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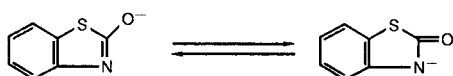
Monsanto Agricultural Company, A Unit of Monsanto Company,
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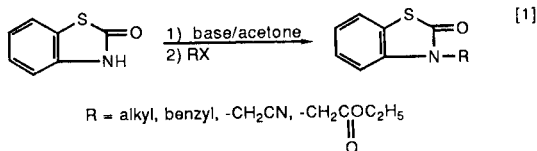
The reaction of 2-oxo-3-benzothiazolineacetic acid (5) and the 5-chloro analogue 6 with thionyl chloride afforded the titled compounds 7 and 8. The reaction of 7 or 8 with substituted hydrazines, amines or substituted anilines, alcohols and mercaptans furnished the hydrazides 9-14, acetamides and acetanilides 16-21, esters 26-30 and thioesters 31-37, respectively. Alternate routes for the synthesis of hydrazide 15, acetamides and acetanilides 22-25 and thioesters 35-36 are described. The reaction of 2-oxo-3(2*H*)-benzothiazolineacetonitrile with thioacetic acid under acidic conditions afforded 2-oxo-3-benzothiazolineethanethioamide (38).

J. Heterocyclic Chem., **25**, 1183 (1988).

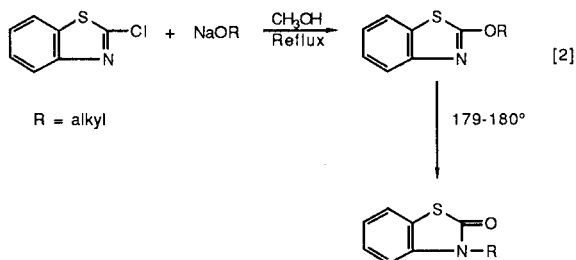
Due to the ambident nature of 2-benzothiazolinone anion in nucleophilic displacement reactions under basic



conditions, either the *N* or *O*-substituted products are possible. However, almost exclusively under a variety of reaction conditions, the *N*-substituted products are obtained. For example, the following reactions afforded the *N*-substituted compounds:

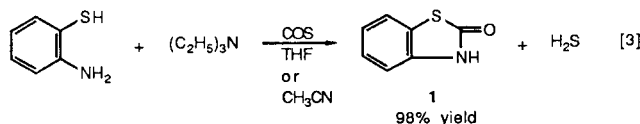


However, Davies and Sexton [1] prepared the *O*-substituted products by the following reaction and, upon heating at 175-180°, the *O*-substituted product was thermally rearranged to the *N*-substituted product.

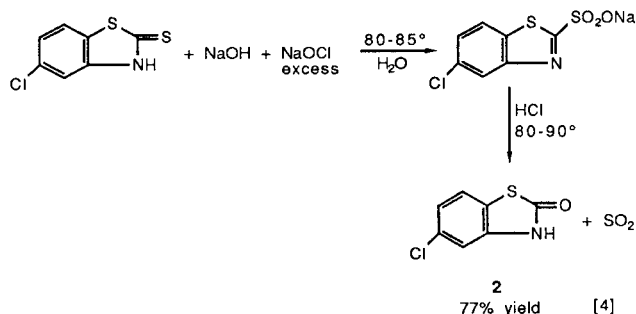


The purpose of this investigation was to prepare 2-oxo-3-benzothiazolineacetyl chloride (7) and 5-chloro-2-oxo-3-benzothiazolineacetyl chloride (8) and to react these acetyl chlorides with various nucleophiles.

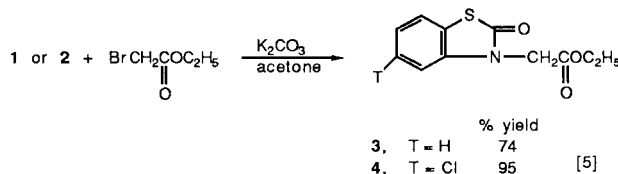
The intermediates 1-6 were prepared by well known procedures (Reactions [1-7]). 2-Benzothiazolinone (1) was prepared in 98% yield by our new method [2] as illustrated by the following reaction:



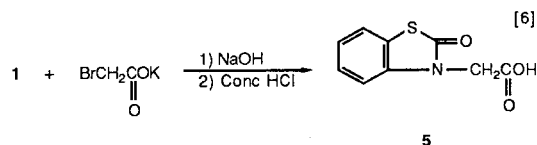
Substituting 5-chlorobenzothiazoline-2-thione for benzothiazoline-2-thione, 5-chloro-2-benzothiazolinone (2) was prepared by the method of Herdieckeroff and Tschunkur [3] and Colonna [4].



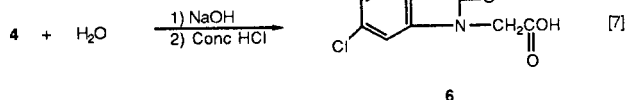
Ethyl 2-oxo-3-benzothiazolineacetate (3) and ethyl 5-chloro-2-oxo-3-benzothiazolineacetate (4) were synthesized by the reaction of 1 or 2 with ethyl bromoacetate under basic conditions.



