Synthesis of 3-Substituted-2-benzothiazolinone, 2-Benzoxazolinone and Benzothiazoline-2-thione

John J. D'Amico* and Frederic G. Bollinger

Monsanto Agricultural Company, A Unit of Monsanto Company, 800 N. Lindbergh Blvd., St. Louis, MO 63167

Received March 20, 1989

Dedicated to Professor Ernest Campaigne on the occasion of his 75th birthday

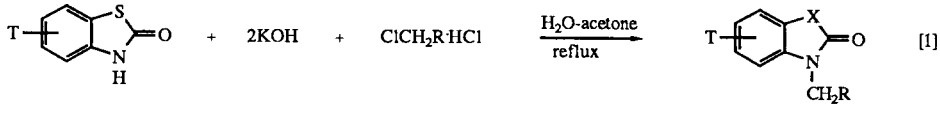
The reaction of 2-benzothiazolinone, 2-benzoxazolinone or benzothiazoline-2-thione under basic conditions with various electrophiles afforded the titled compounds **1-13**, **29-31** and **40-48**. The 3-(substituted-aminomethyl)-2-benzothiazolinone and related compounds **14-25** were prepared by the reaction of 3-(hydroxymethyl)-2-benzothiazolinone or the appropriate 2-benzothiazolinone and formaldehyde with the appropriate amine or substituted aniline. The reaction of **9**, **13** or **25** with methyl iodide afforded the quaternary ammonium iodides **26-28**. The reaction of the appropriate potassium salts of various phenol with 3-(chloromethyl)-2-benzothiazolinone afforded the 3-(substituted-phenoxymethyl)-2-benzothiazolinone and related compounds **32-39**. The ethyl or isopropylxanthates **49-54** were synthesized by the reaction of 3-(chloromethyl)-2-benzothiazolinone and appropriate compounds with potassium ethyl or isopropyl xanthate. The reaction of 3-(chloromethyl)-2-benzothiazolinone with sodium sulfide afforded the sulfide **55**.

J. Heterocyclic Chem., **26**, 1245 (1989).

Since derivatives of 2-benzothiazolinone, 2-benzoxazolinone and benzothiazoline-2-thione [1-10] exhibited biological activity, it appeared expedient to continue our research efforts in this area of Chemistry.

The purpose of this investigation was to react (a) 2-benzothiazolinone and 2-benzoxazolinone under basic conditions with various electrophiles and (b) 3-(chloromethyl)-2-benzothiazolinone, 3-(hydroxymethyl)-2-benzothiazolinone and related compounds with various nucleophiles.

The reaction of the appropriate 2-benzothiazolinone or 2-benzoxazolinone with 2- or 3-picolyl chloride hydrochloride under basic conditions afforded *N*-(2 or 3-pyridyl)-2-benzothiazolinone and related products **1-8** [Table 1].



T = H, 6-OCH_2H_5 or 5-Cl, X = S
T = H, X = O

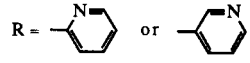
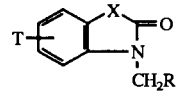


Table 1

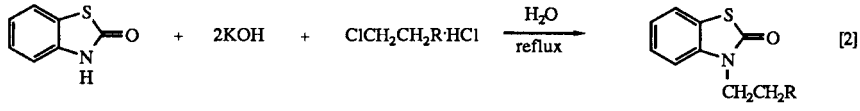


1,2,3,5, and 7 **4,6, and 8**

No.	T	X	Mp°C	Crude % Yield	Empirical formula	%C Calcd.	%C Found	%H Calcd.	%H Found	%N Calcd.	%N Found	%S Calcd.	%S Found
1	H	S	102-103 [a]	90	$C_{13}H_{10}N_2OS$	64.44	64.36	4.16	4.18	11.56	11.56	13.23	13.25
2	6-OC_2H_5	S	89-90 [b]	84	$C_{15}H_{14}N_2O_2S$	62.92	62.88	4.93	4.95	9.78	9.79	11.20	11.13
3	6-Br	S	114-115 [a]	84	$C_{13}H_9BrN_2OS$	48.61	48.79	2.82	2.57	8.72	8.76	9.98	10.05
4	H	S	93-95 [c]	66	$C_{13}H_{10}N_2OS$	64.44	64.57	4.16	4.23	11.56	11.57	13.23	13.17
5	5-Cl	S	105-106 [a]	92	$C_{13}H_9ClN_2OS$	56.42	56.50	3.28	3.33	10.12	10.09	11.59	11.55
6	H	O	138-140 [b]	53	$C_{13}H_{10}N_2O_2$	69.02	68.94	4.46	4.48	12.38	12.34	---	---
7	H	O	108-109 [b]	59	$C_{13}H_{10}N_2O_2$	69.02	68.97	4.46	4.46	12.38	12.35	---	---
8	H	S	115-116 [c]	91	$C_{13}H_{10}N_2OS$	64.44	64.47	4.16	4.20	11.56	11.56	13.23	13.23

[a] Recrystallization from methyl alcohol. [b] Recrystallization from isopropyl alcohol. [c] Recrystallization from isopropyl alcohol-heptane-3:1.

