

Derivatives of 2-Oxo-3(2*H*)-benzothiazolineacetonitrile and Related Compounds. II. Synthesis of 2-Oxo-alkyl Esters of 3(2*H*)-Benzothiazolineacetimidic Acids and Related Products

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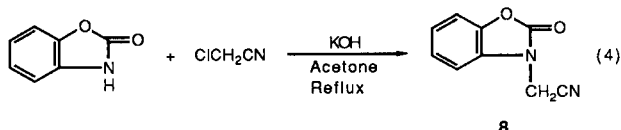
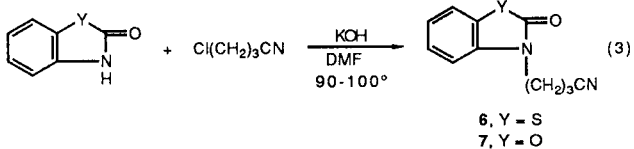
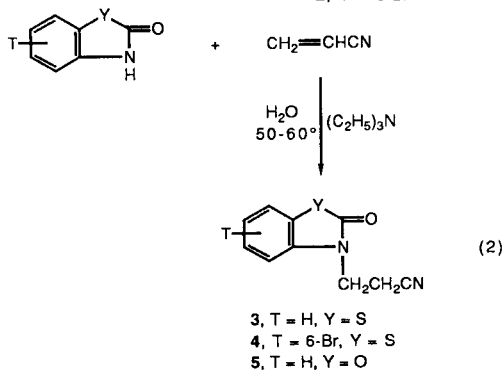
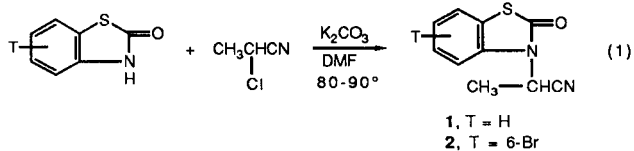
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The reaction of the appropriate 2-benzothiazolinone or 2-benzoxazolinone under basic conditions with (1) 2-chloropropionitrile, (2) acrylonitrile, (3) 4-chlorobutyronitrile or (4) chloroacetonitrile afforded the nitriles **1-8**. The reaction of various nitriles with alcoholic-hydrogen chloride solutions at low temperatures afforded the hydrogen chloride salts of the imino-ester which upon neutralization with potassium carbonate yielded the titled compounds.

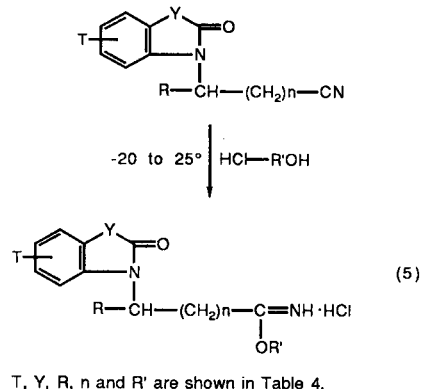
J. Heterocyclic Chem., **25**, 1487 (1988).

In a previous communication [1] we reported the synthesis of *N*-hydroxy-2-oxo or thio-3(2*H*)-benzothiazolineethanimidamides and related products by the reaction of various nitriles with hydroxylamine. Since the above compounds exhibited biological activity, it appeared expedient to continue our investigation to synthesize additional derivatives of nitriles. Thus, the object of this investigation was to prepare additional nitriles and to react these nitriles with alcoholic-hydrogen chloride solutions to afford the hydrogen chloride salts of imino-ester which upon neutralization with potassium carbonate would yield the titled compounds.

The reaction of the appropriate 2-benzothiazolinone or 2-benzoxazolinone under basic conditions with (1) 2-chloropropionitrile, (2) acrylonitrile, (3) 4-chlorobutyronitrile or (4) chloroacetonitrile afforded the intermediate nitriles **1-8**.



The reaction of the appropriate nitrile with a large excess of absolute methyl, ethyl, isopropyl or propyl alcohol containing a large excess of dry hydrogen chloride at low temperatures afforded the hydrogen chloride salts of the titled compounds **9-20** in excellent yields.



The neutralization of hydrogen chloride salts **9-20** with an aqueous solution of potassium carbonate in diethyl ether furnished the titled compounds **21-32** in good yields.

