-cyanoethylated products **1**, **2** and **3** or the *N*-amidoethylated products **4**, **5** and **6**, respectively. The reaction of the sodium salts of the same thiazolethiols with 3-chloropropionitrile furnished a mixture containing the *N*-cyanoethylated products **1**, **2** and **3** and the unknown *S*-cyanoethylated products **7**, **8** and **9**, respectively. Whereas, substituting 3-chloropropionamide for 3-chloropropionitrile in the same reaction gave only the *S*-substituted products **10**, **11**, and **12**, respectively. The treatment of **10**, **11** or **12** with phosphorus oxychloride or thionyl chloride in DMF afforded **7**, **8** and **9** in excellent yields. Possible mechanisms and supporting nmr data are discussed.

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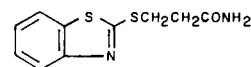
Considerable confusion existed concerning the assignment of the correct structure for the product isolated in the reaction of 2-mercaptobenzothiazole and related compounds with acrylonitrile under basic conditions. With insufficient evidence, Clifford and Liehty [2], Harman [3] and Hurd and Gershbein [4] reported this reaction furnished the *S*-cyanoethylated structure **A**. Whereas based on either uv, ir or nmr data or the aromatic protons, Stewart and Mathes [5], Gaul and co-workers [6] and Halasa and Smith [7] assigned structure **B** for the product isolated in the cyanoethylation reaction.



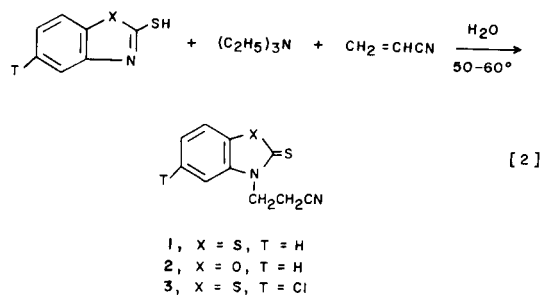
We wish to report (1) based on further nmr studies that structure **B** is the correct assignment, (2) replacement of acrylonitrile with acrylamide in reaction 1 afforded the



N-substituted product, (3) the reaction of 2-mercaptobenzothiazole and related compounds with 3-chloro or bromopropionitrile under basic conditions gave a mixture containing the structures **A** and **B**, (4) replacement of 3-chloropropionitrile with 3-chloropropionamide in the above reaction furnished only one product, the *S*-substituted product and (5) an improved method for the synthesis of the unknown *S*-cyanoethylated structures **A** is described.



The reaction of an aqueous solution containing the triethylamine salt of 2-mercaptobenzothiazole, 2-mercaptobenzoxazole or 5-chloro-2-mercaptobenzothiazole with acrylonitrile afforded 2-thioxo-3(2*H*)-benzothiazolepropanenitrile (**1**), 2-thioxo-3(2*H*)-benzoxazolepropanenitrile (**2**), and 5-chloro-2-thioxo-3(2*H*)-benzothiazolepropanenitrile (**3**), respectively (Table 1).



Substituting acrylamide for acrylonitrile in reaction 2 furnished 2-thioxo-3(2*H*)-benzothiazolepropanamide (**4**), 2-thioxo-3(2*H*)-benzoxazolepropanamide (**5**), and 5-chloro-2-thioxo-3(2*H*)-benzothiazolepropanamide (**6**), respectively (Table 2).