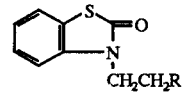
The 3-(2-substituted-aminoethyl)-2-benzothiazolinone and related products **9-13** [Table 2] were synthesized by the reaction of 2-benzothiazolinone [2] with the appropriate 2-chloroethylamine hydrochloride under basic conditions.



9, R = –N⟨ ⟩, **10**, R = –N⟨ ⟩O, **11**, R = $-N(C_2H_5)_2$

12, R = $-NH_2$, **13**, R = $-N(CH_3)_2$

Table 2



R = –N⟨ ⟩, –N⟨ ⟩O, $-N(C_2H_5)_2$, $-NH_2$, $-N(CH_3)_2$

No.	Physical state	bp °C	% Yield	Empirical formula	%C Calcd.	%C Found	%H Calcd.	%H Found	%N Calcd.	%N Found	%S Calcd.	%S Found
9	[a]	----	86	$C_{14}H_{18}N_2OS$	64.09	63.88	6.92	6.98	10.68	10.55	12.22	12.36
10	[a]	----	68	$C_{13}H_{16}N_2O_2S$	59.06	59.30	6.10	6.16	10.60	10.60	12.13	12.29
11	[a]	150-2/0.2 mm (N_D^{25} = 1.5704)	75	$C_{13}H_{18}N_2OS$	62.37	62.10	7.25	7.30	11.19	11.02	12.81	13.00
12	[a]	----	88	$C_9H_{10}N_2OS$	55.64	55.48	5.19	4.96	14.42	14.29	16.51	16.34
13	[a]	154-60/0.2 mm (N_D^{25} = 1.5889)	69	$C_{11}H_{14}N_2OS$	59.43	59.23	6.35	6.25	12.60	12.40	14.42	14.23

[a] Very viscous dark amber liquid.

In Method 1, the reaction of 3-(hydroxymethyl)-2-benzothiazolinone [1] with the appropriate amine or substituted aniline in methanol or 2-propanol at reflux afforded the 3-(substituted-aminomethyl)-2-benzothiazolinone and related compounds **14-20** [Table 3].

Method 1

In Method 2, the 3-(substituted-aminomethyl)-2-benzothiazolinone and related products **21-25** [Table 4] were synthesized by the reaction of 2-benzothiazolinone [2] or 6-bromo-2-benzothiazolinone [6] with formaldehyde and the appropriate amine or aniline.

Method 2

The reaction of **9**, **13** or **25** with methyl iodide furnished the quaternary ammonium iodides **26-28** [Table 5].

3-(3-Substituted-phenoxypropyl)-2-benzothiazolinone and related products **29-31** [Table 6] were synthesized by the reaction of the appropriate 2-benzothiazolinone or 2-benzoxazolinone with 3-phenoxypropyl bromide under basic conditions.

The reaction of the appropriate potassium salts of phenol with 3-(chloromethyl)-2-benzothiazolinone [1] in an acetate-water medium afforded 3-(substituted-phenoxymethyl)-2-benzothiazolinone and related products **32-39** [Table 7].

The reaction of the appropriate 2-benzothiazolinone with substituted chloroformate and triethylamine in an acetone-water medium at 0-10° furnished the substituted-2-oxo-3-benzothiazolinecarboxylates **40-48** [Table 8].

(2-Oxo or thioxobenzothiazolin-3-yl)methyl ethyl or isopropyl xanthate and related compounds **49-54** [Table 9] were prepared by the reaction of potassium ethyl or isopropyl xanthate with 3-(chloromethyl)-2-benzothiazolinone [1], 3-(chloromethyl)-2-benzoxazolinethione [1], or 6-ethoxy-3-(chloromethyl)-2-benzothiazolinethione.

