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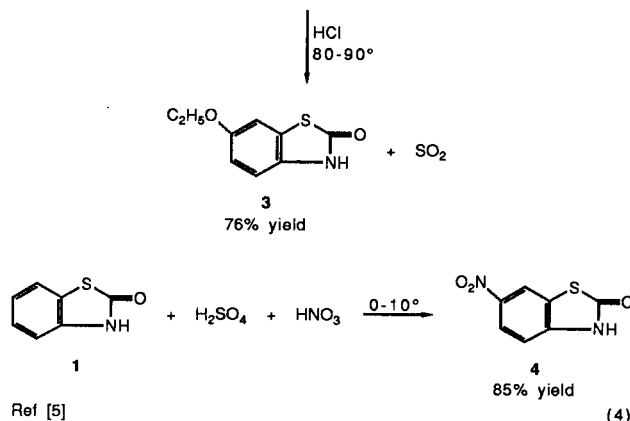
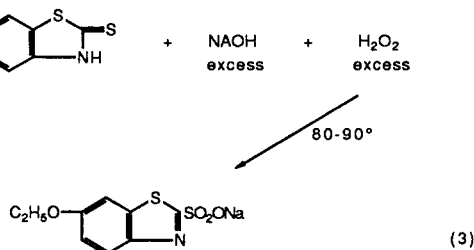
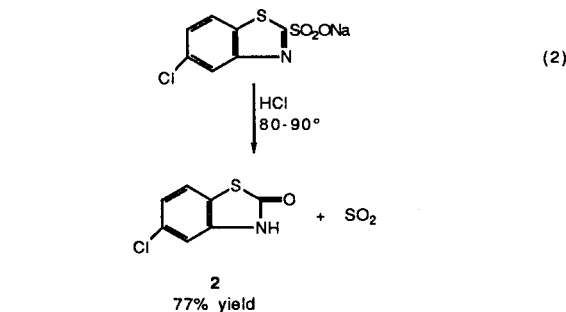
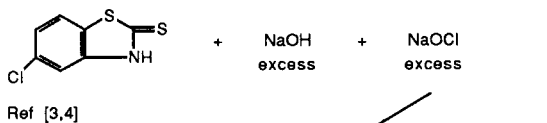
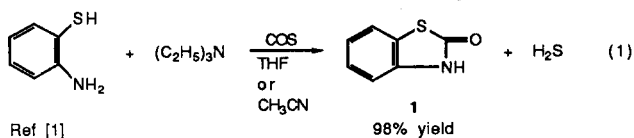
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The reaction of the appropriate 2-benzothiazolinone with 2-chloroacetamide under basic conditions afforded the 2-oxo-3(2*H*)-benzothiazolineacetamides **6-9**. The 2-thioxo-3(2*H*)-benzothiazolineacetamide (**10**) was prepared by the reaction of 3-(carboxymethyl)benzothiazoline-2-thione with ammonium hydroxide. The reaction of acetamides **6-10** with the appropriate anhydride containing a catalytic amount of the sodium salt of the acid corresponding to the anhydride afforded the titled compounds **11-18** in excellent yields. The omission of the catalyst in the same reaction furnished a mixture containing 57% of the titled compound, 37% of the nitrile and 6% of an unknown. Possible mechanism and supporting nmr, ir and mass spectral data are discussed.

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The purpose of this investigation was (1) the synthesis of 2-oxo and thioxo-3(2*H*)-benzothiazoleacetamides and related compounds and (2) to react the acetamides with acetic, propionic or butyric anhydride containing a catalytic amount of the sodium salt of the acid corresponding to the anhydride.

The unsubstituted and substituted-2-benzothiazolinones **1-5** were prepared by the following reactions:



For **2-5**, modified procedures, described by references [2,3,4] and [5], were employed in order to increase the yield and quality of the product (see Experimental).

The 2-oxo-3(2*H*)-benzothiazolineacetamides and related products **6-9** were prepared by the reaction 1, 2, 4, or 5 with 2-chloroacetamide under basic conditions (Table 1).