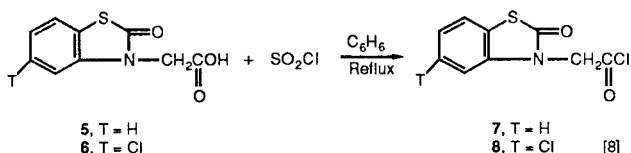
The reaction 1 with bromoacetic acid under basic conditions afforded 2-oxo-3-benzothiazolineacetic acid (5) in 80% yield.



The hydrolysis of **4** with dilute sodium hydroxide afforded 5-chloro-2-oxo-3-benzothiazolineacetic acid (**6**) in 90% yield.

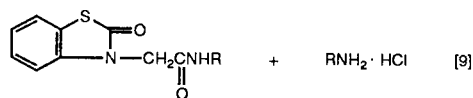
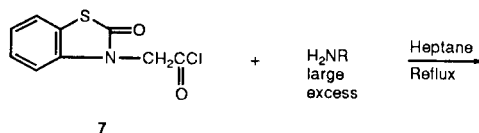


The two key intermediates 2-oxo-3-benzothiazolineacetyl chloride (**7**) and 5-chloro-2-oxo-3-benzothiazolineacetyl chloride (**8**) were prepared by the reaction of **5** and **6** with thionyl chloride.



In Method A, the reaction of **7** with a *large excess* of the appropriate substituted hydrazines in refluxing heptane afforded the hydrazides **9-13** [Table 1].

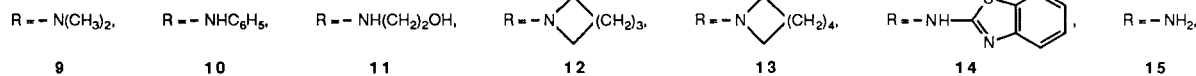
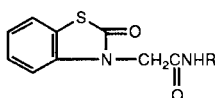
Method A.



- 9; R = -N(CH₃)₂,
 10; R = -NHC₆H₅,
 11; R = -NHCH₂CH₂OH,
 12; R = -N(CH₂)₃,
 13; R = -N(CH₂)₄.

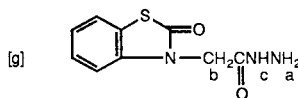
In Method B, the hydrazide **14** was synthesized by the reaction of **7** with 2-hydrazinobenzothiazole in a mole/mole ratio in refluxing heptane containing a mole of triethylamine [Table 1].

Table 1
Hydrazides

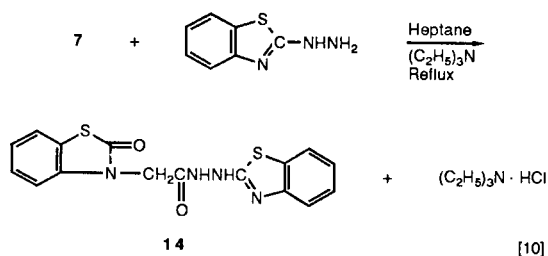


No.	Method	mp °C	Yield %	Empirical Formula	%C		%H		%N		%S	
					Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
9	A	204-205 [a]	63	C ₁₁ H ₁₃ N ₃ O ₂ S	52.57	52.33	5.21	5.21	16.72	16.64	12.76	12.82
10	A	222-223 [b]	73	C ₁₅ H ₁₃ N ₃ O ₂ S	60.18	60.27	4.38	4.39	14.04	13.98	10.71	10.81
11	A	156-157 [c]	48	C ₁₁ H ₁₃ N ₃ O ₃ S	49.43	49.21	4.90	4.97	15.72	15.70	12.00	11.97
12	A	208-209 [d]	78	C ₁₄ H ₁₇ N ₃ O ₂ S	57.71	57.89	5.88	5.94	14.42	14.34	11.00	11.07
13	A	209-210 [c]	75	C ₁₅ H ₁₉ N ₃ O ₂ S	58.99	58.78	6.27	6.29	13.76	13.68	10.50	10.57
14	B	260-261 [e]	87	C ₁₆ H ₁₂ N ₄ O ₂ S ₂	53.92	53.68	3.39	3.49	15.72	15.57	17.99	17.75
15 [g]	C	213-214 [f]	45	C ₉ H ₉ N ₃ O ₂ S	48.42	48.34	4.06	4.05	18.82	18.83	14.36	14.27

[a] Recrystallization from isopropyl alcohol. [b] Recrystallization from ethyl acetate. [c] Recrystallization from methyl alcohol. [d] Recrystallization from toluene. [e] Recrystallization from dimethylformamide. [f] Recrystallization from acetonitrile.

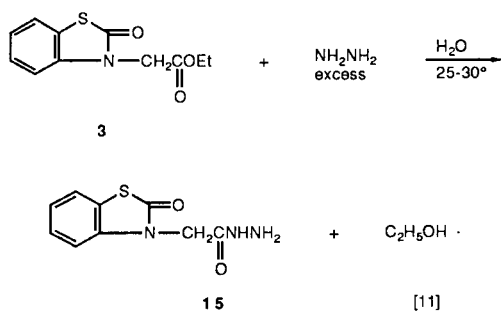


Method B.



