Novel Synthesis of 3-Amino-4-oxo-(2*H*)-pyrazolo[3',4':4,5]pyrimido-[2,1-*b*]benzothiazole and its 2- and 3-Substituted Derivatives

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Received November 27, 2001
Revised September 6, 2002

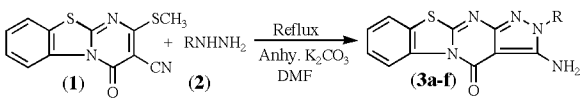
Reaction of 4*H*-pyrimido[2,1-*b*]benzothiazole-2-thiomethyl-3-cyano-4-one (**1**) with hydrazine hydrate/aryl hydrazine/heteryl hydrazine in the presence of anhydrous potassium carbonate and dimethyl formamide afforded 3-amino-4-oxo-(2*H*)/aryl/heteryl pyrazolo[3',4':4,5]pyrimido[2,1-*b*]benzothiazoles in good yield. These pyrazole derivatives on diazotization followed by replacement with hydroxy, chloro, bromo, iodo and on reduction gave the corresponding 3-substituted derivatives.

J. Heterocyclic Chem., **40**, 547 (2003).

A literature survey reveals that very few references are available on the synthesis of pyrazolo pyrimido benzothiazole [1-3]. Garin Javier *et al*. [1-2] reported synthesis of 1-substituted derivatives of pyrazolo [3',4':4,5]pyrimido[2,1-*b*]benzothiazole from respective diphenyl pyrazolo pyrimidine thione and *N*-chlorosuccinimide in sulphuric acid. In continuation of our earlier work [4] on the synthesis of fused heterocycles containing bridgehead nitrogen atom, we report in this paper a convenient route for the synthesis of 3-amino-4-oxo-(2*H*)/aryl/heteryl pyrazolo[3',4':4,5]-pyrimido[2,1-*b*]benzothiazoles (**3a-f**) starting from 4*H*-pyrimido[2,1-*b*]benzothiazole-2-thiomethyl-3-cyano-4-one (**1**).

2-Amino benzothiazole in dimethyl formamide in the presence of anhydrous potassium carbonate was refluxed with ethyl-2-cyano-3,3-bismethylthio acrylate to get the required starting compound (**1**) which contains reactive thiomethyl group at the 2-position and a cyano group at the 3-position [4]. Compound (**1**) on heating independently with hydrazine hydrate, phenyl hydrazine, 2-hydrazino benzothiazole [5], 4-nitro phenyl hydrazine, 2,4-dinitro phenyl hydrazine and 6-nitro-2-hydrazino benzothiazole [5] in the presence of dimethyl formamide and a catalytic amount of potassium carbonate afforded 3-amino-4-oxo-(2*H*)/aryl/heteryl pyrazolo [3',4':4,5]pyrimido[2,1-*b*]benzothiazoles(**3a-f**) respectively in 42-60% yield(Scheme I).

Scheme I



(**1**) (**2**) (**3a-f**)

No.	R	Mp (°C)	Yield (%)
3a	hydrogen	338	60
b	phenyl	305	51
c	2-benzothiazolyl	320	57
d	4-nitro phenyl	>360	44
e	2,4-dinitro phenyl	>360	42
f	6-nitro-2-benzothiazolyl	>360	50

