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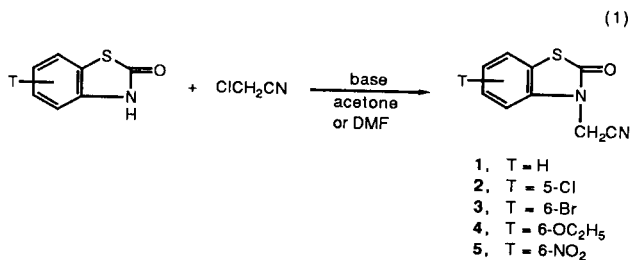
The following methods afforded the titled acetonitriles **1-5** in excellent yields: (1) the reaction of the appropriate 2-benzothiazolinones with chloroacetonitrile under basic conditions and (2) the dehydration of the appropriate 2-oxo-3(2*H*)-benzothiazolineacetamides with phosphorus oxychloride or pentoxide. The reaction of the acetonitriles **1-5** and 2-thioxo-3(2*H*)-benzothiazolineacetonitrile with hydroxylamine afforded the titled compounds **6-11**. Supporting nmr and mass spectral data are discussed.

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The object of the present investigation was to prepare 2-oxo-3(2*H*)-benzothiazolineacetonitriles and related compounds by various methods and to utilize these nitriles as intermediates in the synthesis of the titled compounds.

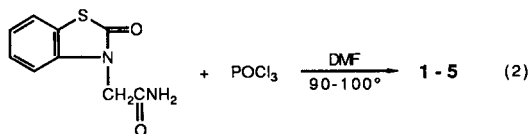
The reaction of the appropriate 2-benzothiazolinone with chloroacetonitrile under basic conditions afforded the 2-oxo-3(2*H*)-benzothiazolineacetonitrile and related compounds **1-5** in 81 to 95% yields.

#### Method 1



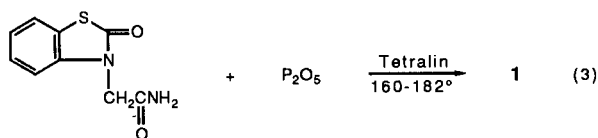
The dehydration of the appropriate 2-oxo-3(2*H*)-benzothiazolineacetamides in dried dimethylformamide with phosphorus oxychloride furnished **1-5** in excellent yields.

#### Method 2



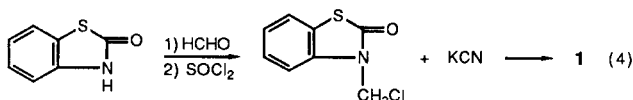
Replacing phosphorus oxychloride and dimethylformamide with phosphorus pentoxide and dried tetralin in reaction 2 and by heating the reaction mixture at 160-182° for one hour yielded **1** in 98% yield.

#### Method 3

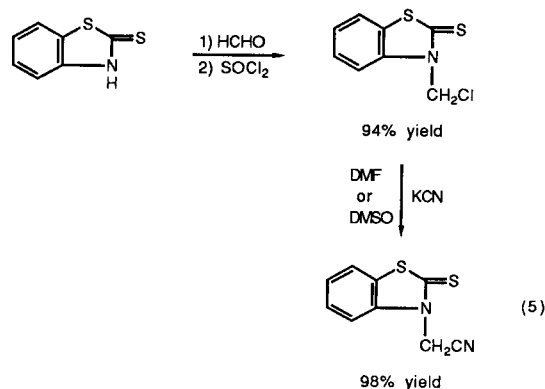


We recently reported [1] that the reaction of 3-(chloromethyl)-2-benzothiazolinone with potassium cyanide in acetone, dimethylformamide or acetonitrile afforded **1** in 87 to 91% yield.