In Method C, the reaction of **3** with an excess of hydrazine in a water medium at 25-30° afforded the hydrazide **15** [Table 1].

Method C.



The reaction of **7** or **8** with an excess of the appropriate amines or anilines in refluxing heptane afforded the acetamides and acetanilides **16-21** [Table 2].

Method A.

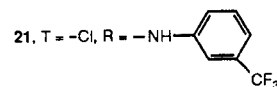
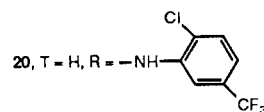
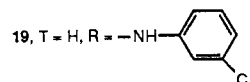
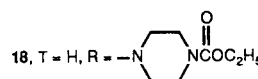
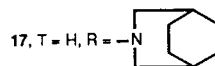
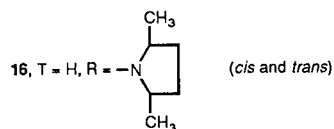
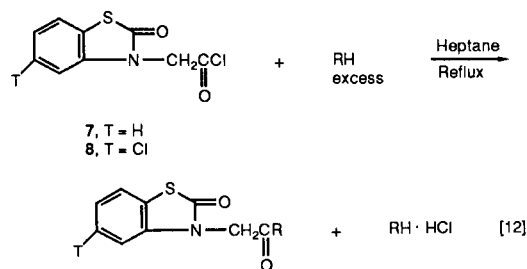
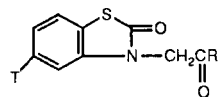
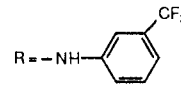
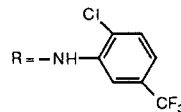
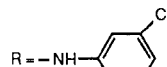
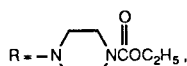
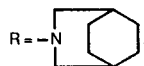
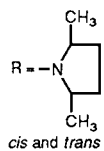


Table 2

Acetamides and Acetanilides



Method A

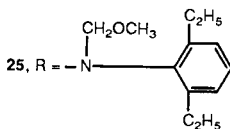
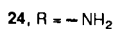
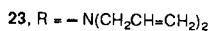
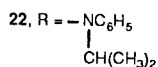
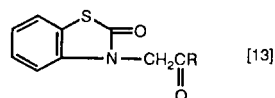
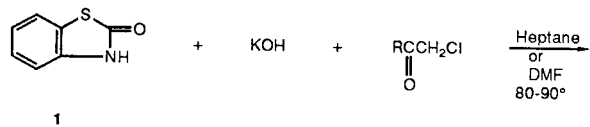


No.	mp °C	Yield	T	Empirical Formula	%C		%H		%N		%S	
					Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
16	167-168 [a]	74	H	C ₁₅ H ₁₈ N ₂ O ₂ S	62.04	61.94	6.25	6.30	9.65	9.71	11.04	11.07
17	198-199 [b]	81	H	C ₁₇ H ₂₀ N ₂ O ₂ S	64.53	64.52	6.37	6.41	8.85	8.88	10.13	10.08
18	165-166 [c]	57	H	C ₁₆ H ₁₉ N ₃ O ₄ S	55.00	55.19	5.48	5.53	12.03	12.00	9.18	9.11
19	242-243	98	H	C ₁₅ H ₁₁ ClN ₂ O ₂ S	56.52	56.40	3.48	3.49	8.79	8.81	10.06	10.16
20	212-213	89	H	C ₁₈ H ₁₀ ClF ₃ N ₂ O ₂ S	49.69	50.00	2.61	2.77	7.24	7.22	8.28	8.40
21	241-242 [c]	94	Cl	C ₁₈ H ₁₀ ClF ₃ N ₂ O ₂ S	49.69	49.64	2.61	2.60	7.24	7.27	8.28	8.33

[a] Recrystallization from isopropyl alcohol. [b] Recrystallization from toluene. [c] Recrystallization from ethyl acetate.

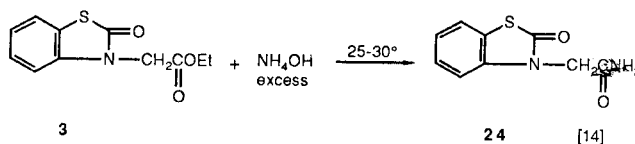
The acetamide and acetanilides **22-25** were synthesized by the reaction of the potassium salt of **1** with 2-chloro-*N*-isopropylacetanilide [5], 2-chloro-*N,N*-diallylacetamide [6], 2-chloroacetamide or 2-chloro-*N*-(2,6-diethylphenyl)-*N*-methoxymethylacetamide [7] [Table 3].

Method B.

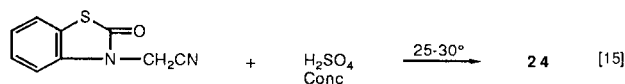


The treatment of **3** with excess concentrated ammonia hydroxide or the reaction of 2-oxo-3(2*H*)-benzothiazoline-acetonitrile [8] with concentrated sulfuric acid afforded 2-oxo-3(2*H*)-benzothiazolineacetamide (**24**) in 89 and 64% yields, respectively.