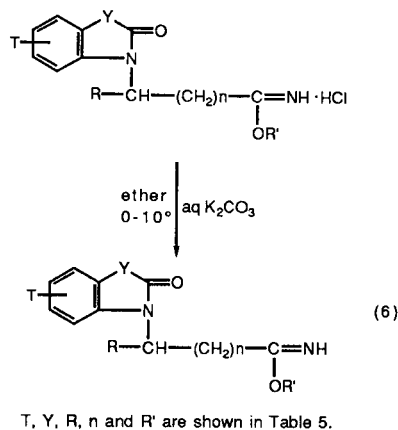
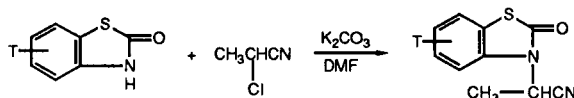


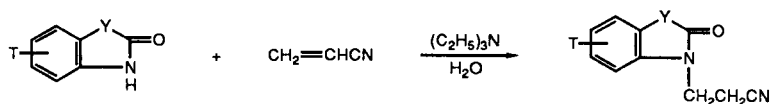
Table 1



No.	T	Mp °C	% Yield	Empirical formula	NMR- δ ppm CDCl ₃ -TMS	Chemical Analysis	
1	H	107-108 [a]	83	C ₁₀ H ₈ N ₂ OS	1.83 (d, 3, CH ₂ -C), 5.88 (q, 1, CHCN), 7.10- 7.75 (m, 4, ArH)	%C	%H
						Calcd. 58.80	Calcd. 3.95
						Found 58.81	Found 3.89
						%N	%S
						Calcd. 13.72	Calcd. 15.70
						Found 13.70	Found 15.81
2	6-Br	170-171 [b]	86	C ₁₀ H ₇ BrN ₂ OS	1.67 (d, 3, CH ₂ -C), 5.95 (q, 1, CHCN), 7.30-7.75 (m, 2, ArH), 7.90-8.10 (m, 1, ArH), (Solvent DMSO-d ₆)	%C	%H
						Calcd. 42.42	Calcd. 2.49
						Found 42.31	Found 2.52
						%N	%S
						Calcd. 9.89	Calcd. 11.32
						Found 9.81	Found 11.44

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

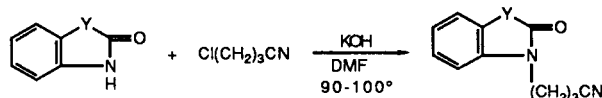
Table 2



No.	T	Y	Mp °C	% Yield	Empirical formula	NMR- δ ppm CDCl ₃ -TMS	Chemical Analysis	
3	H	S	116-117 [a]	96	C ₁₀ H ₈ N ₂ OS	2.85 (t, 2, CH ₂ CN), 4.27 (t, 2, NCH ₂), 7.0-7.7 (m, 4, ArH)	%C	%H
							Calcd. 58.80	Calcd. 3.95
							Found 59.00	Found 3.70
							%N	%S
						Calcd. 13.72	Calcd. 15.70	
						Found 13.78	Found 15.61	
4	6-Br	S	145-146 [a]	92	C ₁₀ H ₇ BrN ₂ OS	2.83, J = 7 Hz (t, 2, CH ₂ CN), 4.24, J = 7 Hz (t, 2, NCH ₂), 7.07, J = 9 Hz (d, 1, ArH), 7.53, J = 9 Hz (d, 1, ArH), 7.65, J = 2 Hz (d, 1, ArH)	%C	%H
							Calcd. 42.42	Calcd. 2.49
							Found 42.52	Found 2.51
							%N	%S
						Calcd. 9.89	Calcd. 11.32	
						Found 9.86	Found 11.28	
5	H	O	118-119 [b]	72	C ₁₀ H ₈ N ₂ O ₂	2.87 (t, 2, CH ₂ CN), 4.15 (t, 2, NCH ₂), 7.00- 7.44 (m, 4, ArH)	%C	%H
							Calcd. 63.82	Calcd. 4.29
							Found 64.02	Found 4.31
							%N	%S
						Calcd. 14.89		
						Found 15.01		