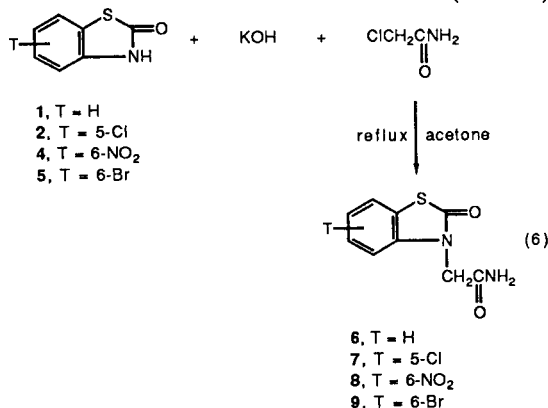
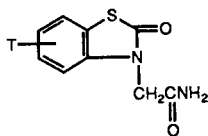


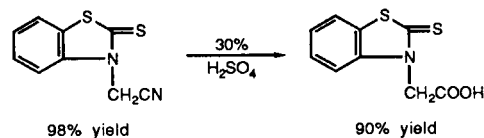
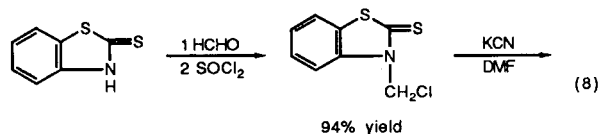
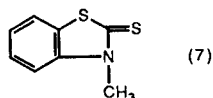
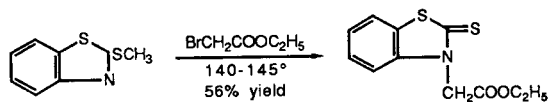
Table 1



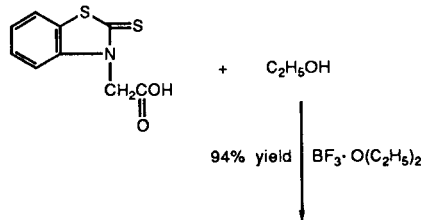
No.	T	Mp °C	% Yield	Empirical formula	NMR- $\delta$ ppm DMSO- $d_6$ -TMS	Chemical Analysis	
						%C	%H
6	H	253-254	79	$C_9H_9N_2O_2S$	4.58 (s, 2, NCH <sub>2</sub> ), 7.0-8.0 (m, 6, ArH + NH <sub>2</sub> ), NH <sub>2</sub> protons exchanged with deuterium oxide	Calcd. 51.91	Calcd. 3.87
						Found 51.80	Found 3.80
						%N	%S
						Calcd. 13.45	Calcd. 15.40
7	5-Cl	284-285 [a]	84	$C_9H_7ClN_2O_2S$	4.56 (s, 2, NCH <sub>2</sub> ), 6.95-7.91 (m, 5, ArH + NH <sub>2</sub> )	Calcd. 44.54	Calcd. 2.91
						Found 44.62	Found 2.90
						%N	%S
						Calcd. 11.54	Calcd. 13.21
8	6-NO <sub>2</sub>	297-298 [a]	54	$C_9H_7N_3O_4S$	4.58 (s, 2, NCH <sub>2</sub> ), 7.00-8.26 (m, 3, ArH), 8.59 (d, 2, NH <sub>2</sub> )	Calcd. 42.69	Calcd. 2.79
						Found 42.62	Found 2.79
						%N	%S
						Calcd. 16.59	Calcd. 12.66
9	6-Br	278-279	80	$C_9H_7BrN_2O_2S$	4.50 (s, 2, NCH <sub>2</sub> ), 6.90-7.90 (m, 5, ArH + NH <sub>2</sub> )	Calcd. 37.65	Calcd. 2.46
						Found 37.77	Found 2.51
						%N	%S
						Calcd. 9.76	Calcd. 11.17
						Found 9.70	Found 11.27

[a] Recrystallization from dimethylformamide.

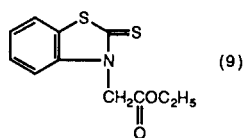
The synthesis of 3-(carboethoxymethyl)benzothiazoline-2-thione was first prepared by Chen [6] by the reaction of 2-(methylthio)benzothiazole with ethyl bromoacetate at 140-145°.