Method C.



Method D.

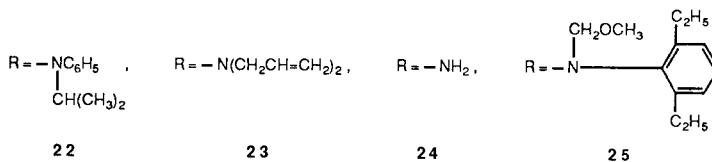
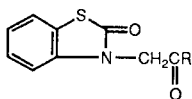


The mixture melting points of **24** derived by methods B, C and D were not depressed and their nmr spectra were identical [Table 3].

The reaction of **7** with the appropriate alcohols afforded the substituted 2-oxo-3-benzothiazolineacetate **26-30** [Table 4].

Table 3

Acetamides and Acetanilides



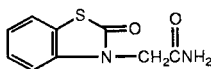
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23

24

25

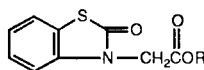
No.	mp °C	Yield %	Empirical Formula	%C		%H		%N		%S	
				Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
22	165-166	89	C ₁₈ H ₁₈ N ₂ O ₂ S	66.23	66.17	5.56	5.59	8.58	8.63	9.82	9.89
23	117-118	84	C ₁₅ H ₁₆ N ₂ O ₂ S	62.48	62.41	5.59	5.61	9.71	9.72	11.12	11.20
24 [a]	253-254	79	C ₇ H ₈ N ₂ O ₂ S	51.91	51.80	3.87	3.80	13.45	13.61	15.40	15.62
25	163-164	86	C ₂₁ H ₂₄ N ₂ O ₃ S	65.60	65.62	6.29	6.29	7.29	7.28	8.34	8.39



24

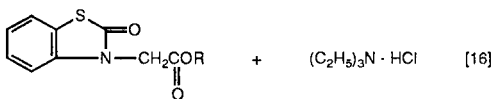
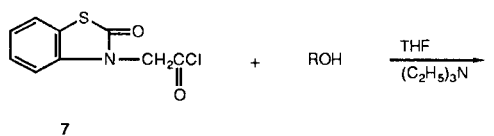
[a] Nmr (DMSO-d₆): δ 4.58 (s, 2, NCH₂), 7.0-8.0 (m, 6, ArH + NH₂). The NH₂ protons exchanged with deuterium oxide.

Table 4
Substituted 2-Oxo-3-benzothiazolineacetate



No.	mp °C	Yield %	Empirical Formula	%C		%H		%N		%S	
				Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
26	101-102 [a]	72	C ₁₆ H ₁₃ NO ₃ S	64.20	64.12	4.38	4.41	4.68	4.68	10.71	10.64
27	97-98 [a]	67	C ₁₂ H ₉ Cl ₂ NO ₃ S	45.30	45.50	2.85	2.89	4.40	4.47	10.08	10.01
28	168-169 [b]	73	C ₁₂ H ₉ NO ₃ S	58.29	58.32	3.67	3.70	5.66	5.68	12.97	12.97
29	80-81 [a]	61	C ₁₇ H ₁₂ F ₃ NO ₃ S	55.58	55.43	3.29	3.31	3.81	3.83	8.73	8.83
30	43-44 [c]	44	C ₁₂ H ₁₃ NO ₃ S ₂	50.86	51.00	4.62	4.65	4.94	4.96	22.63	22.52

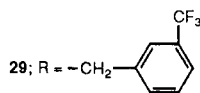
[a] Recrystallization from heptane-isopropyl alcohol. [b] Recrystallization from ethyl acetate. [c] Recrystallization from heptane.



26; R = -CH₂C₆H₅

27; R = -CH₂CCl=CHCl [*cis* and *trans*]

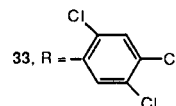
28; R = -CH₂C≡CH



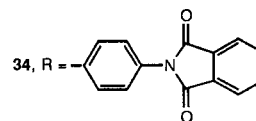
29; R = -CH₂-[pentafluorophenyl]

30; R = -(CH₂)₂SCH₃

32, R = -C₆H₅



33, R = -[2,4,6-trichlorophenyl]



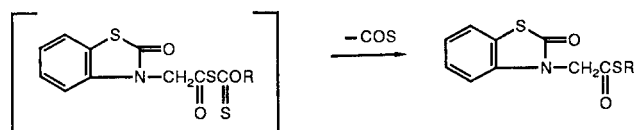
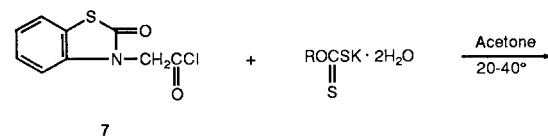
35, R = -CH₂C₆H₅

36, R = -CH₃

37, R = -C(CH₃)₃

Utilization of our novel method for synthesis of thioesters [9], the reaction of 7 with potassium benzyl or methyl dithiocarbonate dihydrate afforded 35 and 36 in 79 and 50% yields, respectively.

Method B.