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

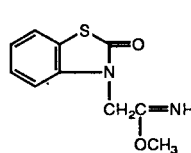
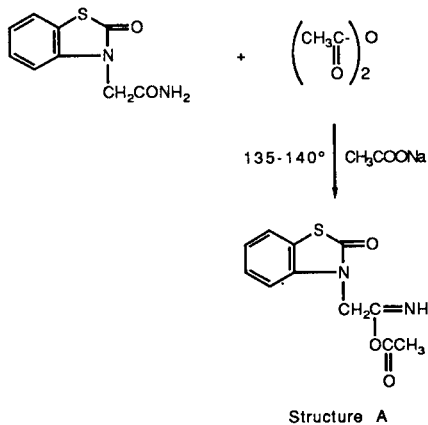
Table 3



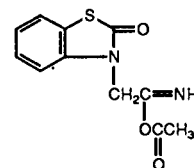
No.	Y	Mp °C	% Yield	Empirical formula	NMR- δ ppm CDCl ₃ -TMS	Chemical Analysis	
6	S	61-62 [a]	94	C ₁₁ H ₁₀ N ₂ OS	1.75-2.69 (m, 4, -CH ₂ -CH ₂ CN), 4.07 (t, 2, NCH ₂), 6.88-7.60 (m, 4, ArH)	% C	% H
						Calcd. 60.53	Calcd. 4.62
7	O	78-79 [b]	67	C ₁₁ H ₁₀ N ₂ O ₂	1.95-2.55 (m, 4, CH ₂ -CH ₂ CN), 3.90 (t, 2, NCH ₂), 6.9-7.3 (m, 4, ArH)	Found 60.49	Found 4.68
						Calcd. 12.83	Calcd. 14.69
						Found 12.80	Found 14.64
						% C	% H
						Calcd. 65.34	Calcd. 4.98
						Found 65.40	Found 5.01
						% N	% S
						Calcd. 13.85	Calcd. 14.69
						Found 13.88	Found 14.64

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

The analysis and nmr spectral data (Table 5) confirmed the proposed structures for **21-32**. In a recent paper [2] we reported the synthesis of 2-oxo-3(2H)-benzothiazoleethanimic acid anhydride with acetic acid (Structure A) by the reaction of 2-oxo-3(2H)-benzothiazolineacetamide with acetic anhydride containing a catalytic amount of sodium acetate.

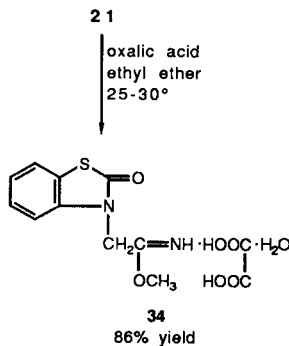
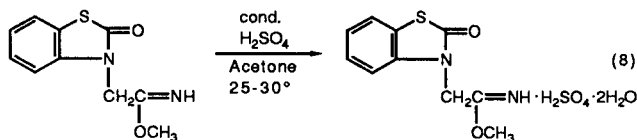


3.80 (s, 3, OCH₃)
4.60 (s, 2, NCH₂)
6.70-7.70 (m, 5, ArH + NH)



2.25 (s, 3, OCH₃)
5.00 (s, 2, NCH₂)
6.70-7.55 (m, 4, ArH)
10.8 (br s, 1, NH)

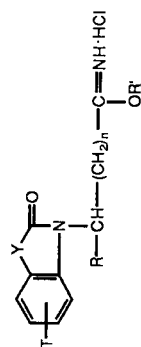
The reaction of imino-ester **21** with concentrated sulfuric acid or oxalic acid at 25-30° furnished the sulfuric and oxalic acid salts, respectively.



It is noteworthy to contrast the chemical shifts for **21** and structure A.

In structure A, the NH proton appeared at 10.8 ppm whereas in **21** it was found at 6.70-7.70 ppm along with the aromatic protons.