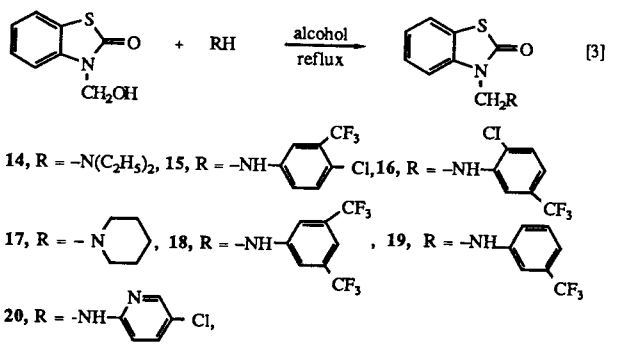
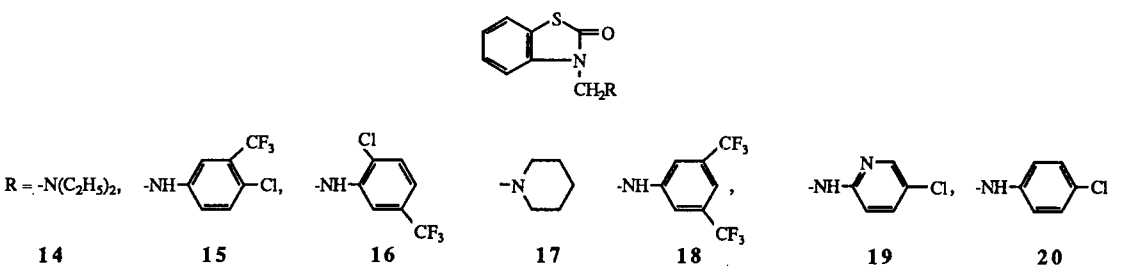


Table 3 (Method 1)



14 **15** **16** **17** **18** **19** **20**

No.	Solvent A CH_3OH Ml	Solvent A $(CH_3)_2CHOH$ Ml	Reflux	25-30°C	Solvent B Heptane Ml	Solvent B H_2O Ml	Mp°C	Crude % Yield	Empirical formula	%C Calcd.	%C Found	%H Calcd.	%H Found	%N Calcd.	%N Found	%S Calcd.	%S Found
14	40	--	0.5	24	--	--	53-54 [a]	89	$C_{12}H_{16}N_2OS$	60.98	60.87	6.82	6.64	11.85	11.67	13.57	13.47
15	--	50	1.0	--	100	--	158-159 [b]	84	$C_{15}H_{10}ClF_3N_2OS$	50.21	50.33	2.81	2.84	7.81	7.81	8.94	8.94
16	--	50	6.0	18	100	--	141-142 [b]	47	$C_{15}H_{10}ClF_3N_2OS$	50.21	50.47	2.81	3.09	7.81	7.64	8.94	8.70
17	--	40	1.0	--	--	25	93-94 [c]	81	$C_{13}H_{16}N_2OS$	62.87	62.68	6.49	6.51	11.28	11.25	12.91	12.84
18	--	50	6.0	18	--	800	139-140 [d]	51	$C_{16}H_{10}F_6N_2OS$	48.98	49.92	2.57	2.61	7.14	7.11	8.17	8.83
19	20	--	0.5	--	--	--	121-122 [d]	96	$C_{15}H_{11}F_3N_2OS$	55.55	55.62	3.42	3.42	8.64	8.63	9.89	9.91
20	--	100	1.0	--	50	--	179-180 [e]	38	$C_{13}H_{10}ClN_3OS$	53.51	53.50	3.45	3.46	14.40	14.44	10.99	10.92

[a] Methanol removed *in vacuo* (1-2 mm) at max temp 80-90°. [b] Recrystallization from 2-propanol. [c] Recrystallization from heptane. [d] Recrystallization from heptane-2-propanol. [e] Recrystallization from toluene.

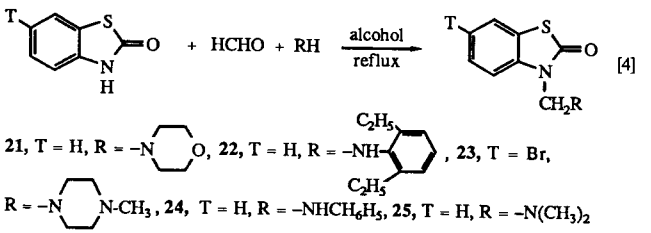
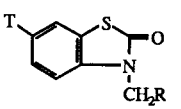
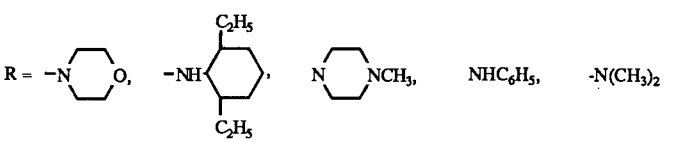


Table 4 (Method 2)