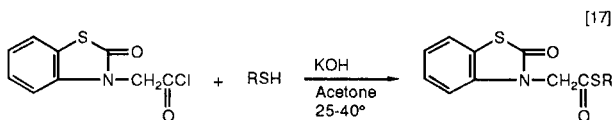


35, R = -CH₂C₆H₅

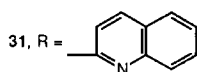
36, R = -CH₃

The *S*-substituted-2-oxo-3-benzothiazoline ethanethioates **31-37** were synthesized by the reaction of **7** with the appropriate mercaptans under basic conditions [Table 5].

Method A.



7



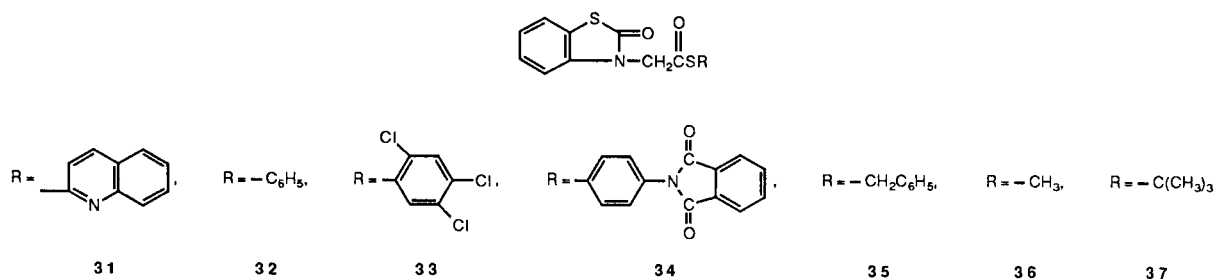
31, R = -[2-quinolineylmethyl]

[18]

Table 5

S-Substituted-2-oxo-3-benzothiazolineethanethiolates

Method A

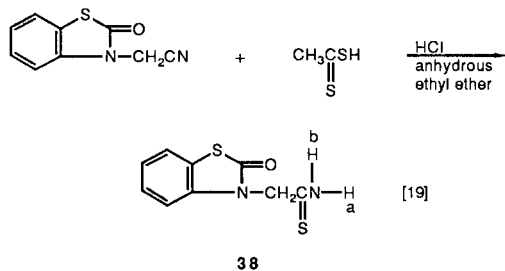


No.	mp °C	Yield %	Empirical Formula	NMR, δ (ppm) CDCl ₃ -Me ₄ Si	%C		%H		%N		%S	
					Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
31	99-100	74	C ₁₈ H ₁₂ N ₂ O ₂ S ₂		61.34	61.07	3.43	3.54	7.95	8.04	18.20	18.26
32	120-122	67	C ₁₅ H ₁₁ NO ₂ S ₂		59.78	59.74	3.68	3.72	4.65	4.63	21.28	21.35
33	169-170 [a]	86	C ₁₅ H ₈ Cl ₃ NO ₂ S ₂		44.52	44.45	1.99	1.95	3.46	3.39	15.84	15.57
34	191-193	74	C ₂₃ H ₁₄ N ₂ O ₄ S ₂		61.87	61.56	3.16	3.32	6.27	5.98	14.36	14.10
35	112-113 [b]	79	C ₁₆ H ₁₃ NO ₂ S ₂	4.17 (s, 2, SCH ₂) 4.83 (s, 2, NCH ₂) 6.78-7.55 (m, 9, ArH)	60.93	60.83	4.15	4.39	4.44	4.26	20.33	20.36
36	146-147	63	C ₁₀ H ₉ NO ₂ S ₂	2.3 (s, 3, SCH ₃) 4.81 (s, 2, NCH ₂) 6.8-7.6 (m, 4, ArH)	50.19	50.22	3.79	3.84	5.85	5.83	26.80	26.90
37	90-91 [c]	46	C ₁₃ H ₁₅ NO ₂ S ₂		55.49	55.52	5.37	5.38	4.98	5.00	22.79	22.62

[a] Recrystallization from toluene. [b] Recrystallization from isopropyl alcohol. [c] Recrystallization from heptane-isopropyl alcohol.

The mixture melting points of **35** and **36** with the products derived by Method A were not depressed and their nmr spectra were identical [Table 5].

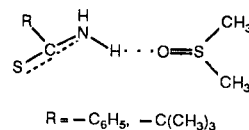
2-Oxo-3-benzothiazolineethanethioamide (**38**) was obtained in 85% yield by the reaction of 2-oxo-3(2*H*)-benzothiazolineacetonitrile [8] with thioacetic acid under acidic conditions.



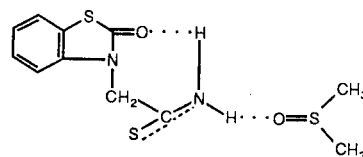
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Compound **38** had nmr (deuteriodimethylsulfoxide): δ 4.75 (s, 2, NCH₂), 6.85-7.25 (m, 4, ArH), 9.46 (br s, 1, a), 9.78 (br s, 1, b). Restricted internal rotation in primary thioamides RCSNH₂ has been observed for benzoic and pivalic acid thioamides in deuteriodimethylsulfoxide but not in deu-

teriochloroform. This effect was explained by a specific astatic association of the solvent molecule with one proton, which is not shielded by the bulky R group phenyl or *t*-butyl [10,11].