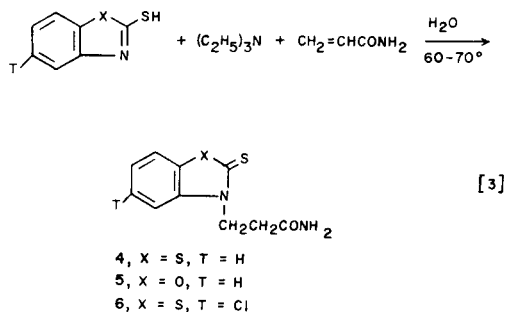
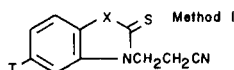


Table 1



No.	X	T	% Yield [a]	mp °C	NMR: δ ppm DMSO- d_6 /TMS	Empirical Formula	Chemical Analysis	
1 [b]	S	H	91	169-170	2.88 (t, 2, -NCH ₂ CH ₂ CN) 4.51 (t, 2, -NCH ₂ CH ₂ CN) 6.91-7.69 (m, 4, ArH)	C ₁₀ H ₈ N ₂ S ₂	%C	%N
							Calcd. 54.54	Calcd. 12.72
							Found 54.44	Found 12.70
							%H	%S
							Calcd. 3.66	Calcd. 29.01
							Found 3.70	Found 29.00
2 [b]	O	H	91	175-176	3.00 (t, 2, -NCH ₂ CH ₂ CN) 4.40 (t, 2, -NCH ₂ CH ₂ CN) 7.10-7.70 (m, 4, ArH)	C ₁₀ H ₈ N ₂ OS	%C	%N
							Calcd. 58.80	Calcd. 13.72
							Found 58.88	Found 13.71
							%H	%S
							Calcd. 3.95	Calcd. 15.70
							Found 3.99	Found 15.64
3	S	Cl	79	199-200	2.93 (t, 2, -NCH ₂ CH ₂ CN) 4.64 (t, 2, -NCH ₂ CH ₂ CN) 7.13-8.17 (m, 3, ArH)	C ₁₀ H ₈ ClN ₂ S ₂	%C	%N
							Calcd. 47.15	Calcd. 11.00
							Found 47.01	Found 10.99
							%H	%S
							Calcd. 2.77	Calcd. 25.17
							Found 2.78	Found 25.27

[a] When (C₂H₅)₃N was replaced by aqueous sodium hydroxide as a catalyst and base the yields were decreased. [b] Reference 4 reports mp 167° for **1** and mp 173.0-173.5° for **2** but their assignment of structures are incorrect.

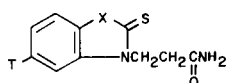
(Chart 1)

no.	X	T	mp°C	% Yield	nmr: δ ppm	Table Number
1	S	H	169-170	18.9	4.51 (-NCH ₂ CH ₂ CN)	1
7	S	H	vis. liquid	39.3	3.51 (-SCH ₂ CH ₂ CN)	Experimental
2	O	H	175-176	28.2	4.40 (-NCH ₂ CH ₂ CN)	1
8	O	H	43-44	8.2	3.51 (-SCH ₂ CH ₂ CN)	3
3	S	Cl	199-200	18.1	4.64 (-NCH ₂ CH ₂ CN)	1
9	S	Cl	86-88	9.5	3.59 (-SCH ₂ CH ₂ CN)	3

(Chart 2)

No.	X	T	mp°C	% Yield	nmr: δ ppm	Table Number
4	S	H	226-227	76	4.58 (-NCH ₂ CH ₂ CONH ₂)	2
10	S	H	145-146	88	3.35 (-SCH ₂ CH ₂ CONH ₂)	4
5	O	H	206-208	48	4.37 (-NCH ₂ CH ₂ CONH ₂)	2
11	O	H	143-144	79	3.31 (-SCH ₂ CH ₂ CONH ₂)	4
6	S	Cl	226-228	70	4.60 (-NCH ₂ CH ₂ CONH ₂)	2
12	S	Cl	200-202	90	3.48 (-SCH ₂ CH ₂ CONH ₂)	4