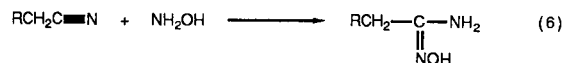
#### Method 4



The mixture melting point of products derived by Methods 1-4 were not depressed and their nmr spectra were identical. In the same communication [1] we also reported the synthesis of 2-thioxo-3(2*H*)-benzothiazolineacetonitrile by the following reactions:



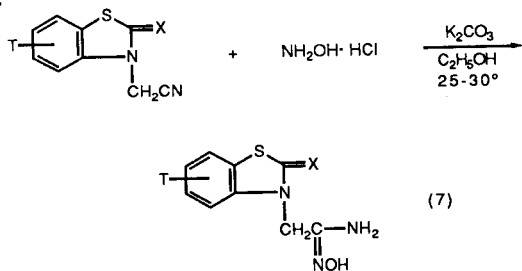
Hydroxylamine is an exceptionally nucleophilic amino compound and reacts readily with all types of nitriles to give amidoximes [2-4].



Hollander and co-workers [3] have reported that a nitrile group in position near an electron-withdrawing substituent undergoes reaction with amines with unusual ease.

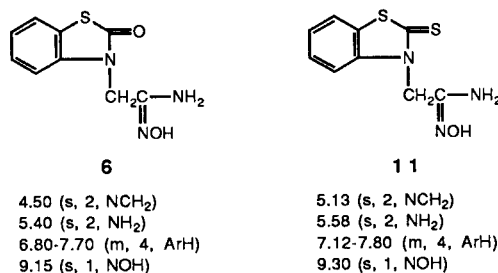
For example, it has been reported that unusually rapid reactions occurred with hydroxylamine and succinonitrile [5], cyanogen [6] and tribromoacetone [7].

The reaction of the appropriate acetonitrile **1-5** or 2-thio-3-(2*H*)-benzothiazolineacetonitrile with hydroxylamine hydrochloride in an ethyl alcohol medium at 25-30° followed by neutralization with potassium carbonate afforded the titled compounds **6-11** in 75-91% yields.



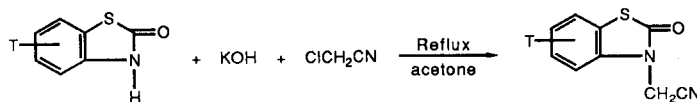
T and X are shown in Table 3.

The analysis and nmr spectral data (Table 3) confirmed the proposed structures for **6-11**. It is noteworthy to contrast the chemical shifts for **6** and **11**.



In **11**, the NCH<sub>2</sub>, NH<sub>2</sub> and NOH protons appeared further downfield when compared to the same groups in **6**. These downfield shifts in **11** are due to the deshielding effect of the thiocarbonyl group.

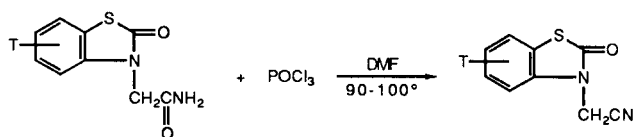
Table 1 (Method 1)



No.	T	Mp °C	% Yield	Empirical formula	NMR-δ ppm DMSO-d <sub>6</sub> -TMS	Chemical Analysis	
						%C	%H
<b>1</b>	H	134-135 [a]	95	C <sub>7</sub> H <sub>6</sub> N <sub>2</sub> OS	4.85 (s, 2, NCH <sub>2</sub> ) 7.00-7.70 (m, 4, ArH)	Calcd. 56.83	Calcd. 3.18
						Found 56.92	Found 3.21
						Calcd. 14.73	Calcd. 16.86
						Found 14.65	Found 17.01
<b>2</b>	5-Cl	202-203 [b]	95	C <sub>5</sub> H <sub>5</sub> ClN <sub>2</sub> OS	5.08 (s, 2, NCH <sub>2</sub> ) 7.00-7.77 (m, 3, ArH)	Calcd. 48.11	Calcd. 2.24
						Found 48.13	Found 2.23
						Calcd. 12.47	Calcd. 14.27
						Found 12.44	Found 14.50
<b>3</b>	6-Br	186-187 [c]	91	C <sub>9</sub> H <sub>5</sub> BrN <sub>2</sub> OS	5.17 (s, 2, NCH <sub>2</sub> ) 7.20-8.05 (m, 3, ArH)	Calcd. 40.17	Calcd. 1.87
						Found 40.22	Found 1.87
						Calcd. 10.41	Calcd. 11.91
						Found 10.46	Found 11.97
<b>4</b>	6-OC <sub>2</sub> H <sub>5</sub>	165-166 [d]	92	C <sub>11</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> S	1.20 (t, 3, OCH <sub>3</sub> ) 3.90 (q, 2, OCH <sub>2</sub> ) 5.08 (s, 2, NCH <sub>2</sub> ) 6.79-7.47 (m, 3, ArH)	Calcd. 56.40	Calcd. 4.30
						Found 56.30	Found 4.27
						Calcd. 11.96	Calcd. 13.69
						Found 12.10	Found 13.88