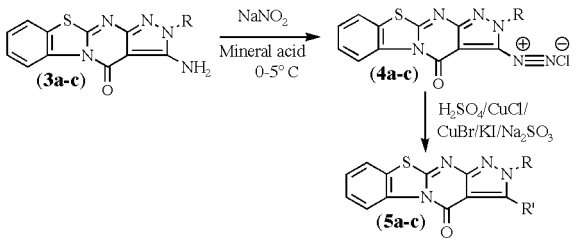
Since compounds (**3a-f**) prepared presently possess a reactive amino group at the 3-position and could be replaced by various substituents, it is surmised that they would become best precursors for the synthesis of 3-substituted derivative of compounds (**3a-f**). Compound **3a**, **3b** and **3c** as they contain a free amino group at 3-position, on diazotization at 0-5 °C with sodium nitrite and mineral acid gave the corresponding diazonium salts (**4a-c**). On hydrolysis, treatment with cuprous chloride, cuprous bromide and potassium iodide **4a-c** afforded 3-hydroxy (**5a-c**), 3-chloro (**5d-f**), 3-bromo (**5g-i**) and 3-iodo (**5j-l**) derivatives respectively. 3-Hydrazino-4-oxo-(2*H*)/phenyl/benzothiazolylpyrazolo[3',4':4,5] pyrimido[2,1-*b*]benzothiazoles (**5m,n,o**) were prepared by reduction of diazonium salts (**4a-c**) with alkaline sodium sulphite. (Scheme II). Structures of these derivatives were confirmed on the basis of elemental analysis and spectral data. The ir and ^{1}H nmr spectra of these compounds showed the absence of bands and peaks respectively due to NH_2 group. Chemical evidence also confirmed the structures of some derivatives. 3-Chloro derivatives (**5d,e,f**) were also obtained by heating the corresponding 3-hydroxy derivatives (**5a,b,c**) with phosphoryl chloride for a period of 1-4 hours. The 3-hydrazino derivatives (**5m,n,o**) were also obtained by heating 3-iodo derivatives (**5j,k,l**) in methanol with 80% hydrazine hydrate for a period of 1-4 hours(Scheme III).

3-Chloro derivatives (**5d,e,f**) and 3-hydrazino derivatives(**5m,n,o**) prepared by two different routes, showed undepressed mixed melting points and exhibited the same Rf values in tlc.

EXPERIMENTAL

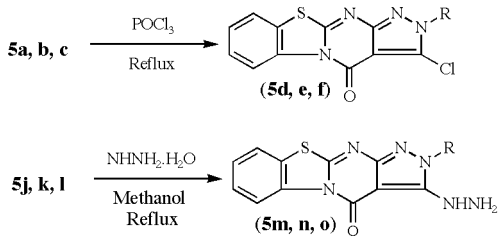
All melting points were determined in capillary tube and are uncorrected. Infrared (ir) spectra were recorded in potassium bromide pellets on a Bomen MB 104 FT Infrared spectrophotometer. Nuclear magnetic resonance (nmr) spectra were obtained on a FT Gemini 60 (60MHz) spectrometer with tetramethyl silane as an internal standard. Mass spectra (ms) were recorded on a FT VG-7070 H Mass spectrophotometer using the EI technique at 70 eV. Microanalysis was performed on a

Scheme II



No	R	R'	Yield(%)
5a	hydrogen	OH	40
b	phenyl	OH	41
c	2-benzothiazolyl	OH	43
d	hydrogen	Cl	27
e	phenyl	Cl	34
f	2-benzothiazolyl	Cl	39
g	hydrogen	Br	29
h	phenyl	Br	36
i	2-benzothiazolyl	Br	39
j	hydrogen	I	28
k	phenyl	I	33
l	2-benzothiazolyl	I	36
m	hydrogen	$NHNH_2$	40
n	phenyl	$NHNH_2$	35
o	2-benzothiazolyl	$NHNH_2$	38

Scheme III



Heraeus CHN-O Rapid analyzer. All the reactions were monitored by thin layer chromatography (tlc), carried out on 0.2 mm silica gel-G plate using iodine vapor for detection.

3-Amino-4-oxo-(2*H*)pyrazolo[3',4':4,5]pyrimido[2,1-*b*]benzothiazole (**3a**).

A mixture of 2.73 g (10 mmoles) of 4*H*-pyrimido[2,1-*b*]benzothiazole-2-thiomethyl-3-cyano-4-one (**1**) and 1.0 g (20 mmoles) of hydrazine hydrate (80%) was refluxed in the presence of a catalytic amount of anhydrous potassium carbonate and 25 ml of dimethylformamide for 3-4 hours. After cooling the solid that appeared was collected by filtration and recrystallized from dimethyl formamide to give 1.54 g (6 mmoles, 60%) of crystalline solid of **3a**, mp 338 °C; ir (potassium bromide): ν max cm^{-1} 3500, 3420 (NH_2), 3310 (NH), 1715 (C=O); ms: m/z 257(M^+,100%): ^{1}H-nmr (deuteriodimethyl sulfoxide): δ 5.2 (broad s, 2H, NH_2, exchangeable with D_2O), 10.9 (s, 1H, NH, exchangeable with D_2O), 7.3-7.7 (m, 4H, aromatic-H).