Likewise in our case, R is a bulky group containing a carbonyl group which also can astatically associate with the other NH proton.



38

These effects would explain the nonequivalence of the two amino protons at 9.46 and 9.78 ppm.

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. The electron impact mass spectra were determined with a Varian-MAT CH-7A mass spectrometer operating at an ionizing potential of 70 eV using the direct insertion probe technique with a source temperature of 250°.

2-Benzothiazolinone (1).

Compound **1** was prepared in 98% yield by our alternate method [2].

5-Chloro-2-benzothiazolinone (2).

To a stirred solution at 80° containing 100.6 g (0.5 mole) of 5-chlorobenzothiazoline-2-thione, 40 g (0.5 mole) of 50% aqueous sodium hydroxide and 200 ml of water, 2240 g (1.5 mole) of 5% aqueous sodium hypochlorite was added slowly at 80-90° over a one hour period. After allowing the stirred reaction mixture to cool to 70°, 55 g (0.55 mole) of concentrated hydrochloric acid was added dropwise at 60-70° over a 30 minute period (foaming and sulfur dioxide evolution). The stirred reaction mixture was heated at 95-100° for 1.5 hours. After cooling to 0°, the solid was collected by filtration, washed with water until neutral to litmus and air-dried at 50°. The product, mp 222-224°, was obtained in 77% yield. After recrystallization from methyl alcohol, it melted at 239-240°.

Anal. Calcd. for C_7H_5ClNOS : C, 45.29; H, 2.17; Cl, 19.10; N, 7.55; S, 17.27. Found: C, 45.16; H, 2.10; Cl, 19.05; N, 7.47; S, 17.42.

Ethyl 2-Oxo-3-benzothiazolineacetate (3) and Ethyl 5-Chloro-2-oxo-3-benzothiazolineacetate (4).

To a stirred slurry containing 0.2 mole of **1** or **2**, 28 g (0.203 mole) of potassium carbonate and 300 ml of acetone, 0.22 mole of ethyl bromoacetate was added in one portion and then heated at reflux for 4 hours. After cooling to 0°, 700 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°. Compound **3**, mp 90-91° after recrystallization from ethyl alcohol and **4**, mp 115-116° after recrystallization from heptane were obtained in 74 and 95% yields, respectively.

Anal. **3**, Calcd. for $C_{11}H_{11}NO_3S$: C, 55.68; H, 4.67; N, 5.90; S, 13.51. Found: C, 55.60; H, 4.56; N, 6.12; S, 13.50.

Anal. **4**, Calcd. for $C_{11}H_9ClNO_3S$: C, 48.62; H, 3.71; Cl, 13.05; N, 5.16; S, 11.80. Found: C, 48.40; H, 3.68; Cl, 13.36; N, 5.13; S, 12.10.

2-Oxo-3-benzothiazolineacetic Acid (5).

A stirred charge containing 37.8 g (0.25 mole) of **1**, 40 g (0.25 mole) of 25% aqueous sodium hydroxide and 200 ml of water was heated to 90° and filtered hot to remove a small amount of impurities. To a stirred solution containing 35 g (0.25 mole) of bromoacetic acid in 100 ml of water, 18.6 g (0.125 mole) of potassium carbonate was added in small portions (foaming) until pH 8 was obtained. This solution was added to the stirred solution of the sodium salt **1** and then heated at 90-100° for 6 hours. After stirring at 25-30° for 18 hours, 25 g of concentrated hydrochloric acid in 500 ml of water was added dropwise until pH 3 was obtained. After stirring at 0-20° for 30 minutes, the solid was collected by filtration, washed with water until neutral to litmus and air-dried at 45°. Compound **5** had mp 184-185° after recrystallization from toluene-acetone and was obtained in 80% yield.

Anal. Calcd. for $C_9H_7NO_3S$: C, 51.67; H, 3.37; N, 6.70; S, 15.32. Found: C, 51.55; H, 3.30; N, 6.75; S, 15.08.

5-Chloro-2-oxo-3-benzothiazolineacetic Acid (6).

To a stirred refluxing solution containing 0.2 mole of **4** in 200 ml of methyl alcohol, 34.4 g (0.215 mole) of 25% aqueous sodium hydroxide in 165 ml of water was added dropwise over a 30 minute period and then heated at reflux for 30 minutes. The solvent (180 ml) was removed by dis-

tillation. To this stirred solution, 30 g (0.3 mole) of concentrated hydrochloric acid was added dropwise at 20-30° until pH 2 or 3 was obtained. After stirring at 25-30° for one hour, the solid was collected by filtration, washed with water until neutral and air-dried at 25-30°. Compound **6**, had mp 250-251° after recrystallization from ethyl alcohol and was obtained in 90% yield.

Anal. Calcd. for $C_9H_6ClNO_3S$: C, 44.36; H, 2.48; Cl, 14.55; N, 5.75; S, 13.16. Found: C, 44.20; H, 2.36; Cl, 14.25; N, 5.98; S, 13.07.