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

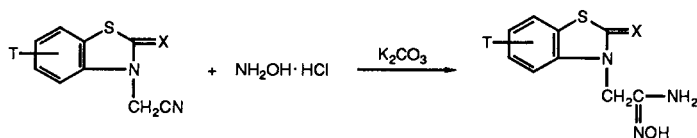
Table 2 (Method 2)



No.	T	Mp °C	% Yield	Empirical formula	%C		%H		%N		%S	
					Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
1 [e]	H	134-135 [a]	95	C <sub>9</sub> H <sub>6</sub> N <sub>2</sub> OS	56.83	56.85	3.18	3.22	14.73	14.73	16.86	16.79
2 [e]	5-Cl	202-203 [b]	97	C <sub>9</sub> H <sub>5</sub> ClN <sub>2</sub> OS	48.11	48.03	2.24	2.27	12.47	12.43	14.27	14.20
3 [e]	6-Br	186-187 [c]	67	C <sub>9</sub> H <sub>5</sub> BrN <sub>2</sub> OS	40.17	39.91	1.87	1.89	10.41	10.37	11.91	11.78
4 [e]	6-OC <sub>2</sub> H <sub>5</sub>	165-166 [d]	90	C <sub>11</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> S	56.40	56.37	4.30	4.38	11.96	11.89	13.69	13.61
5 [e]	6-NO <sub>2</sub>	199-200 [c]	96	C <sub>9</sub> H <sub>5</sub> N <sub>3</sub> O <sub>3</sub> S	45.96	45.91	2.14	2.16	17.86	17.82	13.63	13.63

[a] Recrystallization from isopropyl alcohol. [b] Recrystallization from toluene. [c] Recrystallization from ethyl acetate. [d] Recrystallization from isopropyl alcohol-ethyl acetate. [e] A mixture melting points of 1-5 derived by Methods 1 or 2 were not depressed and their nmr spectra were identical.