Anal. Calcd. for $C_{11}H_7N_5OS$: C,51.36; H, 2.72; N, 27.23. Found C, 51.34; H, 2.70; N, 27.25.

3-Amino-4-oxo-2-phenylpyrazolo[3',4':4,5]pyrimido[2,1-*b*]benzothiazole (**3b**).

This compound (1.7 g, 5.1 mmoles) was prepared from (**1**) (2.73 g, 10 mmoles) and phenyl hydrazine (2.16, 20 mmoles) in 51% yield in a manner similar to that described for the preparation of **3a,** mp 305 °C; ir (potassium bromide): ν max cm^{-1} 3490, 3410 (NH_2), 1703 (C=O); ms: m/z 333 (M^+, 100%); ^{1}H-nmr (deuteriodimethyl sulfoxide): δ 6.5 (broad s, 2H, NH_2, exchangeable with D_2O), 7.2-8.3 (m, 9H, aromatic-H).

Anal. Calcd. for $C_{17}H_{11}N_5OS$: C, 61.26; H, 3.30; N, 21.02. Found C, 61.20; H, 3.32; N, 21.00.

3-Amino-4-oxo-2(2'-benzothiazolyl)pyrazolo[3',4':4,5]pyrimido[2,1-*b*]benzothiazole(**3c**).

This compound (2.25 g, 5.76 mmoles) was prepared from (**1**) (2.73 g, 10 mmoles) and 2-hydrazino benzothiazole (1.65 g, 10 mmoles) in 57 % yield in a manner similar to that described for the preparation of **3a**, mp 320 °C; ir (potassium bromide): ν max cm^{-1} 3470, 3400 (NH_2), 1715 (C=O); ms: m/z 390 (M^+,100%); ^{1}H-nmr (deuteriodimethyl sulfoxide): δ 5.2 (broad s, 2H, NH_2, exchangeable with D_2O), 7.3-8.4 (m, 8H, aromatic-H).

Anal. Calcd. for $C_{18}H_{10}N_6OS_2$: C,55.38; H, 2.58; N, 21.52. Found C, 55.40; H, 2.54; N, 21.56.

3-Amino-4-oxo-2(4'-nitrophenyl)pyrazolo[3',4':4,5]pyrimido[2,1-*b*]benzothiazole (**3d**).

This compound (1.6 g, 4.39 mmoles) was prepared from (**1**) (2.73 g, 10 mmoles) and 4-nitro phenyl hydrazine (1.53 g, 10 mmoles) in 44 % yield in a manner similar to that described for the preparation of **3a**, mp >360 °C; ir (potassium bromide): ν max cm^{-1} 3480, 3415 (NH_2), 1695 (C=O); ms: m/z 378 (M^+, 100%); ^{1}H-nmr (deuteriodimethyl sulfoxide): δ 5.6 (broad s, 2H, NH_2, exchangeable with D_2O), 7.2-8.4 (m, 8H, aromatic-H).

Anal. Calcd. for $C_{17}H_{10}N_6O_3S$: C, 53.96; H, 2.66; N, 22.21. Found C, 53.90; H, 2.60; N, 22.19.

3-Amino-4-oxo-2(2',4'-dinitrophenyl)pyrazolo[3',4':4,5]pyrimido[2,1-*b*]benzothiazole (**3e**).

This compound (1.75 g, 4.2 mmoles) was prepared from (**1**) (2.73 g, 10 mmoles) and 2,4-dinitro phenyl hydrazine (1.98 g, 10 mmoles) in 42 % yield in a manner similar to that described for the preparation of **3a**, mp >360 °C; ir (potassium bromide): ν max cm^{-1} 3480, 3390 (NH_2), 1700 (C=O); ms: m/z 423 (M^+, 100%); ^{1}H-nmr (deuteriodimethyl sulfoxide): δ 5.8 (broad s, 2H, NH_2, exchangeable with D_2O), 7.1-8.0 (m, 7H, aromatic-H).