Table 4



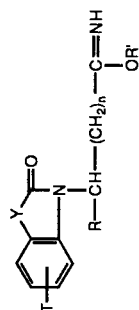
No.	T	Y	R	n	R'	alcohol HCl g	Molar Ratio Nitrile/Alcohol/HCl	Mp °C	% Yield	Empirical formula	Chemical Analysis			
											%C	%H	%N	%S
9	H	S	H	0	-CH ₃	[a]	1/15.6/13.7	249-250	90	C ₁₀ H ₁₀ N ₂ O ₂ S·HCl	%C	%H	%N	%S
											Calcd. 46.42	Calcd. 4.29	Found 46.20	Found 4.32
10	H	S	H	0	-C ₂ H ₅	[b]	1/10.9/11.9	249-250	76	C ₁₁ H ₁₂ N ₂ O ₂ S·HCl	%C	%H	%N	%S
											Calcd. 48.44	Calcd. 4.80	Found 48.32	Found 4.99
11	H	S	H	1	-CH ₃	[a]	1/15.6/13.7	193-194	98	C ₁₁ H ₁₂ N ₂ O ₂ S·HCl	%C	%H	%N	%S
											Calcd. 48.44	Calcd. 4.80	Found 48.22	Found 4.78
12	5-Cl	S	H	0	-CH ₃	[a]	1/24.0/21.0	286-288	95	C ₁₀ H ₈ ClN ₂ O ₂ S·HCl	%C	%H	%N	%S
											Calcd. 40.97	Calcd. 3.44	Found 41.06	Found 3.46
13	6-OC ₂ H ₅	S	H	0	-CH ₃	[a]	1/15.7/13.8	214-215	96	C ₁₂ H ₁₄ N ₂ O ₂ S·HCl	%C	%H	%N	%S
											Calcd. 47.60	Calcd. 4.99	Found 47.37	Found 5.07
14	H	S	H	0	-CH(CH ₃) ₂	[c]	1/ 8.4/ 9.7	224-226	62	C ₁₂ H ₁₄ N ₂ O ₂ S·HCl·H ₂ O	%C	%H	%N	%S
											Calcd. 47.29	Calcd. 5.62	Found 47.59	Found 5.39
											%C	%H	%N	%S
											Calcd. 9.19	Calcd. 10.52	Found 9.49	Found 10.68

Table 4 (continued)

No.	T	Y	R	n	R'	alcohol	Molar Ratio Nitrile/Alcohol/HCl	Mp °C	% Yield	Empirical formula	Chemical Analysis
15	H	S	H	0	-C ₃ H ₇	[d]	1/ 8.4/ 8.4	241-242	94	C ₁₂ H ₁₄ N ₂ O ₂ S·HCl	%C Calcd. 50.25 Found 50.35
											%H Calcd. 5.27 Found 5.32
16	H	S	H	2	-CH ₃	[a]	1/15.6/12.2	127-128	90	C ₁₂ H ₁₄ N ₂ O ₂ S·HCl	%N Calcd. 9.77 Found 9.69
											%S Calcd. 11.18 Found 11.00
17	H	S	-CH ₃	0	-CH ₃	[a]	1/16.0/15.2	106-108	95	C ₁₁ H ₁₂ N ₂ O ₂ S·HCl	%C Calcd. 48.44 Found 48.09
											%H Calcd. 4.80 Found 4.74
18	6-Br	S	H	0	-CH ₃	[a]	1/16.0/14.0	277-278	99	C ₁₀ H ₈ BrN ₂ O ₂ S·HCl	%N Calcd. 10.27 Found 10.24
											%S Calcd. 11.76 Found 11.57
19	6-Br	S	-CH ₃	0	-CH ₃	[a]	1/15.7/13.7	202-203	91	C ₁₁ H ₁₁ BrN ₂ O ₂ S·HCl	%C Calcd. 35.57 Found 35.35
											%H Calcd. 2.99 Found 2.99
20	H	O	H	0	-CH ₃	[a]	1/15.7/13.7	252-253	95	C ₁₀ H ₁₀ N ₂ O ₂ ·HCl	%N Calcd. 8.30 Found 8.25
											%S Calcd. 9.50 Found 9.49
											%C Calcd. 37.57 Found 37.57
											%H Calcd. 3.44 Found 3.43
											%N Calcd. 7.97 Found 8.00
											%S Calcd. 9.12 Found 9.06
											%C Calcd. 49.50 Found 49.10
											%H Calcd. 4.57 Found 4.55
											%N Calcd. 11.54 Found 11.49
											%S Calcd. 14.61 Found 15.02

[a] Methyl alcohol. [b] Ethyl alcohol. [c] Isopropyl alcohol. [d] Propyl alcohol.