The treatment of the acid with ethanol and boron trifluoride ether complex provided a new route to the ester [8] in 94% yield.



Recently we reported [7] the synthesis of 2-thioxo-(3*H*)-benzothiazoline-3-acetic acid in an overall yield of 83% by the following reactions:



The reaction of the ethyl ester of 2-thioxo-3(2*H*)-benzothiazole-3-acetic acid [6 and 8] with ammonia hydroxide

afforded 2-thioxo-3(2*H*)-benzothiazoleacetamide (10) in 91% yield.

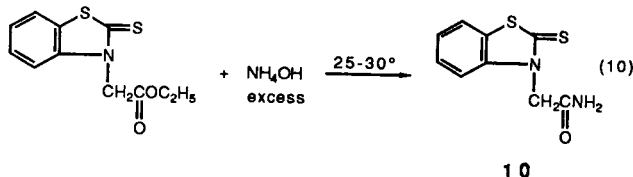
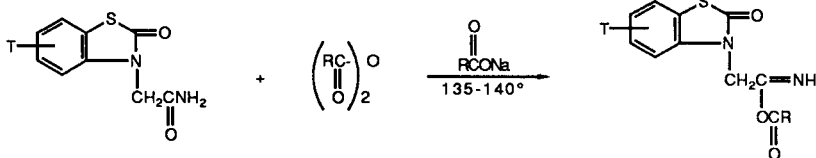


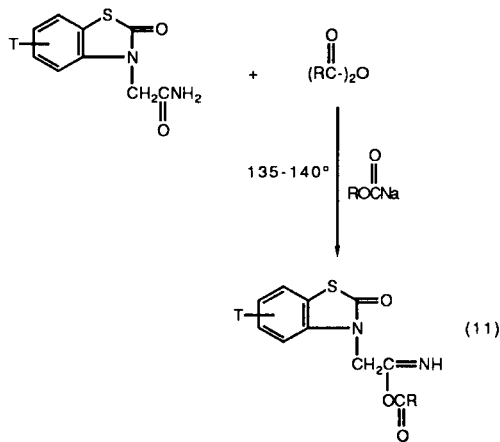
Table 2



No.	T	R	Reactant acetamide	mp °C	% Yield	Empirical formula	NMR-δ ppm DMSO-d <sub>6</sub> -TMS	Chemical Analysis	
								%C	%H
11 [a], [d], [e]	H	-CH <sub>3</sub>	6	148 [b]	74	C <sub>11</sub> H <sub>10</sub> N <sub>2</sub> O <sub>3</sub> S	2.25 (s, 3, -COCH <sub>3</sub> ), 5.00 (s, 2, NCH <sub>2</sub> ), 6.70-7.75 (m, 4, ArH), 10.80 (br s, 1, NH),	Calcd. 52.79	Calcd. 4.03
								Found 52.94	Found 4.05
12	5-Cl	-CH <sub>3</sub>	7	209-211 [b]	82	C <sub>11</sub> H <sub>9</sub> ClN <sub>2</sub> O <sub>3</sub> S	2.22 (s, 3, -COCH <sub>3</sub> ), 5.11 (s, 2, NCH <sub>2</sub> ), 7.10-7.87 (m, 3, ArH), 11.21 (br s, 1, NH)	Calcd. 46.40	Calcd. 3.19
								Found 46.43	Found 3.19
13	6-NO <sub>2</sub>	-CH <sub>3</sub>	8	227-228 [c]	86	C <sub>11</sub> H <sub>9</sub> N <sub>3</sub> O <sub>3</sub> S	2.15 (s, 3, -COCH <sub>3</sub> ), 5.08 (s, 2, NCH <sub>2</sub> ), 7.50 (d, 1, ArH), 8.18 (2d, 1, ArH), 8.65 (d, 1, ArH), 11.19 11.19 (br s, 1, NH)	Calcd. 44.75	Calcd. 3.07
								Found 44.68	Found 3.09
14	6-Br	-CH <sub>3</sub>	9	216-218 [b]	91	C <sub>11</sub> H <sub>9</sub> BrN <sub>2</sub> O <sub>3</sub> S	2.10 (s, 3, -COCH <sub>3</sub> ), 4.95 (s, 2, NCH <sub>2</sub> ), 7.05-7.59 (m, 2, ArH), 7.82 (d, 1, ArH), 11.10 (br s, 1, NH)	Calcd. 40.14	Calcd. 2.76
								Found 40.14	Found 2.76
15	H	-C <sub>2</sub> H <sub>5</sub>	6	189-189 [b]	60	C <sub>13</sub> H <sub>12</sub> N <sub>2</sub> O <sub>3</sub> S	0.97 (t, 3, C-CH <sub>3</sub> ), 2.41 (q, 2, -COCH <sub>2</sub> -), 4.98 (s, 2, NCH <sub>2</sub> ), 6.95-7.70 (m, 4, ArH), 11.03 (br s, 1, NH)	Calcd. 54.53	Calcd. 4.58
								Found 54.55	Found 4.58
16	H	-C <sub>2</sub> H <sub>5</sub>	6	152-153	57	C <sub>13</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub> S	0.90 (t, 3, C-CH <sub>3</sub> ), 1.61 (sextet, 2, C-CH <sub>2</sub> -C)-2, 2.35 (t, 2, -COCH <sub>2</sub> -), 5.03 (s, 2, NCH <sub>2</sub> ), 6.70-7.50 (m, 4, ArH), 9.40 (s, 1, NH)	Calcd. 56.10	Calcd. 5.07
								Found 56.14	Found 5.09