21 22 23 24 25

No.	T	Solvent A CH_3OH Ml	Solvent A $(CH_3)_2CHOH$ Ml	Reaction Time (hours) Reflux	Reaction Time (hours) 25-30°C	Solvent B Solvent	Solvent B Ml	Mp°C	Crude % Yield	Empirical formula	%C Calcd.	%C Found	%H Calcd.	%H Found	%N Calcd.	%N Found	%S Calcd.	%S Found
21	H	20	--	0.5	–	Water	50	86-87	96	$C_{12}H_{14}N_2O_2S$	57.58	57.61	5.64	5.67	11.19	11.21	12.81	12.83
22	H	–	20	24	–	Heptane 2-propanol	25 37	184-185 [a]	78	$C_{18}H_{20}N_2OS$	69.20	69.10	6.45	6.35	8.97	8.58	10.26	10.00
23	Br	40	--	1	24	Methanol	25	140-141 [b]	93	$C_{13}H_{17}BrN_3OS$	45.62	45.68	4.71	4.76	12.18	12.24	9.37	9.38
24	H	–	20	1	–	Heptane	50	163-164 [c]	96	$C_{14}H_{12}N_2OS$	65.60	65.58	4.72	4.75	10.93	10.90	12.51	12.51
25	H	20	--	–	48	Ethyl ether	300	viscous liquid	94	$C_{10}H_{12}N_2OS$	57.67	57.39	5.81	5.57	13.45	13.63	15.40	15.67

[a] Recrystallization from toluene. [b] Recrystallization from 2-propanol. [c] Recrystallization from ethyl acetate.

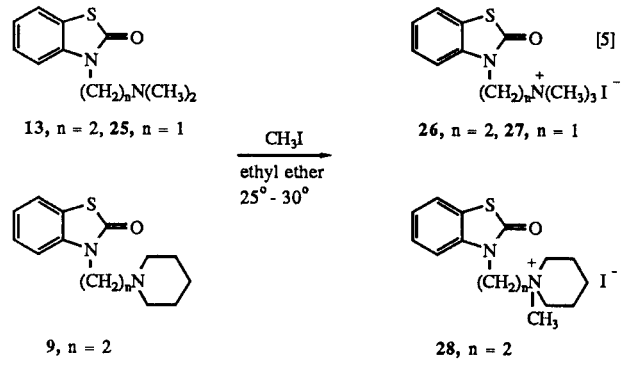
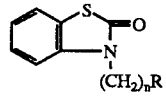
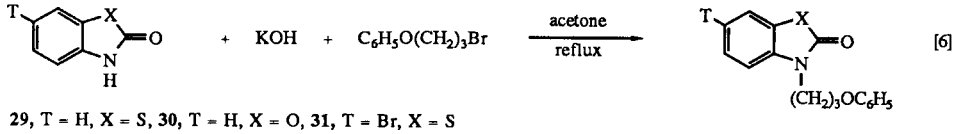


Table 5

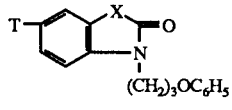


No.	n	R	Mp °C	% Yield	Empirical formula	%C Calcd.	%C Found	%H Calcd.	%H Found	%N Calcd.	%N Found	%S Calcd.	%S Found
26	2	$-\overset{+}{N}(CH_3)_3\ I^-$	288-290	41	$C_{12}H_{17}IN_2OS$	39.57	39.48	4.70	4.60	7.69	7.92	8.80	8.82
27	1	$-\overset{+}{N}(CH_3)_3\ I^-$	114-116	57	$C_{11}H_{15}IN_2OS$	37.73	38.88	4.32	4.40	8.00	7.88	9.16	9.04
28	2		238-240	72	$C_{11}H_{15}IN_2OS$	44.56	44.80	5.24	5.19	6.93	6.84	7.93	8.18



29, T = H, X = S, **30**, T = H, X = O, **31**, T = Br, X = S

Table 6



No.	T	X	Mp °C	Crude % Yield	Empirical formula	%C Calcd.	%C Found	%H Calcd.	%H Found	%N Calcd.	%N Found	%S Calcd.	%S Found
29	H	S	60-61 [a]	99	$C_{16}H_{15}NO_2S$	67.34	67.14	5.30	5.34	4.91	4.85	11.24	11.10
30	H	O	57-59 [b]	93	$C_{16}H_{15}NO_3$	71.36	71.32	5.61	5.65	5.20	5.19	---	---
31	Br	S	101-102 [b]	88	$C_{16}H_{14}BrNO_2S$	52.76	52.67	3.87	3.91	3.85	3.83	8.80	8.77

[a] Recrystallization from 2-propanol-heptane (1:1). [b] Recrystallization from 2-propanol.