Table 3



No.	T	X	Mp °C	% Yield	Empirical formula	NMR-δ ppm DMSO-d <sub>6</sub> -TMS	Chemical Analysis	
							%C	%H
6	H	O	202-203 [a]	90	C <sub>9</sub> H <sub>6</sub> N <sub>3</sub> O <sub>2</sub> S	4.50 (s, 2, NCH <sub>2</sub> ) 5.40 (s, 2, NH <sub>2</sub> ) 6.80-7.70 (m, 4, ArH) 9.15 (s, 1, NOH)	Calcd. 48.42	Calcd. 4.86
							Found 48.36	Found 4.56
							%N	%S
							Calcd. 18.82	Calcd. 14.36
Found 18.82	Found 14.34							
7	5-Cl	O	222-223 [a]	87	C <sub>9</sub> H <sub>5</sub> ClN <sub>3</sub> O <sub>2</sub> S	4.50 (s, 2, NCH <sub>2</sub> ) 5.47 (s, 2, NH <sub>2</sub> ) 6.90-7.71 (m, 3, ArH) 9.21 (s, 1, NOH)	Calcd. 41.95	Calcd. 3.13
							Found 41.98	Found 3.16
							%N	%S
							Calcd. 16.31	Calcd. 12.44
Found 16.30	Found 12.46							
8	6-Br	O	216-217 [a]	80	C <sub>9</sub> H <sub>5</sub> BrN <sub>3</sub> O <sub>2</sub> S	4.56 (s, 2, NCH <sub>2</sub> ) 5.51 (s, 2, NH <sub>2</sub> ) 7.02-7.96 (m, 3, ArH) 9.28 (s, 1, NOH)	Calcd. 35.78	Calcd. 2.67
							Found 35.75	Found 2.68
							%N	%S
							Calcd. 13.91	Calcd. 10.61
Found 13.91	Found 10.65							
9	6-OC <sub>2</sub> H <sub>5</sub>	O	184-185	75	C <sub>11</sub> H <sub>13</sub> N <sub>3</sub> O <sub>3</sub> S	1.30 (t, 3, OCCH <sub>3</sub> ) 3.98 (q, 2, OCH <sub>2</sub> ) 4.48 (s, 2, NCH <sub>2</sub> ) 5.43 (s, 2, NH <sub>2</sub> ) 6.72-7.34 (m, 3, ArH) 9.21 (s, 1, NOH)	Calcd. 49.43	Calcd. 4.90
							Found 49.48	Found 4.95
							%N	%S
							Calcd. 15.72	Calcd. 12.00
Found 15.74	Found 12.04							

							%C	%H
10 [c]	6-NO <sub>2</sub>	O	207-208	91	C <sub>9</sub> H <sub>6</sub> N <sub>4</sub> O <sub>4</sub> S	4.68 (s, 2, NCH <sub>2</sub> )	Calcd. 40.30	Calcd. 3.01
						5.67 (s, 2, NH <sub>2</sub> )	Found 40.39	Found 3.03
						7.45 (d, J = 7 ppm,	%N	%S
						1, ArH), 8.29 (d, J =	Calcd. 20.89	Calcd. 11.95
						7 ppm, 2nd order splitting, J = 2 ppm, 1, ArH), 9.35 (s, 1, NOH)	Found 20.82	Found 12.00
11	H	S	187-188 [b]	90	C <sub>6</sub> H <sub>5</sub> N <sub>3</sub> OS <sub>2</sub>	5.13 (s, 2, NCH <sub>2</sub> )	Calcd. 45.17	Calcd. 3.79
						5.58 (s, 2, NH <sub>2</sub> )	Found 45.18	Found 3.81
						7.12-7.80 (m, 4, ArH)	%N	%S
						9.30 (s, 1, NOH)	Calcd. 17.56	Calcd. 26.80
						Found 17.53	Found 26.77	

[a] Recrystallization from dimethylformamide. [b] Recrystallization from ethyl acetate. [c] Electron impact mass spectrum *m/e* (relative intensity) 268 (83) M<sup>+</sup>, 223 (17), 181 (100), 135 (40), 108 (8), 71 (8), 63 (11), 43 (31) and 42 (49).

### EXPERIMENTAL

The nmr spectra were obtained with a Varian T-60 nmr spectrometer. The chemical shifts are reported in ppm, using tetramethylsilane as reference. All melting points were taken upon a Fisher-Johns block and are uncorrected. The electron impact mass spectrum for **10** was 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 267°.

2-Oxo-3(2*H*)-benzothiazolineacetoneitrile (**1**), 5-Chloro-2-oxo-3(2*H*)-benzothiazolineacetoneitrile (**2**), 6-Bromo-2-oxo-3(2*H*)-benzothiazolineacetoneitrile (**3**) and 6-Ethoxy-2-oxo-3(2*H*)-benzothiazolineacetoneitrile (**4**) [Method 1].

To a stirred solution containing 0.1 mole of the appropriate 2-benzothiazolinone, 6.6 g (0.1 mole) of 85% potassium hydroxide, 200 ml of acetone and 10 ml of water, 7.7 g (0.1 mole) of 97% chloronitrile was added in one portion. The stirred reaction mixture was heated at reflux for 6 hours and then at 25-30° for 18 hours. After the addition of 800 ml of water, stirring was continued at 25-30° 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 1.