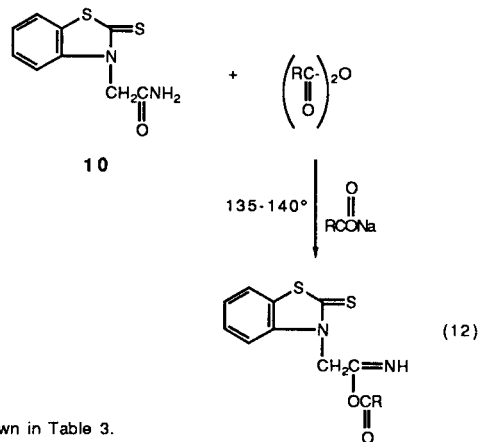
[a] Calcd. M. W. 250.3 Found 252 (THF). [b] Recrystallization from isopropyl alcohol. [c] Recrystallization from ethyl acetate. [d] Ir (potassium bromide) 1674 (C = NH), 1703 (C = O cyclic lactam) and 1747 (C = O of acetyl group) cm<sup>-1</sup>. [e] Electron impact mass spectrum and m/e (relative intensity) 250 (46) M<sup>+</sup>, 208 (7), 191 (100), 164 (13), 136 (86), 109 (24), 65 (12) and 43 (47).

The reaction of **6**, **7**, **8** or **9** with acetic, propionic or butyric anhydride containing a catalytic amount of the sodium salt of the acid corresponding to the anhydride at 135-140° for two hours afforded 2-oxo-3(2*H*)-benzothiazoleethanimic acid anhydride with acetic acid and related products **11-16**.



T and R are shown in Table 2.

The reaction of **10** with acetic or propionic anhydride containing a catalytic amount of the sodium salt of the acid corresponding to the anhydride at 135-140° for two hours gave 2-thioxo-3(2*H*)-benzothiazoleethanimic acid anhydride with acid and related products **17-18**.



R is shown in Table 3.

Based on elemental analysis and molecular weight data, compound **11** isolated in reaction 11 (Table 2) had a molecular weight of 250 with an empirical formula of  $C_{11}H_{10}N_2O_3S$ . From this limited data we considered the possible structures as the *O* substituted derivative (**11**) or the *N*-substituted derivative (Structure A). The nmr, ir and mass spectral data completely substantiated the proposed