Table 5



No.	T	Y	R	n	R'	Mp °C	% Yield	Empirical formula	NMR- δ ppm CDCl ₃ , TMS	Chemical Analysis
21	H	S	H	0	-CH ₃	100-101 [a]	78	C ₁₀ H ₁₀ N ₂ O ₂ S	3.80 (s, 3, OCH ₃), 4.60 (s, 2, NCH ₂), 6.70-7.70 (m, 5, ArH + NH)	%C Calcd. 54.04 Found 53.91 %N Calcd. 12.60 Found 12.53 %H Calcd. 4.54 Found 4.57
22	H	S	H	0	-C ₂ H ₅	99-100 [b]	64	C ₁₁ H ₁₂ N ₂ O ₂ S	1.40 (t, 3, C-CH ₃), 4.30 (q, 2, OCH ₂), 4.67 (s, 2, NCH ₂), 6.80-7.80 (m, 5, ArH + NH)	%C Calcd. 55.91 Found 55.41 %N Calcd. 11.86 Found 11.49 %H Calcd. 5.12 Found 5.02
23	H	S	H	1	-CH ₃	56-57	98	C ₁₁ H ₁₂ N ₂ O ₂ S	2.60 (t, 2, CH ₂ = N), 3.60 (s, 3, OCH ₃), 4.10 (t, 2, NCH ₂), 6.75-7.55 (m, 5, ArH + NH)	%C Calcd. 55.91 Found 55.72 %N Calcd. 11.86 Found 11.89 %H Calcd. 5.12 Found 5.08
24	5-Cl	S	H	0	-CH ₃	125-126 [6]	93	C ₁₀ H ₉ ClN ₂ O ₂ S	3.75 (s, 3, OCH ₃), 4.60 (s, 2, NCH ₂), 6.80-7.50 (m, 4, ArH + NH)	%C Calcd. 46.79 Found 46.68 %N Calcd. 10.91 Found 10.89 %H Calcd. 3.53 Found 3.53
25	6-OC ₂ H ₅	S	H	0	-CH ₃	116-117 [b]	60	C ₁₂ H ₁₄ N ₂ O ₂ S	1.33 (t, 3, CH ₃ C), 3.75 (s, 3, OCH ₃), 3.95 (q, 2, CH ₂ O), 4.48 (s, 2, NCH ₂), 6.50-7.30 (m, 4, ArH + NH)	%C Calcd. 54.12 Found 53.80 %N Calcd. 10.52 Found 10.18 %H Calcd. 5.30 Found 5.19
26	H	S	H	0	-CH(CH ₃) ₂	46-47	85	C ₁₂ H ₁₄ N ₂ O ₂ S	1.20 (2d, 6, C(CH ₃) ₂), 4.52 (2s, 2, NCH ₂), 5.00 (septet, 1, OCH), 6.65-7.50 (m, 5, ArH + NH)	%C Calcd. 57.58 Found 57.18 %N Calcd. 11.19 Found 11.00 %H Calcd. 5.64 Found 5.33

Table 5 (continued)

No.	T	Y	R	n	R'	Mp °C	% Yield	Empirical formula	NMR- δ ppm CDCl ₃ -TMS	Chemical Analysis	
										%C	%H
27	H	S	H	0	-C ₃ H ₇	52-53	94	C ₁₃ H ₁₄ N ₂ O ₂ S	0.90 (t, 3, C-CH ₃), 1.70 (sextet, 2, C-CH ₂ -C), 4.10 (t, 2, OCH ₃), 4.60 (s, 2, NCH ₃), 6.70-7.70 (m, 5, ArH + NH)	Calcd. 57.58 Found 57.30	Calcd. 5.64 Found 5.36
										%N	%S
28	H	S	H	2	-CH ₃	viscous liquid	94	C ₁₃ H ₁₄ N ₂ O ₂ S	1.60-2.70 (m, 4, CH ₂ CH ₂ , C=N), 3.70 (s, 3, OCH ₃), 4.00 (t, 2, NCH ₃), 6.50-7.70 (m, 5, ArH + NH)	Calcd. 57.58 Found 57.18	Calcd. 5.64 Found 5.24
										%N	%S
29	H	S	-CH ₃	0	-CH ₃	viscous liquid	95	C ₁₁ H ₁₃ N ₂ O ₂ S	1.65 (d, 3, CH ₃ C), 3.65 (s, 3, OCH ₃), 5.38 (q, 1, CH), 6.80-7.80 (m, 5, ArH + NH)	Calcd. 55.91 Found 55.70	Calcd. 5.12 Found 5.13
										%N	%S
30	6-Br	S	H	0	-CH ₃	132-133 [a]	95	C ₁₀ H ₉ BrN ₂ O ₂ S	3.80 (s, 3, OCH ₃), 4.60 (s, 2, NCH ₃), 6.60-7.70 (m, 4, ArH + NH)	Calcd. 39.88 Found 39.93	Calcd. 3.01 Found 3.02
										%N	%S
31	6-Br	S	-CH ₃	0	-CH ₃	93-95 [b]	92	C ₁₁ H ₁₁ BrN ₂ O ₂ S	1.65 (d, 3, CH ₃ C), 3.70 (s, 3, OCH ₃), 5.45 (q, 1, CH), 6.70- 7.80 (m, 4, ArH + NH)	Calcd. 41.92 Found 42.00	Calcd. 3.52 Found 3.55
										%N	%S
32	H	O	H	0	-CH ₃	100-101 [b]	99	C ₁₀ H ₁₀ N ₂ O ₂ S	3.80 (s, 3, OCH ₃), 4.45 (s, 2, NCH ₃), 6.70-7.50 (m, 5, ArH + NH)	Calcd. 58.25 Found 58.41	Calcd. 4.89 Found 5.04
										%N	%S