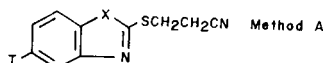
Table 2



No.	X	T	% Yield [a]	mp °C	NMR: δ ppm DMSO- d_6 /TMS	Empirical Formula	Chemical Analysis	
							% C	% N
4	S	H	76	226-227	2.50 (t, 2, $-\text{CH}_2\text{CH}_2\text{CO}-$) 4.58 (t, 2, $-\text{CH}_2\text{CH}_2\text{CO}-$) 6.90 (br s, 2, $-\text{CONH}_2$) 7.20-7.80 (m, 4, ArH)	$\text{C}_{10}\text{H}_{10}\text{N}_2\text{OS}_2$	Calcd. 50.40	Calcd. 11.75
							Found 50.28	Found 11.72
							Calcd. 4.23	Calcd. 26.91
							Found 4.28	Found 26.79
5	O	H	48	206-208	2.62 (t, 2, $-\text{CH}_2\text{CH}_2\text{CO}-$) 4.37 (t, 2, $-\text{CH}_2\text{CH}_2\text{CO}-$) 6.90 (br s, 2, $-\text{CONH}_2$) 7.10-7.66 (m, 4, ArH)	$\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}_2\text{S}$	Calcd. 54.04	Calcd. 12.60
							Found 53.82	Found 12.52
							Calcd. 4.54	Calcd. 14.43
							Found 4.57	Found 14.39
6	S	Cl	70	226-228	2.52 (t, 2, $\text{CH}_2\text{CH}_2\text{CO}-$) 4.60 (t, 2, $-\text{CH}_2\text{CH}_2\text{CO}-$) 6.92 (br s, 2, $-\text{CONH}_2$) 7.28-7.90 (m, 3, ArH)	$\text{C}_{10}\text{H}_9\text{ClN}_2\text{OS}$	Calcd. 44.03	Calcd. 10.27
							Found 44.00	Found 10.27
							Calcd. 3.33	Calcd. 23.51
							Found 3.34	Found 23.49

[a] Replacement of $(\text{C}_2\text{H}_5)_3\text{N}$ with aqueous sodium hydroxide as a catalyst and base gave decreased yields.

Table 3



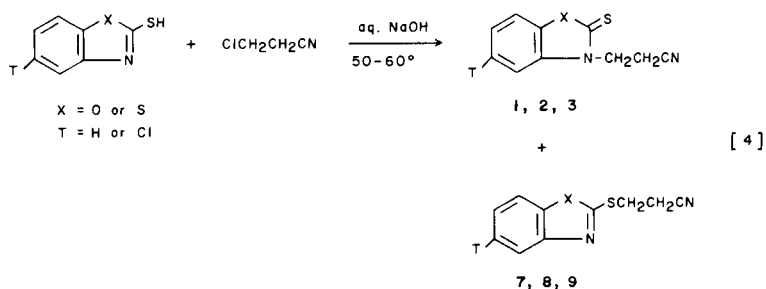
No.	X	T	% Yield	% Conversion	Mp °C	NMR: δ ppm DMSO- d_6 /TMS	Empirical Formula	Chemical Analysis	
								% C	% N
8	O	H	8.2	18.1	43-44	3.06 (t, 2, $-\text{SCH}_2\text{CH}_2\text{CN}$) 3.51 (t, 2, $-\text{SCH}_2\text{CH}_2\text{CN}$) 6.96-7.69 (m, 4, ArH)	$\text{C}_{10}\text{H}_8\text{N}_2\text{OS}$	Calcd. 58.80	Calcd. 13.72
								Found 58.60	Found 13.63
								Calcd. 3.95	Calcd. 15.70
								Found 3.97	Found 15.83

Compound **2**, mp 176-177°, was obtained in 28% yield (63% conversion). A mixture melting point with the product obtained in Method I was not depressed and the nmr spectra of the two were identical (Table 1). *Anal.* Calcd. for $\text{C}_{10}\text{H}_8\text{N}_2\text{OS}$: C, 58.80; H, 3.95; N, 13.71; S, 15.70. Found: C, 58.90; H, 3.97; N, 13.71; S, 15.64.

Twenty-five g (0.165 mole) mp 196-198°, of 2-mercaptobenzothiazole was recovered. A mixture melting point with an authentic sample was not depressed and the nmr spectra of the two were identical; (DMSO- d_6): δ 6.81-7.41 (m, 4, ArH); 13.68 (br s, 1, NH). *Anal.* Calcd. for $\text{C}_7\text{H}_5\text{NOS}$: C, 55.61; H, 3.33; N, 9.26; S, 21.21. Found: C, 55.58; H, 3.35; N, 9.26; S, 21.13.