2-Oxo-3-benzothiazolineacetyl Chloride (7) and 5-Chloro-2-oxo-3-benzothiazolineacetyl Chloride (8).

To a stirred slurry containing 0.4 mole of **5** or **6** and 300 ml of benzene, 59.5 g (0.5 mole) of thionyl chloride was added in one portion and then heated at reflux for 3 hours. After cooling to 0°, stirring was continued at 0-10° for 30 minutes. The solid was collected by filtration and air-dried at 25-30°. Compound **7** mp 122-123° and **8** mp 125-126°, were obtained in 72 and 76% yield, respectively.

Anal. **7**, Calcd. for $C_9H_6ClNO_2S$: C, 47.48; H, 2.66; Cl, 15.57; N, 6.15; S, 14.08. Found: C, 47.80; H, 2.70; Cl, 15.44; N, 6.19; S, 14.14.

Anal. **8**, Calcd. for $C_9H_4Cl_2NO_2S$: C, 41.24; H, 1.92; Cl, 27.05; N, 5.34; S, 12.23. Found: C, 41.23; H, 1.93; Cl, 26.98; N, 5.31; S, 12.25.

Hydrazides 9-15.

Method A. 9-13.

To a stirred slurry containing 15.9 g (0.07 mole) of **7** in 200 ml of heptane, 0.2 mole of the appropriate substituted hydrazine was added in one portion. The stirred reaction mixture was heated at reflux for 6 hours and then stirred at 25-30° for 18 hours. After the addition of 600 ml of water, stirring was continued for 30 minutes. The solid was collected by filtration, washed with 100 ml of water and air-dried at 25-30°. The data are summarized in Table 1.

Hydrazide 14.

Method B.

To a stirred slurry containing 22.8 g (0.1 mole) of **7**, 11.3 g (0.11 mole) of triethylamine, 16.5 g (0.1 mole) of 2-hydrazinobenzothiazole and 400 ml of heptane was heated at reflux for 6 hours and then held at 25-30° for 18 hours. The product **14** was isolated as described in Method A. The data are summarized in Table 1.

Hydrazide 15.

Method C.

A stirred charge containing 11.9 g (0.05 mole) of **3**, 33.8 g (1.0 mole) of 95% hydrazine and 100 ml of water was stirred at 25-30° for six days. After the addition of 500 ml of water, stirring was continued at 25-30° for 10 minutes. The solid was collected by filtration, washed with 200 ml of water and air-dried at 25-30°. Crude **5**, mp 211-212°, was obtained in 45% yield. The data are summarized in Table 1.

Acetamides and Acetanilides 16-21.

Method A.

To a stirred slurry containing 0.07 mole of **7** or **8** in 300 ml of heptane, 0.2 mole of the appropriate amine or aniline was added in one portion. The stirred mixture was heated at reflux for six hours and held at 25-30° for 18 hours. After the addition of 800 ml of water 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 25-30°. The data are summarized in Table 2.

Acetamides and Acetanilides 22-24.

Method B.

To a stirred solution containing 15.1 g (0.1 mole) of **1**, 6.6 g (0.1 mole) of 85% potassium hydroxide, 200 ml of acetone and 10 ml of water, 0.1 mole of 2-chloro-*N*-isopropylacetanilide [5], 2-chloro-*N,N*-diallylacetamide [6] or 2-chloroacetamide was added in one portion. The stirred reaction mixture was heated at reflux for 6 hours and then held at

25-30° for 18 hours. After addition of 800 ml of water, stirring was continued at 25-30° for 30 minutes. The solid was collected by filtration, washed with water until neutral and air-dried at 25-30°. The data are summarized in Table 3.

Acetanilide 25.

Method B.

To a stirred solution containing 16.1 g (0.11 mole) of **1**, 7.3 g (0.11 mole) of 85% potassium hydroxide, 100 ml of DMF and 10 ml of water, 27 g (0.1 mole) of 2-chloro-*N*-(2,6-diethylphenyl)-*N*-methoxymethylacetamide [7] was added in one portion. The stirred reaction mixture was heated at 80-90° for 24 hours. After cooling to 20°, 800 g of ice water was added and stirring continued at 25-30° for 30 minutes. The solid was collected by filtration, washed with 500 ml of water and air-dried at 25-30°. The data are summarized in Table 3.

2-Oxo-3(2*H*)-benzothiazolineacetamide (24).

Method C.

A charge containing 0.07 mole of **3** and 250 ml of concentrated ammonia hydroxide was stirred at 25-30° for 5 hours. After the addition of 750 ml of water, stirring was continued at 15-30° for 5 minutes. The solid was collected by filtration, washed with water until neutral to litmus and air-dried at 50°. Compound **24**, mp 253-254°, was obtained in 89% yield. The mixture melting point of **24** with the product derived by Method B was not depressed and their nmr spectra were identical.

Anal. Calcd. for C₉H₈N₂O₂S: C, 51.91; H, 3.87; N, 13.45; S, 15.40. Found: C, 51.88; H, 3.89; N, 13.45; S, 15.38.

Method D, 24.