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

Discussion.

Pinner [3] was the first to describe the synthesis of imino-esters. According to Pinner [3b] the optimal ratio of the three reagents (nitrile, alcohol and hydrogen chloride) is when they are practically equimolar. However, different ratios were employed and various authors obtained good results with nitrile/alcohol $\frac{1}{2}$ [4,5] or even up to $\frac{1}{3}$ [6,7]. Other reports that a large excess of alcohol (1/10) sometimes improves the yield [8,9], whereas in other cases this ratio must be decreased [10]. However, in our case, with exception of compound **14**, we obtained excellent yields (90-99%) of the imino-ester hydrogen chloride salts employing a molar ratio of nitrile/alcohol/hydrogen chloride of 1/15.6-24.0/12.2-15.2. (See Table 4 and the following Figures 1-4).

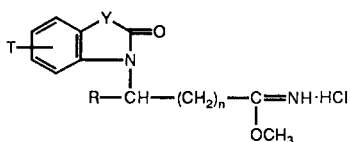


Figure 1

T = H, 5-Cl, 6-OC₂H₅, or 6-Br, Y = S or O. R = H n = zero.

No.	T	Y	% Yield	Alcohol	Molar Ratio		
					Nitrile / Alcohol / HCl		
9	H	S	90	CH ₃ OH	1	15.6	13.7
12	5-Cl	S	95	CH ₃ OH	1	24.0	21.0
13	6-OC ₂ H ₅	S	96	CH ₃ OH	1	15.7	13.8
18	6-Br	S	99	CH ₃ OH	1	16.0	14.0
20	H	O	95	CH ₃ OH	1	15.7	13.7

When the molar ratio of the nitrile/methyl alcohol was 1/15.6 to 1/24.0, the % yield of the imino-ester hydrogen chloride salts ranged from 90 to 99%.

Increasing the length of the aliphatic chain while maintaining the high molar ratio of nitrile/methyl alcohol (1/15.6) afforded **11** and **16** in yields of 98 and 90%, respectively.

Figure 2

T = H, Y = S or O, R = H

No.	n	Y	% Yield	Alcohol	Molar Ratio			Remarks
					Nitrile / Alcohol / HCl			
11	1	S	98	CH ₃ OH	1	15.6	13.7	-----
16	2	S	90	CH ₃ OH	1	15.6	12.2	-----
20	zero	O	95	CH ₃ OH	1	15.7	13.7	See Figure 1
9	zero	S	90	CH ₃ OH	1	15.6	13.7	See Figure 1

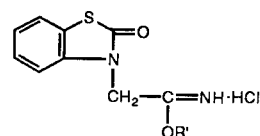
Figure 3

T = H or 6-Br, Y = S, R = -CH₃, n = zero

No.	T	% Yield	Alcohol	Molar Ratio		
				Nitrile / Alcohol / HCl		
17	H	95	CH ₃ OH	1	16.0	15.2
19	6-Br	91	CH ₃ OH	1	15.7	13.7

As expected, employing a high molar ratio (1/15.7 to 16.0) of the nitrile to methyl alcohol furnished **17** and **19** in yields of 95 and 91%, respectively.