9	S	Cl	9.5	33.8	86-88	3.07 (t, 2, $-\text{SCH}_2\text{CH}_2\text{CN}$) 3.59 (t, 2, $-\text{SCH}_2\text{CH}_2\text{N}$) 7.15-8.10 (m, 3, ArH)	$\text{C}_{10}\text{H}_7\text{ClN}_2\text{S}_2$	Calcd. 47.15	Calcd. 11.00
								Found 47.17	Found 10.99
								Calcd. 2.77	Calcd. 25.17
								Found 2.81	Found 25.08

Compound **3**, mp 199-200°, was obtained in 18% yield (64% conversion). A mixture melting point with the product obtained in Method I was not depressed and the nmr spectra of the two were identical (Table 1). Forty-four g (0.214 mole) mp 205-207° of 5-chloro-2-mercaptobenzothiazole was recovered. A mixture melting point with an authentic sample was not depressed and the nmr spectra of the two were identical.

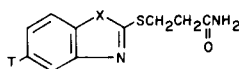


The reaction of an aqueous solution containing the sodium salt of 2-mercaptobenzothiazole, 2-mercaptobenzoxazole or 5-chloro-3-mercaptobenzothiazole with either 3-bromopropionitrile or 3-chloropropionitrile gave a mixture containing **1** and the unknown 3-(2-benzothiazolythio)propanenitrile (**7**), **2** and the unknown 3-(2-benzoxazolythio)propanenitrile (**8**) and **3** and the unknown 5-chloro-(2-benzothiazolythio)propanenitrile (**9**), respectively (Table 3).

Proof of structures for **1** and **7**, **2** and **8**, and **3** and **9** were based on nmr spectra data. It is noteworthy to contrast the chemical shifts for the methylene protons in **1**

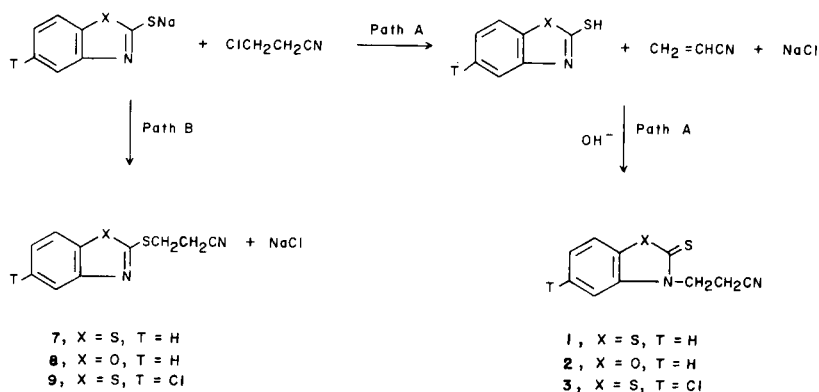
and **7**, **2** and **8**, and **3** and **9**. The $-\text{SCH}_2-$ protons in **7**, **8** and **9** appeared at δ 3.51, δ 3.51, and δ 3.59, respectively whereas their rearranged counterparts the $-\text{NCH}_2-$ protons in **1**, **2**, and **3** were found at δ 4.51, δ 4.40, and δ 4.64, respectively. The large downfield shifts for **1**, **2** and **3** are due to the deshielding effects of the thiocarbonyl group. The same effect has been observed with 2-methylthiobenzimidazole (δ $-\text{SCH}_3 = 2.72$) and its rearranged product 1-methyl-2-benzimidazolinethione (δ $-\text{N-CH}_3 = 3.69$) [8]. Another example of this effect was reported with 2-methylthiobenzothiazole (δ $-\text{SCH}_3 = 2.75$) and its rearranged product 3-methylbenzothiazoline-2-thione (δ $-\text{N-CH}_3 =$