6-Nitro-2-oxo-3(2*H*)-benzothiazolineacetoneitrile (**5**) [Method 1].

To a stirred slurry containing 59 g (0.3 mole) of 6-nitro-2-benzothiazolinone [8], 42 g of potassium carbonate and 200 ml of dimethylformamide, 46.2 g (0.6 mole - 100% excess of 97% chloroacetoneitrile) was added in one portion. The stirred reaction mixture was heated at 80-90° for 6 hours and then at 25-30° for 18 hours. After the addition of 1500 ml of water, stirring was continued at 25-30° for 1 hour. The solid was collected by filtration, washed with water until neutral and air-dried at 50°. Compound **5**, mp 193-195°, was obtained in 81% yield. After recrystallization from ethyl acetate **5** melted at 199-200°; nmr (deuteriodimethyl sulfoxide): δ 5.25 (s, 2, NCH<sub>2</sub>); 7.66 (d, 1, ArH); 7.67 (d, 1, ArH); 8.13-8.42 (2d, 1, ArH).

Anal. Calcd. for C<sub>9</sub>H<sub>5</sub>N<sub>3</sub>O<sub>3</sub>S: C, 45.96; H, 2.14; N, 17.86; S, 13.63. Found: C, 46.14; H, 2.21; N, 17.72; S, 13.53.

Compounds **1-5** [Method 2].

To a stirred solution containing 0.1 mole of the appropriate 2-oxo-3(2*H*)-benzothiazolineacetamide and 100 ml of dried dimethylformamide, 15.4 g (0.1 mole) of phosphorus oxychloride was added dropwise at 90-100° over a 5 minute period and then heated at 90-100° for 1 hour. After cooling to 5°, 800 g of ice water was added and stirring continued at 25-30° for 30 minutes. The solid was collected by filtration, washed with water until neutral and air-dried at 50°. The data are summarized in Table 2.

Compound **1** [Method 3].

A stirred slurry containing 21 g (0.1 mole) of 2-oxo-3(2*H*)-benzothiazolineacetamide, 8.5 g of phosphorus pentoxide and 200 ml of dried tetralin was heated at 160-182° for 1 hour. After cooling to 10°, 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°. Compound **1**, mp 122-124°, was obtained in 98% yield. After recrystallization from isopropyl alcohol **1** melted at 133-134°. A mixture melting point with **1** obtained by Methods 1 or 2 was not depressed and their nmr spectra were identical.

Anal. Calcd. for C<sub>6</sub>H<sub>5</sub>N<sub>2</sub>OS: C, 56.83; H, 3.18; N, 14.73; S, 16.86. Found: C, 56.98; H, 3.37; N, 14.78; S, 16.50.

Compound **1** [Method 4].

We recently reported [1] that the reaction of 3-(chloromethyl)-2-benzothiazolinone with potassium cyanide in acetone, dimethylformamide or acetonitrile furnished **1** in 87 to 91% yield.

*N*-Hydroxy-2-oxo or Thioxo-3(2*H*)-benzothiazoleethanimidamide and Related Products **6-11**.

A stirred slurry containing 0.1 mole of **1**, **2**, **3**, **4**, **5** or 2-thioxo-3(2*H*)-benzothiazolineacetoneitrile [1] in 900 ml of ethyl alcohol was heated to 60° and then allowed to cool to room temperature. To this stirred mixture, a solution containing 7 g (0.1 mole) of hydroxylamine hydrochloride in 25 ml of water was added in one portion and stirring continued at 25-30° for 7 hours. A solution containing 6.4 g (0.06 mole) of potassium carbonate in 25 ml of water was added and stirring continued at 25-30° for 18 hours. After the addition of one liter of water, stirring was continued at 25-30° 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 3.

### REFERENCES AND NOTES

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