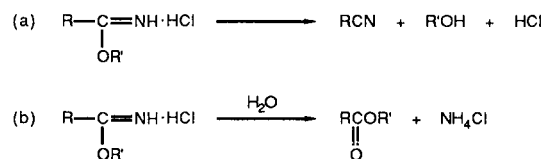
Figure 4



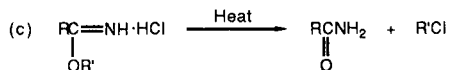
No.	R'	% Yield	Alcohol	Molar Ratio		
				Nitrile / Alcohol / HCl		
14	-CH(CH ₃) ₂	62	isopropyl	1	8.4	9.7
15	-CH ₂ H ₇	94	propyl	1	8.4	8.4

The low yield (62%) for **14** can be explained on the basis that some of the isopropyl alcohol reacted with hydrogen chloride to give isopropyl chloride [11], thus lowering the molar ratio of the nitrile to isopropyl alcohol. However under the same reaction conditions and substituting propyl alcohol for isopropyl alcohol furnished **15** in 94% yield. Since propyl alcohol is a primary alcohol no reaction occurred with hydrogen chloride.

Pinner [3b] and Derby [12] have pointed out the instability of imino-ester hydrochlorides. Decomposition in aqueous solution occurs as follows:



Thus some salts of imino-ester are difficult to keep, since traces of moisture will cause the above side reactions to take place. Pinner [3b] gives the following reaction takes place during the recrystallization of salts of imino-ester.



Due to the inherent instability of some salts of imino-ester, they should be neutralized as soon as possible to the imino-esters. However, Ashley and co-workers [6] found no evidence of the existence of unstable salts of imino-esters in their work, in which they used aromatic nitriles of higher molecular weight.

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.

α -Methyl-2-oxo-3-benzothiazolineacetonitrile (**1**) and 6-Bromo- α -methyl-2-oxo-3-benzothiazolineacetonitrile (**2**).

To a stirred charge containing 0.2 mole of 2-benzothiazolinone or 6-bromo-2-benzothiazolinone, 28 g (0.2 mole) of potassium carbonate and 200 ml of dimethylformamide, 20.2 g (0.2 mole) of 97% 2-chloropropionitrile was added in one portion and then heated at 80-90° for 24 hours. After cooling to 0°, 800 g of 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 1.

2-Oxo-3(2H)-benzothiazolinepropionitrile (**3**), 6-Bromo-2-oxo-3(2H)-benzothiazolinepropionitrile (**4**) and 2-Oxo-3(2H)-benzoxazolinepropionitrile (**5**).

To a stirred solution at 50° containing 0.25 mole of 2-benzothiazolinone, 6-bromo-2-benzothiazolinone or 2-benzoxazolinone and 30.4 g (0.3 mole) of triethylamine in 500 ml of water, 15.9 g (0.3 mole) of acrylonitrile was added in one portion. The stirred reaction mixture was heated at 50-60° for 6 hours and then at 25-30° for 18 hours. The solid was collected by filtration, washed with water until neutral and air-dried at 25-30°. The data are summarized in Table 2.

2-Oxo-3(2H)-benzothiazolinebutyronitrile (**6**) and 2-Oxo-3(2H)-benzoxazolinebutyronitrile (**7**).

A charge containing 0.2 mole of 2-benzothiazolinone or 2-benzoxazolinone, 13.2 g (0.2 mole) of 85% potassium hydroxide, 200 ml of dimethylformamide and 15 ml of water was stirred for 10 minutes. To the stirred solution at 38°, 22.8 g (0.2 mole) or 4-chlorobutyronitrile was added in one portion and then heated at 90-100° for 2 days. 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 data are summarized in Table 3.

2-Oxo-3(2H)-benzoxazolineacetonitrile (**8**).