Table 4



No.	X	T	% Yield	mp °C	NMR: δ ppm DMSO- d_6 /TMS	Empirical Formula	Chemical Analysis	
							% C	% N
10	S	H	88	145-146 [a]	2.48 (t, 2, $-\text{CH}_2\text{CO}-$) 3.35 (t, 2, $-\text{SCH}_2-$) 6.84 (br s, 2, $-\text{CONH}_2$) 6.99-8.00 (m, 4, ArH)	$\text{C}_{10}\text{H}_{10}\text{N}_2\text{OS}_2$	Calcd. 50.40	Calcd. 11.75
							Found 50.36	Found 11.73
							% H	% S
							Calcd. 4.23	Calcd. 26.91
							Found 4.23	Found 26.91
11	O	H	79	143-144 [b]	2.51 (t, 2, $-\text{CH}_2\text{CO}-$) 3.31 (t, 2, $-\text{SCH}_2-$) 6.82 (br s, 2, $-\text{CONH}_2$) 6.92-7.62 (m, 4, ArH)	$\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}_2\text{S}$	Calcd. 54.04	Calcd. 12.60
							Found 54.04	Found 12.54
							% H	% S
							Calcd. 4.54	Calcd. 14.43
							Found 4.58	Found 14.39
12	S	Cl	90	200-202	2.59 (t, 2, $-\text{CH}_2\text{CO}-$) 3.48 (t, 2, $-\text{SCH}_2-$) 6.89 (br s, 2, $-\text{CONH}_2$) 7.08-8.50 (m, 3, ArH)	$\text{C}_{10}\text{H}_9\text{ClNOS}_2$	Calcd. 44.03	Calcd. 10.27
							Found 43.82	Found 10.20
							% H	% S
							Calcd. 3.33	Calcd. 23.51
							Found 3.34	Found 23.38

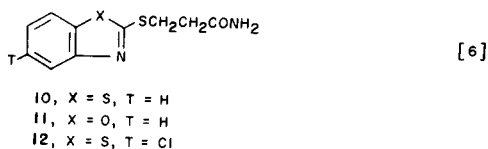
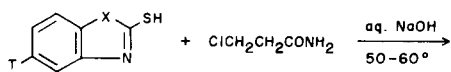
[a] Recrystallization from isopropyl alcohol. [b] Recrystallization from methyl alcohol.



3.80) [9]. In all products the melting point of *S*-substituted products (**7**, **8** and **9**) were markedly lower than their corresponding rearranged products **1**, **2** and **3**.

The formation of a mixture of products in reaction 4, cyanoethylation of both nitrogen and sulfur atoms, can best be explained by paths A and B (Reactions 5).

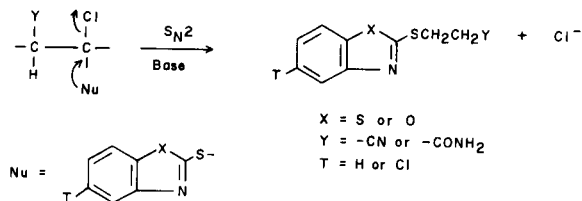
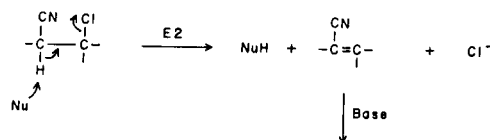
It was anticipated that replacing 3-chloropropionitrile with 3-chloropropionamide in reaction 4 would have afforded a mixture containing both the *S* and *N* substituted products. However, this was not the case for only the *S*-substituted products, 3-(2-benzothiazolythio)propanamide (**10**), 3-(2-benzoxazolythio)propanamide (**11**), and 5-chloro-3-(2-benzothiazolythio)propanamide (**12**) were obtained (Table 4).



A comparison of the nmr spectra for the $-\text{SCH}_2$ protons in **10**, **11** and **12** and the $-\text{NCH}_2$ protons in **4**, **5** and **6** furnished proof for the assignment of structures in reactions 3 and 6. Again the melting point of the *S*-substituted products **10**, **11** and **12** were much lower than their corresponding *N*-substituted products **4**, **5** and **6**.