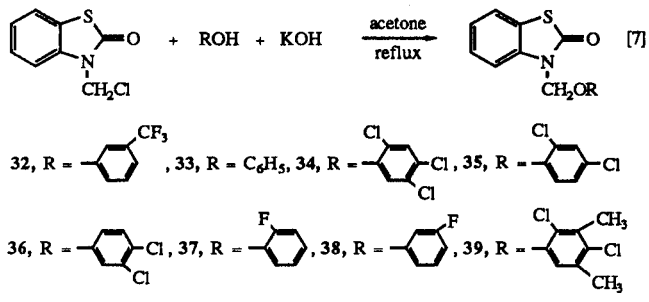
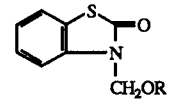
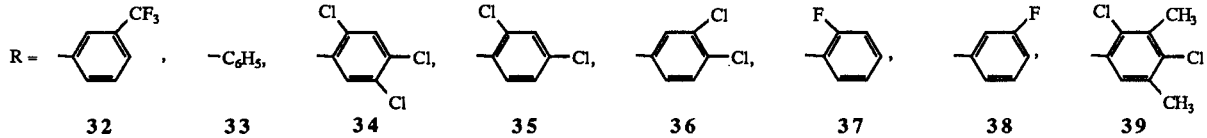


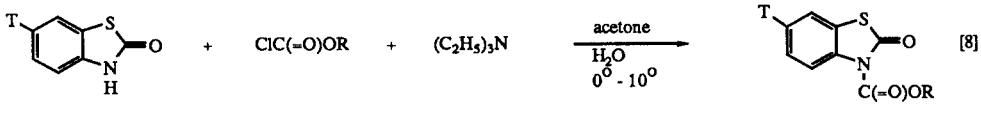
Table 7





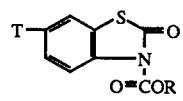
No.	Mp°C	Crude % Yield	Empirical formula	%C Calcd.	%C Found	%H Calcd.	%H Found	%N Calcd.	%N Found	%S Calcd.	%S Found
32	100-101 [a]	92	$C_{15}H_{10}F_3NO_2S$	55.38	55.19	3.10	3.18	4.31	4.36	9.98	10.00
33	58-59 [a]	93	$C_{14}H_{11}NO_2S$	65.35	65.24	4.31	4.19	5.44	5.36	12.46	12.76
34	181-182 [b]	93	$C_{14}H_8Cl_3NO_2S$	46.62	46.67	2.24	2.25	3.88	3.86	8.89	8.97
35	145-146 [a]	97	$C_{14}H_9Cl_2NO_2S$	51.55	51.46	2.78	2.81	4.29	4.30	9.83	9.83
36	132-133 [c]	94	$C_{14}H_9Cl_2NO_2S$	51.55	51.40	2.78	2.83	4.29	4.31	9.83	9.92
37	65-67 [d]	91	$C_{14}H_{10}FNO_2S$	61.08	60.91	3.66	3.70	5.09	5.12	11.65	11.67
38	95-98 [a]	89	$C_{14}H_{10}FNO_2S$	61.08	60.96	3.66	3.46	5.09	5.17	11.65	11.82
39	184-186 [a]	88	$C_{16}H_{13}Cl_2NO_2S$	54.24	54.19	3.70	3.74	3.95	3.97	9.05	9.01

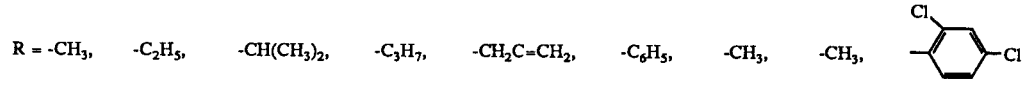
[a] Recrystallization from 2-propanol. [b] Recrystallization from ethyl acetate. [c] Recrystallization from toluene. [d] Recrystallization from heptane-2-propanol (2:1).



40, T = H, R = $-CH_3$, **41**, T = H, R = $-C_2H_5$, **42**, T = H, R = $-CH(CH_3)_2$
43, T = H, R = $-C_3H_7$, **44**, T = H, R = $-CH_2CH{=}CH_2$, **45**, T = H, R = $-C_6H_5$
46, T = Br, R = $-CH_3$, **47**, T = OC_2H_5, R = $-CH_3$, **48**, T = H, R = 