To 75 ml of concentrated sulfuric acid at -15°, 38.2 g (0.2 mole) of 2-oxo-3(2*H*)-benzothiazolineacetonitrile [8] was added in one portion and then stirring was continued at 25-30° for 2 days. After cooling to -10°, 800 g of ice water was added slowly at -10 to 20°. After cooling again to -10°, 250 ml of concentrated ammonia hydroxide was added dropwise at -10 to 20°. After stirring at 25-30° for 30 minutes, the solid was collected by filtration, washed with water until neutral to litmus and air-dried at 50°. Compound **24**, mp 253-254°, was obtained in 64% yield. The mixture melting points of **24** with the products derived from Methods B or C were not depressed and their nmr spectra were identical.

Anal. Calcd. for C₉H₈N₂O₂S: C, 51.91; H, 3.87; N, 13.45; S, 15.40. Found: C, 51.89; H, 3.91; N, 13.42; S, 15.43.

Substituted 2-Oxo-3-benzothiazolineacetate 26-30.

To a stirred solution containing 22.8 g (0.1 mole) of **7** and 0.1 mole of the appropriate alcohol in 200 ml of tetrahydrofuran, 11.3 g (0.11 mole) of triethylamine was added in one portion. An exothermic reaction set in causing a temperature rise from 28° to 60°. The stirred mixture was heated at reflux for 24 hours. After cooling to 0°, 800 g of ice water was added and stirring continued at 0-10° for one hour. The solid was collected by filtration, washed with cold water and air-dried at 25-30°. The data are summarized in Table 4.

S-Substituted-2-oxo-3-benzothiazoline ethanethiolates 31-37.

Method A.

A charge containing 0.1 mole of the appropriate mercapto compound, 6.6 g (0.1 mole) of 85% potassium hydroxide and 250 ml of acetone was stirred for 10 minutes. To this stirred mixture was added in one portion 0.1 mole of **7**. An exothermic reaction set in causing a temperature rise from 25° to 40°. After stirring at 25-30° for 24 hours, 800 g of ice water was added and stirring continued at 0-10° for 1 hour. The solid was collected by filtration, washed with cold water until neutral to litmus and air-dried at 25-30°. The data are summarized in Table 5.

Method B, 35-36.

To a stirred slurry containing 0.12 mole of potassium benzyl or methyl thiocarbonate dihydrate in 200 ml of acetone, 22.8 g (0.1 mole) of **7** was

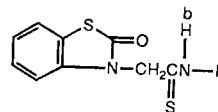
added in one portion. An exothermic reaction set in causing a temperature rise from 22° to about 40°. The reaction was stirred at 25-30° for 18 hours and during this period carbonyl sulfide was liberated. After the addition of 800 g of ice water, stirring was continued at 0-10° for 2 hours. The solid was collected by filtration, washed with water until neutral to litmus and air-dried at 25-30°. Compound **35**, mp 113-114° after recrystallization from isopropyl alcohol and **36**, mp 146-147° after recrystallization from methyl alcohol, were obtained in 79 and 50% yields, respectively. The mixture melting point of **35** and **36** with the product derived by Method A were not depressed and their nmr spectra were identical.

Anal. 35. Calcd. for C₁₆H₁₃NO₂S₂: C, 60.93; H, 4.15; N, 4.44; S, 20.33. Found: C, 60.99; H, 4.21; N, 4.42; S, 20.40.

Anal. 36. Calcd. for C₁₀H₉NO₂S₂: C, 50.19; H, 3.79; N, 5.85; S, 26.80. Found: C, 50.26; H, 3.83; N, 5.85; S, 26.87.

2-Oxo-3-benzothiazolineethanethioamide (38).

To a stirred slurry containing 38 g (0.2 mole) of 2-oxo-3(2*H*)-benzothiazolineacetonitrile [8], 15.2 g (0.2 mole) of thioacetic acid (dried over magnesium sulfate) 300 ml of anhydrous ethyl ether, dry hydrogen chloride gas was bubbled through the suspension at -5 to 0° for 3 hours. External cooling was removed and the reaction mixture was stirred at 25-30° for 18 hours. The solid was collected by filtration, washed with 500 ml of anhydrous ethyl ether and air-dried at 25-30° for 1 hour. The solid (41 g) was slurried with 700 ml of water for 1 hour. After the addition of 300 ml of water and 25 g (0.25 mole) of concentrated hydrochloric acid, stirring was continued at 25-30° for another hour. The solid was collected by filtration, washed with water until neutral to litmus and air-dried at 25-30°. The product, mp 205-207° with decomposition, was obtained in 85% yield. After recrystallization from heptane-tetrahydrofuran (1:1), **38** melted at 216-217°; nmr (deuteriodimethyl sulfoxide): δ 4.75 (s, 2, NCH₂), 6.85-7.25 (m, 4, ArH), 9.46 (br s, 1, a), 9.78 (br s, 1, b).



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Anal. Calcd. for C₉H₈N₂OS₂: C, 48.19; H, 3.60; N, 12.49; S, 28.59. Found: C, 48.23; H, 3.60; N, 12.44; S, 28.49.

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