Anal. Calcd. for $C_{17}H_9N_7O_5S$: C, 48.22; H, 2.14; N, 23.16. Found C, 48.19; H, 2.08; N, 23.08.

3-Amino-4-oxo-2(6'-nitro-2'-benzothiazolyl)pyrazolo[3',4':4,5]-pyrimido[2,1-*b*]benzothiazole (**3f**).

This compound (2.20 g, 5.05 mmoles) was prepared from (**1**) (2.73 g, 10 mmoles) and 6-nitro-2-hydrazino benzothiazole (2.10 g, 10 mmoles) in 50 % yield in a manner similar to that described for the preparation of **3a**, mp >360 °C; ir (potassium bromide): ν max cm^{-1} 3470, 3410 (NH_2), 1710 (C=O); ms: m/z 435 (M^+, 100%): ^{1}H-nmr (deuteriodimethyl sulfoxide): δ 5.1 (broad s, 2H, NH_2, exchangeable with D_2O), 6.9-7.9 (m, 7H, aromatic-H).

Anal. Calcd. for $C_{18}H_9N_7O_3S_2$: C,49.64;H, 2.08; N, 22.52. Found C, 49.60; H, 2.01; N, 22.50.

3-Hydroxy-4-oxo-(2*H*)-pyrazolo[3',4':4,5]pyrimido[2,1-*b*] benzothiazole (**5a**).

Compound **3a** (0.257 g, 1 mmole) was dissolved in 2 ml of conc. sulphuric acid and 2 ml of water. The mixture was cooled to 0-5 °C, diazotized by adding 0.069 g (1 mmole) of sodium nitrite in 1 ml of water. A mixture of 5 ml of sulphuric acid and 5 ml of water was added to above mixture with stirring Followed by heating on water bath for 30 minutes. The solid that appeared was collected by filtration and recrystallized from ethanol to give 0.105 g (0.4 mmoles, 40%) of crystalline solid of **5a**, mp 152 °C; ir (potassium bromide): ν max cm^{-1} 3475-3375 (broad OH), 1693 (C=O); ms: m/z 258 (M^+, 100%); ^{1}H-nmr (deuteriodimethyl sulfoxide): δ 4.6 (s, 1H, OH, exchangeable with D_2O), 11.0 (s, 1H, NH, exchangeable with D_2O), 7.3-7.6 (m, 4H, aromatic-H).

Anal. Calcd. for $C_{11}H_6N_4O_2S$: C, 51.16; H, 2.30; N, 21.70. Found C, 51.10; H, 2.25; N, 21.65.

3-Hydroxy-4-oxo-2-phenylpyrazolo[3',4':4,5]pyrimido[2,1-*b*]benzothiazole (**5b**).

This compound (0.14 g, 0.41mmole) was prepared from **3b** (0.333 g, 1 mmole) in 41% yield in a manner similar to that described for **5a**, mp 202 °C; ir (potassium bromide): ν max cm^{-1} 3427-3360(broad, OH), 1698(C=O); ms: m/z 334(M^+,100%); ^{1}H-nmr (deuteriodimethyl sulfoxide): δ 5.4 (s, 1H, OH, exchangeable with D_2O), 7.3-7.9 (m, 9H, aromatic-H).

Anal. Calcd. for $C_{17}H_{10}N_4O_2S$: C, 61.07; H, 2.99; N, 16.76. Found C, 61.05; H, 2.92; N, 16.78.

3-Hydroxy-4-oxo-2(2'-benzothiazolyl)pyrazolo[3',4':4,5]pyrimido[2,1-*b*]benzothiazole (**5c**).

This compound (0.17 g, 0.43 mmole) was prepared from **3c** (0.39 g, 1 mmole) in 43% yield in a manner similar to that described for **5a**, mp 230 °C; ir (potassium bromide): ν max cm^{-1} 3400-3200(broad OH), 1703(C=O); ms: m/z 391(M^+,100%); ^{1}H-nmr (deuteriodimethyl sulfoxide): δ 6.1 (s, 2H, OH, exchangeable with D_2O), 7.3-8.1 (m, 8H, aromatic-H).

Anal. Calcd. for $C_{18}H_9N_5O_2S_2$: C, 55.24; H, 2.30; N, 17.90. Found C, 55.20; H, 2.28; N, 17.88.