Table 8

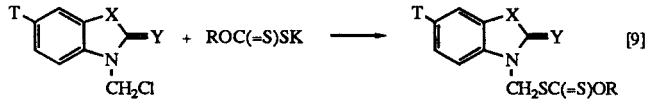




40 41 42 43 44 45 46 47 48

No.	T	Mp°C	Crude % Yield	Empirical formula	%C Calcd.	%C Found	%H Calcd.	%H Found	%N Calcd.	%N Found	%S Calcd.	%S Found
40	H	47-48 [a]	93	$C_9H_7NO_3S$	51.66	51.65	3.37	3.37	6.70	6.67	15.33	15.31
41	H	67-68	96	$C_{10}H_9NO_3S$	53.80	53.91	4.06	4.10	6.27	6.24	14.36	14.33
42	H	74-75 [a]	67	$C_{11}H_{11}NO_3S$	55.68	55.50	4.67	4.71	5.90	5.85	13.51	13.60
43	H	64-65 [a]	98	$C_{11}H_{11}NO_3S$	55.68	55.73	4.67	4.69	5.90	5.88	13.51	13.51
44	H	78-79 [a]	85	$C_{11}H_9NO_3S$	56.16	56.10	3.86	3.84	5.95	5.78	13.63	13.67
45	H	92-93 [a]	99	$C_{14}H_9NO_3S$	61.98	61.90	3.34	3.37	5.16	5.15	11.82	11.79
46	Br	167-168	83	$C_9H_6BrNO_3S$	37.51	37.58	2.10	2.13	4.86	4.85	11.13	11.13
47	$OC2H_5$	151-152 [b]	93	$C_{11}H_{11}NO_4S$	52.16	52.27	4.38	4.43	5.53	5.52	12.66	12.72
48	H	82-84	77	$C_{14}H_7Cl_2NO_3S$	49.43	49.80	2.07	2.24	4.12	4.29	9.43	9.25

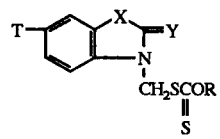
[a] Recrystallization from heptane-3-propanol. [b] Recrystallization from 2-propanol.



[9]

49, T = H, X = S, Y = O, R = $-C_2H_5$
50, T = H, X = S, Y = O, R = $CH(CH_3)_2$
51, T = H, X = S, Y = S, R = $-C_2H_5$
52, T = H, X = S, Y = S, R = $CH(CH_3)_2$
53, T = H, X = O, Y = S, R = $-C_2H_5$
54, T = $-OC_2H_5$, X = S, Y = S, R = $-C_2H_5$

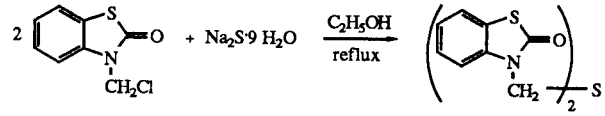
Table 9



No.	T	X	Y	R	Solvent	Mp°C	Crude % Yield	Empirical formula	%C Calcd.	%C Found	%H Calcd.	%H Found	%N Calcd.	%N Found	%S Calcd.	%S Found
49	H	S	O	$-C_2H_5$	[a]	75-76 [c]	98	$C_{11}H_{11}NO_2S_3$	46.29	46.18	3.89	3.92	4.91	4.89	33.71	33.63
50	H	S	O	$-CH(CH_3)_2$	[b]	83-84 [c]	83	$C_{12}H_{13}NO_2S_3$	48.13	48.10	4.38	4.41	4.68	4.70	32.13	32.02
51	H	S	S	$-C_2H_5$	[a]	86-87 [d]	93	$C_{11}H_{11}NOS_4$	43.82	43.80	3.68	3.67	4.65	4.67	42.55	42.46
52	H	S	S	$-CH(CH_3)_2$	[b]	64-65	94	$C_{12}H_{13}NOS_4$	45.68	45.69	4.15	4.15	4.44	4.53	40.65	40.53
53	H	O	S	$-C_2H_5$	[a]	85-87	95	$C_{11}H_{11}NO_2S_3$	46.29	46.55	3.89	3.88	4.91	4.99	33.71	33.51
54	$-OC_2H_5$	S	S	$-C_2H_5$	[a]	117-119 [e]	98	$C_{13}H_{15}NO_2S_4$	45.19	45.24	4.38	4.38	4.05	4.04	37.12	37.02

[a] Ethanol. [b] 2-Propanol. [c] Recrystallization from heptane-3-propanol. [d] Recrystallization from heptane-ethyl acetate. [e] Recrystallization from ethyl acetate.

Bis-(2-oxobenzothiazolin-3-ylmethyl) sulfide (**55**) was prepared by the reaction of 3-(chloromethyl)-2-benzothiazolinone [1] with sodium sulfide in refluxing ethanol.