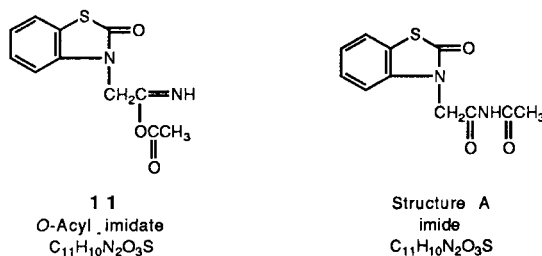


Table 3

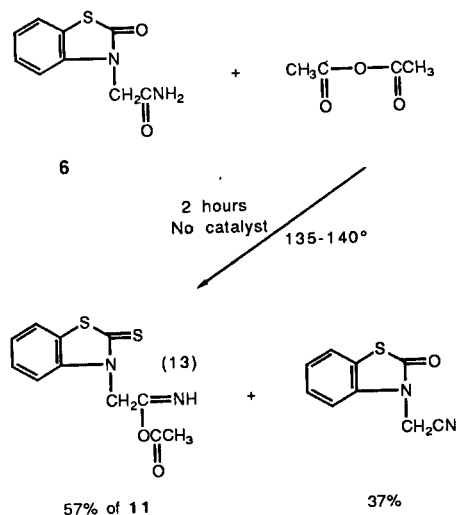
No.	R	Mp °C	% Yield	Empirical formula	NMR- $\delta$ ppm DMSO- $d_6$ -TMS	Chemical Analysis	
						% C	% H
17	-CH <sub>3</sub>	203-204 [a]	94	$C_{11}H_{10}N_2O_2S_2$	2.07 (s, 3, -COCH <sub>3</sub> ), 5.42 (s, 2, NCH <sub>2</sub> ), 7.00-7.80 (m, 4, ArH), 11.10 (br s, 1, NH)	Calcd. 49.61	Calcd. 3.78
						Found 49.64	Found 3.78
						Calcd. 10.52	Calcd. 24.08
						Found 10.52	Found 24.04
18	-C <sub>2</sub> H <sub>5</sub>	207 [b]	82	$C_{12}H_{12}N_2O_2S_2$	0.95 (t, 3, C-CH <sub>3</sub> ), 2.40 (q, 2, -COCH <sub>2</sub> -), 5.50 (s, 2, NCH <sub>2</sub> ), 7.07-7.80 (m, 4, ArH), 11.11 (br s, 1, NH)	Calcd. 51.41	Calcd. 4.31
						Found 51.42	Found 4.33
						Calcd. 9.99	Calcd. 22.87
						Found 10.00	Found 22.91

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

structure **11** and thus ruled out structure A. In deuteriodimethyl sulfoxide, the following chemical shifts were observed for **11**:  $\delta$  2.25 (s, 3, CCH<sub>3</sub>), 5.00 (s, 2, NCH<sub>2</sub>),

6.70-7.55 (m, 4, ArH), 10.80 (br s, 1, NH). The presence of imino group [C=NH] (1674 cm<sup>-1</sup>), cyclic lactam carbonyl group (1703 cm<sup>-1</sup>) and the carbonyl of the acetyl group (1749 cm<sup>-1</sup>) absorption bands in potassium bromide ir spectrum afforded additional proof for our proposed structure **11**. Furthermore, the electron impact mass spectrum furnished the molecular weight data in the form of M<sup>+</sup>: 250. Electron impact mass spectrum and m/e (relative intensity) 250 (46) M<sup>+</sup>; 208 (7), 191 (100), 164 (13), 136 (86), 109 (24), 65 (12), and 43 (47).

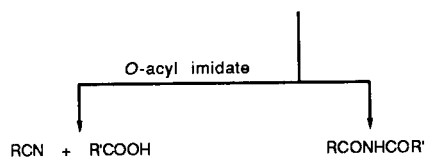
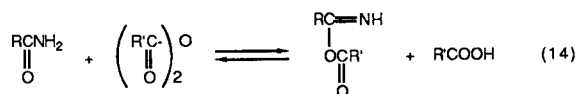
Repeating reaction 11 when T = H and R = CH<sub>3</sub> without the catalyst, sodium acetate, furnished a mixture, mp 117-118° containing 57% of **11**, 37% of 2-oxo-3(2*H*)-benzothiazolineacetonitrile [8] and 6% of an unknown.



## Discussion.

Anhydrides react sluggishly with most amides unless a catalyst such as sulfuric acid, dry hydrogen chloride, an acyl chloride or even ammonium chloride is used [9,10]. Both dehydration to the nitrile and mono-*N*-substitution is observed with primary amides [9]. Most catalysts appear to speed both the nitrile and diacylamide or imide formation [9,10].