3-Chloro-4-oxo-(2*H*)-pyrazolo[3',4':4,5]pyrimido[2,1-*b*] benzothiazole (**5d**).

Compound **3a** (0.257 g, 1 mmoles) was dissolved in 2 ml of conc. sulphuric acid and 2 ml of water. The mixture was cooled to 0-5 °C, diazotized by adding 0.069 g (1 mmole) of sodium nitrite in 1 ml of water. While diazotization was in progress, the calculated amount of a mixture of cuprous chloride in conc. hydrochloric acid was added with stirring. The mixture was stirred for 15 minutes. Then the mixture was heated on water bath for 30 minutes. The solid that appeared was collected by filtration and recrystallized from ethanol to give 0.075 g (0.27 mmoles, 27%) of crystalline solid of **5d**, mp 240-245 °C; ir (potassium bromide): ν max cm^{-1} 3100(NH), 1716(C=O); 690(C-Cl); ms: m/z 278(M+2,10%), 276(M^+, 30%); ^{1}H-nmr (deuteriochloroform): δ 10.7(s, 1H, NH, exchangeable with D_2O), δ 7.4-7.9 (m, 4H, aromatic-H).

Anal. Calcd. for $C_{11}H_5N_4OSCl$:C,47.82;H,1.81;N, 20.28; found C, 47.80; H, 1.80; N, 20.25.

Synthesis of **5d** from **5a** Using Phosphoryl Chloride.

A mixture of 0.129 g (0.5 mmoles) of **5a** and 2 ml of phosphoryl chloride was refluxed for 1 hour. The mixture was poured on crushed ice. The separated solid was filtered, washed with water and recrystallized from ethanol to give 0.05 g (18%) of **5d**, mp 240-242 °C.

3-Chloro-4-oxo-2-phenylpyrazolo[3',4':4,5]pyrimido[2,1-*b*] benzothiazole (**5e**).

This compound (0.120 g, 0.34 mmole) was prepared from **3b** (0.333 g, 1 mmole) in 34% yield in a manner similar to that described for **5d**, mp 220-225 °C; ir (potassium bromide): ν max cm^{-1} 1710(C=O); 710(C-Cl); ms: m/z 354(M+2,15%), 352(M^+,45%); ^{1}H-nmr (deuteriochloroform): δ 7.1-8.1 (m, 9H, aromatic-H).

Anal. Calcd. for $C_{17}H_9N_4OSCl$: C, 57.95; H, 2.55; N, 15.90. Found C, 57.90; H, 2.50; N, 15.82.

Synthesis of **5e** from **5b** Using Phosphoryl Chloride.

A mixture of 0.166 g (0.5 mmoles) of **5b** and 2 ml of phosphoryl chloride was refluxed for 3 hours. The mixture was poured on crushed ice. The solid separated was filtered, washed with water and recrystallized from ethanol to give 0.06 g (34%) of **5e**, mp 225 °C

3-Chloro-4-oxo-2(2'-benzothiazolyl)pyrazolo[3',4':4,5]pyrimido[2,1-*b*]benzothiazole (**5f**).

This compound (0.16 g, 0.39 mmole) was prepared from **3c** (0.39 g, 1 mmole) in 39% yield in a manner similar to that described for **5d**, mp 260-265 °C; ir (potassium bromide): ν max cm^{-1} 1720(C=O), 720(C-Cl); ms: m/z 411(M+2, 25%), 409(M^+, 75%); ^{1}H-nmr (deuteriochloroform): δ 7.1-7.9 (m, 8H, aromatic-H).

Anal. Calcd. For $C_{18}H_8N_5OS_2Cl$: C, 52.81; H, 1.95; N, 17.11. Found C, 52.78; H, 1.92; N, 17.08.

Synthesis of **5f** from **5c** Using Phosphoryl Chloride.

A mixture of 0.179 g (0.5 mmoles) of **5c** and 2 ml of phosphoryl chloride was refluxed for 4 hours. The mixture was poured on crushed ice. The separated solid was collected by filtration, washed with water and recrystallized from ethanol to give 0.06 g (30%) of **5f**, mp 258-260 °C.