Since identical reaction conditions were used in reaction 4 and 6 with the exception that in reaction 4 the reactant was 3-chloropropionitrile and in reaction 6 the electrophile was 3-chloropropionamide, it appears that the acidity of the beta hydrogen of the two reactants determines

whether reactions 4 and 6 proceed by an E_2 , $\text{S}_{\text{N}}2$ or combination of both mechanisms. In reaction 4 the cyano moiety is more electrophilic than the amido group in reaction 6. This effect increases the acidity of the proton to be removed and thus accelerates the elimination reaction (E_2). Thus in reaction 4 the mechanism proceeds by a combination of $\text{S}_{\text{N}}2$ and E_2 pathways. In reaction 6, the acidity of the beta hydrogen is too low to be abstracted by the nucleophile and thus proceeds by the $\text{S}_{\text{N}}2$ mechanism.



The treatment of **10**, **11** and **12** with either phosphorus oxychloride or thionyl chloride in dimethylformamide at 90-100° gave **7**, **8** or **9** in excellent yields (Table 5).

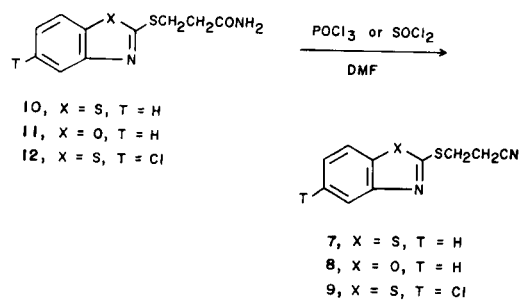
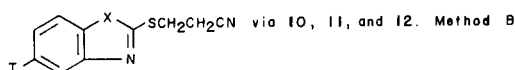


Table 5



No.	X	T	Dehydration Agent	% Yield	mp °C	%C		%H		%N		%S	
						Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
7 [a]	S	H	POCl ₃	99	Visc Liquid	54.52	54.26	3.66	3.59	12.72	12.54	29.11	28.86
			SOCl ₂	95	Visc liquid	54.52	54.33	3.66	3.64	12.72	12.55	29.11	29.25
8 [b]	O	H	POCl ₃	86	46-47	58.80	58.53	3.95	4.01	13.72	13.65	15.70	15.81
			SOCl ₂	84	45-47	58.80	58.66	3.95	4.00	13.72	13.67	15.70	15.73
9 [b]	S	Cl	POCl ₃	98	86-88 [c]	47.15	47.12	2.77	2.81	11.00	10.97	25.17	25.08
			SOCl ₂	94	86-88 [c]	47.15	46.84	2.77	2.74	11.00	10.79	25.17	24.91

[a] The N_D^{25} for **7** derived by methods A and B were identical and the nmr spectra of the two were identical. [b] A mixture melting point with **8** or **9** obtained by method A (Table 3) was not depressed and the nmr spectra of each pair were identical. [c] Recrystallization from isopropyl alcohol.

EXPERIMENTAL

The nmr spectra were obtained with a Varian T-60 nmr spectrometer. The chemical shifts are reported in δ , using tetramethylsilane as reference. All melting points were taken upon a Fisher-Johns block and are uncorrected.

2-Thioxo-3(2H)-benzothiazolepropanenitrile (**1**), 2-Thioxo-3(2H)-benzoxazolepropanenitrile (**2**) and 5-Chloro-2-thioxo-3(2H)-benzothiazolepropanenitrile (**3**) (Method 1).

To a stirred solution at 50° containing 0.6 mole of 2-mercaptobenzothiazole, 2-mercaptobenzoxazole or 5-chloro-2-mercaptobenzothiazole, 60 g (0.6 mole) of triethylamine and 750 ml of water, 37.1 g (0.7 mole) of acrylonitrile was added in one portion. The stirred reaction mixture was heated at 50-60° for 5 hours and thereafter for 18 hours at 25-30°. The product was collected by filtration, washed with water until neutral to litmus and air-dried at 50°. The data are summarized in Table 1.