To a stirred solution containing 0.2 mole of 2-benzoxazolinone, 13.2 g (0.2 mole) of 85% potassium hydroxide, 200 ml of acetone and 10 ml of water, 15.4 g (0.2 mole) of 97% chloroacetonitrile was added in one portion. The stirred reaction mixture was heated at reflux for 6 hours and then a 25-30° for 18 hours. After the addition of 700 ml of water, stirring was continued for 30 minutes at 25-30°. The solid was collected by filtra-

tion, washed with water until neutral and air-dried at 25-30°. Compound **8**, mp 182-183° after recrystallization from ethyl acetate, was obtained in 95% yield; ¹H nmr (deuteriodimethyl sulfoxide): δ 5.09 (s, 2, CH₂CN), 6.90-7.50 (m, 4, ArH).

Anal. Calcd. C₉H₈N₂O₂: C, 62.07; H, 3.47; N, 16.09. Found: C, 62.02; H, 3.49; N, 16.05.

Hydrogen Chloride Salts of the 2-Oxo-alkyl Ester of 3(2H)-Benzothiazolineacetimidic Acid and Related Products **9-20**.

Dry hydrogen chloride gas [61-100 g - see Table 4] was added at a very slow rate at 0-10° to 100 g of the appropriate *absolute* methyl, ethyl, propyl or isopropyl alcohol until a 38-52% hydrogen chloride-alcohol solution was obtained. While stirring this solution at -20°, 0.2 mole of **1**, **2**, **3**, **6**, **8**, 2-oxo-3(2H)-benzothiazolineacetonitrile [**1**], 5-chloro-2-oxo-3(2H)-benzothiazolineacetonitrile [**1**], 6-ethoxy-2-oxo-3(2H)-benzothiazolineacetonitrile [**1**] or 6-bromo-2-oxo-3(2H)-benzothiazolineacetonitrile [**1**] was added in one portion. External cooling was removed and stirring continued for 3 hours. During this period the temperature rose from -20 to 25°. After cooling the reaction mixture to -20°, 500 to 600 ml of *anhydrous* diethyl ether was added, and stirring continued at -20 to -15° for 30 minutes. For all compounds except **16**, the solid was collected by filtration, washed with 100 ml of *anhydrous* diethyl ether and air-dried at 25-30° in a vacuum oven. Since no precipitate resulted in **16**, the bottom colored layer was separated and the solvents were removed *in vacuo* at a maximum temperature of 50° at 1-2 mm. The data are summarized in Table 4.

2-Oxo-alkyl Esters of 3(2H)-Benzothiazolineacetimidic Acid and Related Products **21-32**.

To a stirred solution containing 28 g (0.2 mole) of potassium carbonate in 400 ml of water, 3 liters of diethyl ether were added. After cooling to 0°, 0.1 mole of the appropriate *freshly prepared* imino-ester hydrochloride salt **9-20** was added in one portion, and stirring continued at 0-10° for 3 hours and then at 25-30° for 1 hour. The reaction mixture was filtered to remove any small amount of impurities. The separated ether layer was dried over sodium sulphate and the ether removed *in vacuo* at maximum temperature of 50° at 1-2 mm. The solids were dried in a vacuum oven at 25-30°. The data are summarized in Table 5.

Sulfuric Acid Salt of **21**, **33**.

To a stirred solution containing 15.6 g (0.07 mole) of **21** in 100 ml of acetone, 7.3 g (0.07 mole) of 95-98% concentrated sulfuric acid was added in one portion. An exothermic reaction set in causing a temperature rise from 22 to 40° and the formation of a precipitate. After stirring for 3 hours at 25-30°, the solid was collected by filtration and air-dried at 25-30° in a vacuum oven. Compound **33**, mp 103-104°, was obtained in 84% yield.

Anal. Calcd. for C₁₀H₁₀N₂O₂S·H₂SO₄·2H₂O: C, 33.70; H, 4.53; N, 7.86; S, 17.99. Found: C, 33.55; H, 4.55; N, 7.79; S, 18.39.

Oxalic Salt of **21**, **34**.

To a stirred slurry containing 15.6 g (0.07 mole) of **21** and 100 ml of *anhydrous* ethyl ether, 6.3 g (0.07 mole) of oxalic acid was added in one portion. After stirring at 25-30° for 3 hours, the solid was collected by filtration and air-dried at 25-30° in a vacuum oven. Compound **34**, mp 160-163°, was obtained in 86% yield.

Anal. Calcd. for C₁₂H₁₂N₂O₆S·H₂O: C, 43.63; H, 4.27; N, 8.48; S, 9.71. Found: C, 43.54; H, 4.28; N, 8.46; S, 9.70.

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