3-Bromo-4-oxo-(2*H*)-pyrazolo[3',4':4,5]pyrimido[2,1-*b*]benzothiazole (**5g**).

Compound **3a** (0.257 g, 1 mmoles) was dissolved in 2 ml of conc. sulphuric acid and 2 ml of water. The mixture was cooled to 0-5 °C, diazotized by adding 0.069 g (1 mmole) of sodium nitrite in 1 ml of water. While diazotization was in progress, the calculated amount of a mixture of cuprous bromide in hydrobromic acid was added with stirring. The mixture was stirred for 15 minutes. Then the mixture was heated on water bath for 30 minutes. The solid that appeared was collected by filtration and recrystallized from ethanol to give 0.095 g (0.29 mmoles, 29%) of crystalline solid of **5g**, mp 275-278 °C; ir (potassium bromide): ν max cm-^{1} 3341(NH), 1734(C=O); 576(C-Br); ms: m/z 322(M+2, 67%), 320(M^+, 69%); ^{1}H-nmr (deuteriochloroform): δ 11.1(s, 1H, NH, exchangeable with D_2O), 7.2-7.7 (m, 4H, aromatic-H).

Anal. Calcd. for $C_{11}H_5N_4OSBr$:C, 41.25; H, 1.56; N, 17.50. Found C, 41.20; H, 1.52; N,17.40.

3-Bromo-4-oxo-2-phenylpyrazolo[3',4':4,5]pyrimido[2,1-*b*]-benzothiazole (**5h**).

This compound (0.145 g, 0.36 mmole) was prepared from **3b** (0.333 g, 1 mmole) in 36% yield in a manner similar to that described for **5g**, mp 285-287 °C; ir (potassium bromide): ν max cm-$^{-1}$ 1705(C=O); 550(C-Br); ms: m/z 398(M+2, 59%), 396(M^+, 61%); ^{1}H-nmr (deuteriochloroform): δ 7.1-8.0 (m, 9H, aromatic-H).

Anal. Calcd. for $C_{17}H_9N_4OSCl$:C, 51.51; H, 2.27; N, 14.14. Found C, 51.50; H, 2.25; N, 14.10.

3-Bromo-4-oxo-2(2'-benzothiazolyl)pyrazolo[3',4':4,5]pyrimido[2,1-*b*]benzothiazole (**5i**).

This compound (0.18 g, 0.39 mmole) was prepared from **3c** (0.39 g, 1 mmole) in 39% yield in a manner similar to that described for **5g**, mp 290-292 °C; ir (potassium bromide): ν max cm^{-1} 1690(C=O), 570(C-Br); ms: m/z 455(M+2, 62%), 453(M^+, 64%). ^{1}H-nmr (deuteriochloroform): δ 7.3-7.9 (m, 8H, aromatic-H).

Anal. Calcd. for $C_{18}H_8N_5OS_2Br$: C,47.68; H, 1.77; N, 15.45. Found C, 47.65; H, 1.75; N, 15.40.

3-Iodo-4-oxo-(2*H*)-pyrazolo[3',4':4,5]pyrimido[2,1-*b*]benzothiazole (**5j**).

Compound **3a** (0.257 g, 1 mmoles) was dissolved in 2 ml of conc. sulphuric acid and 2 ml of water. The mixture was cooled to 0-5 °C, diazotized by adding 0.069 g (1 mmole) of sodium nitrite in 1ml of water. While diazotization was in progress, the calculated amount of potassium iodide in 1 ml of water was added with stirring. The mixture was stirred for 15 minutes followed by heating on water bath for 30 minutes. The solid that appeared was collected by filtration and recrystallized from ethanol to give 0.105 g (0.28 mmoles, 28%) of crystalline solid of **5j**, mp 220-225 °C; ir (potassium bromide): ν max cm-$^{-1}$ 3169(NH), 1684(C=O); 570(C-I) ms: m/z 368(M^+, 80%); ^{1}H-nmr (deuteriochloroform): δ 10.7(s, 1H, NH, exchangeable with D_2O), 7.2-7.8 (m, 4H, aromatic-H).

Anal. Calcd. for $C_{11}H_5N_4OSI$: C, 35.86; H, 1.35; N, 15.21. Found C, 35.80; H, 1.34; N, 15.20.