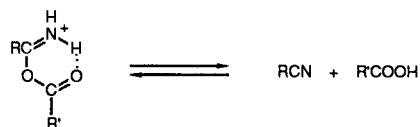
### Acylation of Primary Amides with Acid Anhydride.



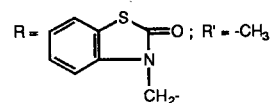
Since the *O*-acylimidates or the titled compounds exhibited biological activity, our research effort was directed towards discovering a catalyst that would afford the *O*-acylimidates in good yields free of the nitrile and imide. After many failures with acidic catalysts, the use of a basic catalysis, in particular, the sodium salt of the acid corresponding to the anhydride afforded the *O*-acylimidates free of the nitrile and imide in yields of 70 to 94%.

The proposed pathway for reactions **11** and **12** is depicted in Scheme 1. The reaction of a primary amide with the catalyst afforded anion **A** which can be stabilized by resonance to give the ambident anion **B** which then can react with the anhydride to give the *O*-acylimidate **C** plus the acid anion R'COO<sup>-</sup>. This is followed by the reaction of the *O*-acylimidate **C** with the acid to yield the isoimidinium carboxylate **D**. Moreover, **C** and **D** are in equilibrium in the presence of the catalyst (R'COONa) which enhances the stability of **C** and thus prevents its decomposition to yield the nitrile and acid.

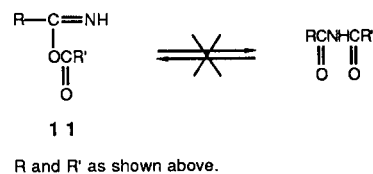
Davidson and Skovronek [9] reported in their study of the propionamide-propionic anhydride reaction that by adjusting the pH of the reaction mixture the isoimidinium carboxylate can decompose into the nitrile under neutral conditions or rearrange into the imide under acidic conditions. They further stated that the decomposition reaction is a six-center type and is not subject to catalysis.



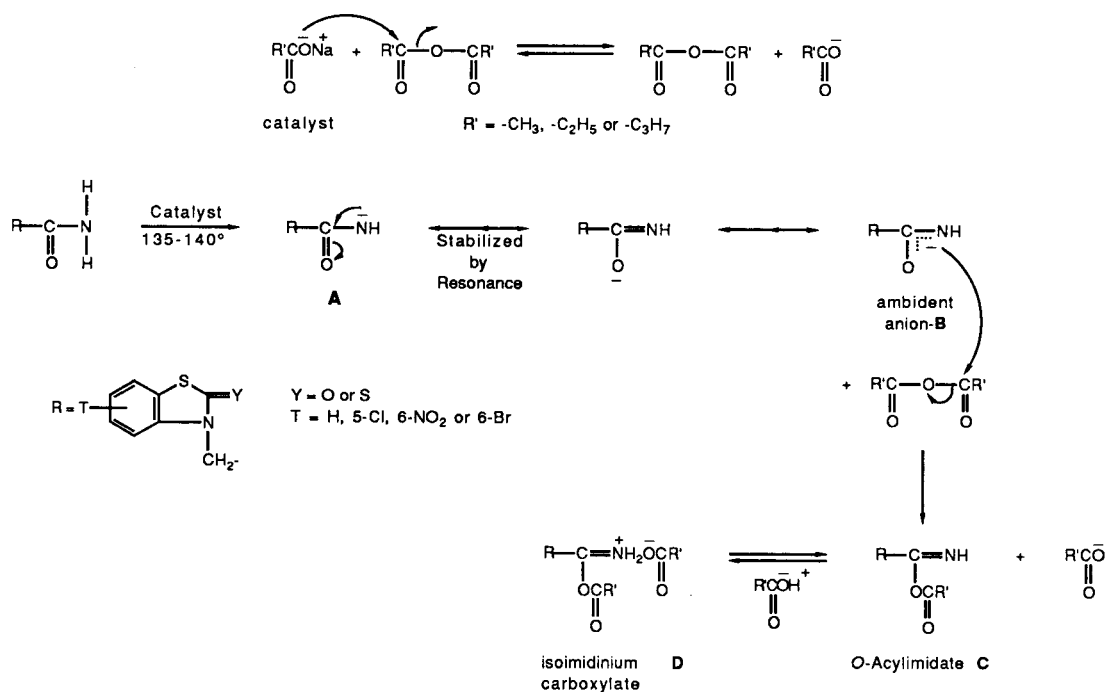
In our case when R and R' are as shown below, the reaction of **6** with acetic anhydride without the catalyst (R'COONa) (Reaction 13) afforded a mixture containing