2-Thioxo-3(2H)-benzothiazolepropanamide (**4**), 2-Thioxo-3(2H)-benzoxazolepropanamide (**5**), and 5-Chloro-2-thioxo-3(2H)-benzothiazolepropanamide (**6**).

To a stirred solution containing 0.25 mole of 2-mercaptobenzothiazole, 2-mercaptobenzoxazole or 5-chloro-2-mercaptobenzothiazole, 0.3 mole of triethylamine and 500 ml of water, 0.3 mole of acrylamide was added in one portion. The stirred reaction mixture was heated at 60-70° for 24 hours. After cooling to 25°, 1 liter of water was added and stirring continued at 25-30° for 30 minutes. The solid was collected by filtration, washed with water until the washings were neutral to litmus and air-dried at 50°. The data are summarized in Table 2.

1 (Method II) and 3-(2-Benzothiazolythio)propanenitrile (**7**). (Method A).

To a stirred solution containing 51 g (0.3 mole) of 2-mercaptobenzothiazole, 24 g (0.3 mole) of 50% aqueous sodium hydroxide and 500 ml of water, 40.2 g (0.3 mole) of 3-bromopropionitrile was added in one portion. The reaction mixture was stirred at 25-30° for 3 days or at 50-60° for 1 day. After the addition of 24 g (0.3 mole) of 50% aqueous sodium hydroxide and 100 ml of water stirring was continued at 25-30° for 15 minutes. This was followed by the addition of 800 ml of ethyl ether. After

stirring at 25-30° for 30 minutes, the solid was collected by filtration, washed with 100 ml of ethyl ether and air-dried at 25-30°. Compound **1**, mp 168-170°, was obtained in 3% yield (12% conversion) for temperatures 25-30° for 3 days and 19% yield (91% conversion) for temperatures 50-60° for 1 day. After recrystallization from toluene **1** melted at 169-170°. A mixture melting point with the product obtained from Method I was not depressed and the nmr spectra of the two were identical (Table 1).

Anal. Calcd. for C₁₀H₈N₂S₂: C, 54.52; H, 3.66; N, 12.72; S, 29.11. Found: C, 54.57; H, 3.67; N, 12.70; S, 29.03.

The separated aqueous layer of the filtrate was made acidic (pH = 2) by the addition of concentrated hydrochloric acid. The recovered 2-mercaptobenzothiazole (MBT) was collected by filtration, washed with 500 ml of water and air-dried at 50°. Thirty-seven g (0.22 mole) and 20 g (0.12 mole) of MBT, mp 181-183°, were recovered for temperatures 25-30° for 3 days and 50-60° for 1 day, respectively. After recrystallization from toluene, MBT melting at 184-185°. A mixture melting point with an authentic sample was not depressed and the nmr spectra of the two were identical; nmr (deuteriodimethylsulfoxide): δ 6.82-7.54 (m, 4, ArH); 13.51 (br s, 1, NH).

Anal. Calcd. for C₇H₅NS₂: C, 50.27; H, 3.01; N, 8.37; S, 38.34. Found: C, 50.19; H, 3.02; N, 8.37; S, 38.26.

The separated top ethyl ether layer of the filtrate was washed with 5% aqueous sodium hydroxide and then 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 60° at 1-2 mm. The product was filtered to remove a small amount of solids. **7**, an amber viscous liquid ($N_D^{25} = 1.6607$) were obtained in 23% yield (86% conversion) and 39% yield (65% conversion) for temperatures 25-30° for 3 days and 50-60° for 1 day, respectively; nmr (deuteriodimethylsulfoxide): δ 2.98 (t, 2, -SCH₂CH₂CN), 3.51 (t, 2, -SCH₂CH₂CN), 6.93-7.94 (m, 4, ArH).