[10]

55

EXPERIMENTAL

The ^1H nmr spectra were obtained with a Varian T-60 NMR spectrometer. The chemical shifts are reported in δ, using tetramethylsilane as the reference. All melting points were taken upon a Fisher-Johns block and are uncorrected.

N-(2 or 3-Pyridyl)-2-benzothiazolinone and Related Products **1-8**.

To a stirred solution containing 0.2 mole of 2-benzothiazolinone [2], 5-chloro-2-benzothiazolinone [5], 6-bromo-2-benzothiazolinone [6], or 2-benzoxazolinone, 26.4 g (0.4 mole) of 85% potassium hydroxide, 150 ml of water and 150 ml of acetone, 34.9 g (0.2 mole) of 2- or 3-picolyl chloride hydrochloride was added in one portion. The stirred reaction mixture was heated at reflux for 24 hours. After cooling to 5°, 800 g of ice water was added and stirring continued at 0-10° for one hour. The solid was collected by filtration, washed with water until neutral and air-dried at 25-30°. The data are summarized in Table 1.

3-(2-Substituted-aminoethyl)-2-benzothiazolinone and Related Compounds **9-13**.

To a stirred solution containing 30.2 g (0.2 mole) of 2-benzothiazolinone [2] and 26.4 g (0.4) of 85% potassium hydroxide in 300 ml of water was added 0.2 mole of *N*-(2-chloroethyl)piperidine, *N*-(2-chlorethyl)morpholine, 2-diethylaminoethyl chloride, 2-aminoethyl chloride or 2-dimethylaminoethyl chloride hydrochloride. The stirred reaction mixture was heated at reflux for 24 horurs. After cooling to 25°, 600 ml of ethyl ether was added and stirring continued at 25-30° for 15 minutes. The separated ether layer was washed with water until neutral and dried over sodium sulfate. The ether was removed *in vacuo* at 1-2 mm at a maximum temperature of 80-90°. The data are summarized in Table 2.

3-(Substituted-aminomethyl)-2-benzothiazolinone and Related Compounds **14-25**.

Method 1, **14-20**.

To a stirred slurry containing 18.1 g (0.1 mole) of 3-(hydroxymethyl)-2-benzothiazolinone [1], in an appropriate amount of solvent A (methanol or 2-propanol) as specified in Table 3, 0.11 mole of the appropriate amine or substituted aniline was added in one portion. The stirred reaction mixture was heated at reflux and then at 25-30° for the time period specified in Table 3. After cooling the stirred reaction mixture to 0°, an appropriate amount of solvent B (heptane or water) as specified in Table 3 was added to the mixture and the resulting mixture was stirred at 0-10° for 30 minutes. The solid was collected by filtration and air-dried at 25-30°. The data are summarized in Table 3.

Method 2, **21-25**.

A stirred slurry containing 0.1 mole of 2-benzothiazolinone [2] or 6-bromo-2-benzothiazolinone [6] and 16 ml of 37% aqueous formaldehyde in an appropriate solvent A (methanol or 2-propanol) as specified in Table 4, was heated at reflux for 30 minutes. After cooling the stirred slurry to 25°, 0.11 mole of the appropriate amine or aniline was added in one portion. The reaction mixture was stirred at reflux and or at 25-30° for the time period as specified in Table 4. For compounds **21-24**, after cooling the stirred reaction mixture to 0°, an appropriate amount of solvent B was added and the resulting mixture was stirred at 0-10° for 1 hour. The solid product was collected by filtration and air-dried at 25-30°. For **20**, after cooling to 25°, 300 ml of ethyl ether was added and stirring continued at 25-30° for 15 minutes. The top ether layer was separated, washed with water until neutral and dried over sodium sulfate. The ether was removed *in vacuo* at 1-2 mm at a maximum temperature of 80-90°. The data are summarized in Table 4.

Quaternary Ammonium Iodides **26-28**.

To a stirred solution containing 0.1 mole of **9**, **13** or **25** in 150 ml of ethyl ether, 28.2 g (0.2 mole) of methyl iodide was added in one portion. After stirring the reaction mixture for 24 hours at 25-30°, the solid product was collected by filtration and air-dried at 25-30°. The data are summarized in Table 5.

3-(3-Substituted-phenoxypropyl)-2-benzothiazolinone and Related Products **29-31**.

To a stirred solution containing 0.2 mole of an appropriate 2-benzothiazolinone or 2-benzoxazolinone, 13.2 g (0.2 mole) of 85% potassium hydroxide, 300 ml of acetone and 10 ml of water was added 0.2 mole of 3-phenoxyphenyl bromide in one portion. The stirred reaction mixture was heated at reflux for 24 hours. After cooling the reaction mixture to 10°, 800 g of ice water was added and stirring continued at 0-10° for 30 minutes. The solid product was collected by filtration, washed with cold water until neutral and air-dried at 25-30°. The data are summarized in Table 6.