37% of 2-oxo-3(2*H*)-benzothiazoleacetonitrile [8], 57% of *O*-acylimidate **11** and 6% of an unknown. Since we employed a basic catalyst and as expected, no acid catalysis occurred to give the imide by the rearrangement of the *O*-acylimidate [9].



Scheme 1



## EXPERIMENTAL

The nmr spectra were obtained with a Varian T-60 NMR spectrometer. The chemical shifts are reported in  $\delta$ , using tetramethylsilane as reference. All melting points were taken upon a Fisher-Johns block and are uncorrected. The electron impact mass spectrum of **11** 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 231°. The infrared spectrum of **11** was obtained with a Beckman IR-12 spectrophotometer. Vapor phase chromatographic analysis of impure **11** obtained in reaction 13 was performed with F and M 720 gas chromatograph. A 0.125 in x 1 ft stainless steel column packed with 10% OV-17 on Chromosorb W-HP 80-100 mesh was operated isothermally at 240° with a pressure of 40 psi.

2-Benzothiazolinone (**1**).

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

5-Chloro-2-benzothiazolinone (**2**).

To a stirred solution at 80° containing 100.6 g (0.5 mole) of 5-chlorobenzothiazolinone-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 SO<sub>2</sub>!). 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 and air-dried at 50°. The product, mp 222-224°, was obtained in 72% yield. After recrystallization from methyl alcohol, it melted at 239-240°.

*Anal.* Calcd. for C<sub>7</sub>H<sub>4</sub>ClNOS: 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.

6-Ethoxy-2-benzothiazolinone (**3**).

To a stirred solution containing 106 g (0.5 mole) of 6-ethoxybenzo-

thiazolinone-2-thione, 120 g (1.5 mole) of 50% aqueous sodium hydroxide and 750 ml of water, 170 g (1.5 mole) of 30% hydrogen peroxide was added dropwise over a 70 minute period. During this period an exothermic reaction set in causing a temperature rise from 30° to 80°. After stirring and heating the reaction mixture at 80-90° for 3 hours, 165 g (1.65 moles) of concentrated hydrochloric acid was added dropwise at 80-90° over a 40 minute period (foaming at SO<sub>2</sub>!). After the addition of 800 ml of hot water, the stirred slurry was heated at 80-90° for 1.5 hours. After cooling to 25°, the solid was collected by filtration, washed with water until neutral and air-dried at 50°. The crude product, mp 142-144°, was obtained in 76% yield. After recrystallization from ethyl alcohol, **3** melted at 148-149°.

*Anal.* Calcd. for C<sub>9</sub>H<sub>9</sub>NO<sub>2</sub>S: C, 55.37; H, 4.65; N, 7.17; S, 16.42. Found: C, 55.23; H, 4.71; N, 7.20; S, 16.55.

6-Nitro-2-benzothiazolinone (**4**).

A charge containing 181.5 g (1.2 moles) of **1** and 1000 g of concentrated sulfuric acid was stirred for 10 minutes resulting in a temperature rise of 25 to 35°. After cooling to 0°, a solution consisting of 160 g of fuming nitric acid and 220 g of concentrated sulfuric acid was added dropwise at 0-5° over a 40 minute period. After stirring at 0-10° for 1 hour, the solution was added slowly to 3000 g of ice water and stirring continued at 0-10° for 1 hour. The precipitate was collected by filtration, washed with water until neutral and air-dried at 50°. Compound **4**, mp 255-257°, after recrystallization from ethyl alcohol, was obtained in 85% yield.