Anal. Calcd. for C₁₀H₈N₂S₂: C, 54.32; H, 3.66; N, 12.72; S, 29.11. Found: C, 54.30; H, 3.73; N, 12.67; S, 28.96.

2 (Method II) and 3-(2-Benzoxazolythio)propanenitrile (**8**) (Method A). **3** (Method II) and 5-Chloro-3-(2-benzothiazolythio)propanenitrile (**9**). (Method A).

The procedure was identical as described for **7** except 26.9 g (0.3 mole)

of 3-chloropropionitrile was used and 2-mercaptobenzothiazole was substituted with either 0.3 mole of 2-mercaptobenzoxazole or 5-chloro-2-mercaptobenzothiazole. The stirred reaction mixture was heated at 50-60° for 1 day. In addition after removal of the ether *in vacuo* at a maximum temperature of 60° no filtration was required. The data are summarized in Table 3.

3-(2-Benzothiazolythio)propanamide (**10**), 3-(2-Benzoxazolythio)propanamide (**11**) and 5-Chloro-3-(2-benzothiazolythio)propanamide (**12**).

To a stirred solution containing 0.3 mole of 2-mercaptobenzothiazole, 2-mercaptobenzoxazole or 5-chloro-2-mercaptobenzothiazole, 24 g (0.3 mole) of 50% aqueous sodium hydroxide and 500 ml of water, 37.4 (0.33 mole) of 95% 3-chloropropionamide was added in one portion. The stirred reaction mixture was heated at 50-60° for 24 hours. After cooling to 25°, 24 g (0.3 mole) of 50% aqueous sodium hydroxide was added and stirring was continued at 25-30° for 30 minutes. The solid was collected by filtration, washed with water until neutral to litmus and air-dried at 50°. The data are summarized in Table 4.

Compounds **7**, **8** and **9** via **10**, **11**, and **12** (Preferred Method B).

To a stirred solution at 90° containing 0.1 mole of **10**, **11** or **12** in 100 ml of dimethylformamide, 0.12 mole of phosphorous oxychloride or thionyl chloride was added dropwise at 90-100°. The stirred reaction mixture was heated at 90-100° for 1 hour. After cooling to 5°, 800 g of ice water was added and stirring continued at 0-10° for 30 minutes. For **8** and **9**, the solid was collected by filtration, washed with cold water until neutral to litmus and air-dried at 25-30°. For **7**, 500 ml of ethyl ether was added

and stirring continued at 25-30° for 30 minutes. The separated top ethyl ether layer was 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 60° at 1-2 mm. The data are summarized in Table 5.

REFERENCES AND NOTES

- [1] Presented at 20th Great Lakes Regional Meeting of the American Chemical Society, Organic Division, Milwaukee, Wisconsin, June 2-4, 1986.
- [2] A. M. Clifford and J. G. Lichty, Wingfoot Corporation, U. S. Patent 2,407,138 (1946); *Chem. Abstr.*, **41**, 488 (1947).
- [3] M. W. Harman, Monsanto Co. U. S. Patent 2,413,917 (1947); *Chem. Abstr.*, **41**, 2246 (1947).
- [4] C. D. Hurd and L. L. Gershbein, *J. Am. Chem. Soc.*, **69**, 2328 (1947).
- [5] F. D. Stewart and R. A. Mathes, *J. Org. Chem.*, **14**, 1111 (1949).
- [6] R. J. Gaul, W. J. Fremuth and M. N. O'Connor, *ibid.*, **26**, 5106 (1961).
- [7] A. F. Halasa and G. E. P. Smith, Jr., *ibid.*, **36**, 631 (1971); *ibid.*, **38**, 1353 (1973).
- [8] J. J. D'Amico, K. Boustany, A. B. Sullivan and R. H. Campbell, *Int. J. Sulfur Chem.*, Part A, **2**, 37 (1972).
- [9] J. J. D'Amico, S. T. Webster, R. H. Campbell, and C. E. Twine, *J. Org. Chem.*, **30**, 3268 (1965).