3-(Substituted-phenoxymethyl)-2-benzothiazolinone and Related Products **32-39**.

To a stirred solution containing 0.1 mole of an appropriate phenol, 6.6 g (0.1 mole) of 85% potassium hydroxide, 200 ml of acetone and 10 ml of water, was added 20 g (0.1 mole) of 3-(chloromethyl)-2-benzothiazolinone [1] in one portion. The remainder of the procedure was identical as described above for compounds **29-31**. The data are summarized in Table 7.

Substituted-2-oxo-3-benzothiazolinonecarboxylates **40-48**.

To a stirred charge at 0° contianing 0.1 mole of the appropriate 2-benzothiazolinone, 11.4 g (0.11 mole) of triethylamine, 300 ml of acetone and 20 ml of water, was added dropwise, 0.1 mole of the appropriate substituted chloroformate at 0-10°. The reaction mixture was stirred at 25-30° for 24 hours. After cooling the stirred mixture to 5°, 800 g of ice water was added and stirring continued at 0-10° for 1 hour. The solid was collected by filtration, washed with water until neutral and air-dried at 25-30°. The data are summarized in Table 8.

(2-Oxo or thioxobenzothiazolin-3-yl)methyl Alkyl Xanthate and Related Compounds **49-54**.

To a stirred slurry containing 0.11 mole of potassium ethyl or isopropyl xanthate in 200 ml of ethanol or 2-propanol, 0.1 mole of 3-(chloromethyl)-2-benzothiazolinone [1], 3-(chloromethyl)-2-benzoxazolethione [1] or 6-ethoxy-3-(chloromethyl)-2-benzothiazolethione was added in one portion. The reaction mixture was stirred at 25-30° for three days. After cooling to 5°, 800 g of ice water was added and stirring continued at 0-10° for one hour. The solid was collected by filtration, washed with water until neutral and air-dried at 25-30°. The data are summarized in Table 9.

Bis(2-oxobenzothiazolin-3-ylmethyl) Sulfide **55**.

To a stirred charge containing 19.2 g (0.08 mole) of sodium sulfide nonahydrate and 300 ml of ethanol, 30 g (0.15 mole) of 3-(chloromethyl)-2-benzothiazolinone [1] was added in one por-

tion. The stirred reaction mixture was heated at reflux for 24 hours. After cooling to 5°, 800 g of ice water was added and stirring continued at 0-10° for 1 hour. The solid was collected by filtration, washed with water until neutral and air-dried at 25-30°. The crude product, mp 184-185°, was obtained in 87% yield. After recrystallization from toluene **55** melted at 185-187°; nmr (deuteriochloroform): δ 5.30 (s, 4, $-NCH_2$), 6.95-7.60 (m, 8, ArH).

Anal. Calcd. for $C_{16}H_{12}N_2O_2S_3$: C, 53.31; H, 3.36; N, 7.77; S, 26.68. Found: C, 53.26; H, 3.40; N, 7.84; S, 26.79.

REFERENCES AND NOTES

[1] J. J. D'Amico, L. Suba and P. G. Ruminski, *J. Heterocyclic Chem.*, **22**, 1479 (1985).

[2] J. J. D'Amico, R. W. Fuhrhop, F. G. Bollinger and W. E. Dahl, *J. Heterocyclic Chem.*, **23**, 641 (1986).

[3] J. J. D'Amico, L. A. Suba and P. G. Ruminski, *J. Heterocyclic Chem.*, **23**, 1629 (1986).

[4] J. J. D'Amico, F. G. Bollinger and W. E. Dahl, *Phosphorus Sulfur*, **35**, 71 (1988).

[5] J. J. D'Amico and F. G. Bollinger, *J. Heterocyclic Chem.*, **25**, 1183 (1988).

[6] J. J. D'Amico, F. G. Bollinger and J. J. Freeman, *J. Heterocyclic Chem.*, **25**, 1503 (1988).

[7] J. J. D'Amico, J. T. Marvel and F. G. Bollinger, *J. Heterocyclic Chem.*, **25**, 1375 (1988).

[8] J. J. D'Amico and F. G. Bollinger, *J. Heterocyclic Chem.*, **25**, 1487 (1988).

[9] J. J. D'Amico and F. G. Bollinger, *J. Heterocyclic Chem.*, **25**, 1601 (1988).

[10] J. J. D'Amico and F. G. Bollinger, *J. Heterocyclic Chem.*, **26**, 655 (1989).