*Anal.* Calcd. for C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>O<sub>3</sub>S: C, 42.85; H, 2.06; N, 14.28; S, 16.34. Found: C, 42.70; H, 1.98; N, 14.41; S, 16.21.

6-Bromo-2-benzothiazolinone (**5**).

To a stirred solution containing 50 g (0.33 mole) of **1** in 1 liter of chloroform, 156 g (0.98 mole) of bromine was added dropwise at 0-3° over a two hour period. The reaction mixture was stirred at 25-30° for three hours. The solid was collected by filtration, washed with 200 ml of chloroform and air-dried at 50°. Crop 1 was 53 g, mp 232-233°. The ex-

cess bromine and chloroform was removed *in vacuo* at maximum temperature of 80-90° at 1-2 mm. Crop 2 was 21 g, mp 232-233°. The total yield was 97% (74 g).

*Anal.* Calcd. for C<sub>7</sub>H<sub>4</sub>BrNOS: C, 36.54; H, 1.75; N, 6.09; S, 13.94. Found: C, 36.62; H, 1.80; N, 6.16; S, 13.91.

#### 2-Oxo-3(2H)-benzothiazolineacetamide and Related Products 6-9.

To a stirred solution containing 0.2 mole of **1**, **2**, **4** or **5**, 13.2 g (0.2 mole) of 85% potassium hydroxide in 250 ml of acetone containing 20 ml of water, 0.2 mole of 2-chloroacetamide 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 700 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 50°. The data are summarized in Table 1.

#### 2-Thioxo-3(2H)-benzothiazoleacetamide (**10**).

To a stirred slurry at 25-30°, containing 70 g (0.276 mole) of the ethyl ester of 2-thioxo-3(2H)-benzothiazoles-3-acetic acid [**6** and **8**] in 800 ml of concentrated ammonia hydroxide, ammonia gas was bubbled into the slurry for 2 to 3 hours each day for a total period of 4 days. The product was collected by filtration, washed with water until neutral and air-dried at 50°. Compound **10**, mp 277-278°, was obtained in 91% yield; <sup>1</sup>H nmr (DMSO-d<sub>6</sub>): δ 5.16 (s, 2, NCH<sub>2</sub>), 7.2-7.6 (m, 4, ArH), 7.73-7.93 (m, 2, NH<sub>2</sub>).

*Anal.* Calcd. for C<sub>8</sub>H<sub>8</sub>N<sub>2</sub>OS<sub>2</sub>: C, 48.19; H, 3.60; N, 12.49; S, 28.59. Found: C, 48.16; H, 3.61; N, 12.49; S, 28.50.

#### 2-Oxo-3(2H)-benzothiazoleethanimic Acid Anhydride with Acetic Acid and Related Products 11-16.

A stirred slurry containing 0.1 mole of **6**, **7**, **8** or **9**, 150 ml of acetic, propionic or butyric anhydride and 2 g of sodium salt of the acid corresponding to the anhydride was heated at 135-140° for 2 hours to form a solution. After cooling the stirred solution to 5°, 800 g of ice water was added and stirring continued at 0-10° for 2 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-Thioxo-3(2H)-benzothiazoleethanimic Acid Anhydride with Acetic Acid and Related Products 17-18.

A stirred slurry containing 0.1 mole of **10**, 250 ml of acetic or propionic anhydride and 2 g of sodium salt of the acid corresponding to the anhydride was heated at 135-140° for 2 hours to form a solution. The product was isolated as described for **11-16**. The data are summarized in Table 3.

#### Reaction of **6** with Acetic Anhydride Without Sodium Acetate.

A stirred charge containing 21 g (0.1 mole) of **6** and 150 ml of acetic anhydride was heated at 135-140° for 2 hours to form a solution. After cooling the stirred solution to 5°, 800 g of ice water was added and stirring continued at 0-10° for 2 hours. The solid was collected by filtration, washed with water until neutral and air-dried at 25-30°. The crude product (19 g) melted at 117-118°. After recrystallization from isopropyl alcohol the melting point remained unchanged. The crude product, mp 117-118°, was analyzed by VPC and found to contain 57% of **11**, 37% of 2-oxo-3(2H)-benzothiazolineacetoneitrile [**7**] and 6% of an unknown.

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