3-Iodo-4-oxo-2-phenylpyrazolo[3',4':4,5]pyrimido [2,1-*b*] benzothiazole (**5k**).

This compound (0.12 g, 0.34 mmole) was prepared from **3b** (0.333 g, 1 mmole) in 34% yield in a manner similar to that described for **5j**, mp 235-240 °C; ir (potassium bromide): ν max cm-$^{-1}$ 1710(C=O); 540(C-I); ms: m/z 444(M^+, 70%); ^{1}H-nmr (deuteriochloroform): δ 7.1-7.9 (m, 9H, aromatic-H).

Anal. Calcd. for $C_{17}H_9N_4OSI$: C, 45.94; H, 2.02; N, 12.61. Found C, 45.92; H, 2.01; N, 12.57.

3-Iodo-4-oxo-2(2'-benzothiazolyl)pyrazolo[3',4':4,5]pyrimido-[2,1-*b*]benzothiazole (**5l**).

This compound (0.185 g, 0.36 mmole) was prepared from **3c** (0.39 g, 1 mmole) in 36% yield in a manner similar to that described for **5j**, mp 240-242 °C; ir (potassium bromide): ν max cm^{-1} 1695(C=O), 570(C-I); ms: m/z 501 (M^+, 74%); ^{1}H-nmr (deuteriochloroform) : δ 7.3-7.8 (m, 8H, aromatic-H).

Anal. Calcd. for $C_{18}H_8N_5OS_2Br$: C,43.11; H,1.59; N, 13.97. Found C, 43.08; H, 1.55; N, 13.95.

3-Hydrazino-4-oxo-(2*H*)-pyrazolo[3',4':4,5]pyrimido[2,1-*b*] benzothiazole (**5m**).

Compound **3a** (0.257 g, 1 mmole) of 3**a** was dissolved in 2 ml of conc. sulphuric acid and 2 ml of water. The mixture was cooled to 0-5 °C, diazotized by adding 0.069 g (1 mmole) of sodium nitrite in 1 ml of water; stirring was continued for 5 minutes. To the above mixture with stirring was added an ice-cold solution of 0.504 g of hydrated sodium sulphite and 1 g of sodium hydroxide in 10 ml of water. The solution was allowed to stand for 10 minutes, acidified with 5 ml of conc. hydrochloric acid and the mixture was heated on water bath for 5 minutes then allowed to stand for overnight. The separated salt was taken up in water and the free base was obtained by adding a saturated solution of sodium acetate. The solid that appeared was collected by filtration, washed with water and recrystallized from ethanol to give 0.11 g (0.4 mmole, 40%) of crystalline solid of **5m**, mp 260 °C; ir (potassium bromide): ν max cm-$^{-1}$ 3320, 3200(NH_2), 3130(NH), 1705(C=O); ms: m/z 272(M^+, 80%); ^{1}H-nmr (deuteriochloroform): δ 4.9 (s, 1H, NH exchangeable with D_2O), 5.8(broad s, 2H, NH_2 exchangeable with D_2O), 10.7 (s, 1H, NH exchangeable with D_2O), 7.1-7.7 (m, 4H, aromatic-H).

Anal. Calcd. for $C_{11}H_8N_6OS$: C, 48.52; H, 2.94; N, 30.88. Found C, 48.35; H, 2.92; N,30.82.

Synthesis of **5m** from **5j** Using Hydrazine Hydrate.

A mixture of 0.138 g (0.5 mmoles) of **5j**, 0.2 ml of hydrazine hydrate (80%) and 2 ml of methanol was refluxed for 2 hours. The separated solid was collected by filtration and recrystallized from ethanol to give 0.03 g (22%) of **5m**, mp 255-260 °C

3-Hydrazino-4-oxo-2-phenylpyrazolo[3',4':4,5]pyrimido[2,1-*b*]-benzothiazole (**5n**).

This compound (0.12 g, 0.35 mmole) was prepared from **3b** (0.333 g, 1 mmole) in 35% yield in a manner similar to that described for **5m**, mp 274-276 °C; ir (potassium bromide): ν max cm-$^{-1}$ 3300, 3270(NH_2), 3190(NH), 1690(C=O); ms: m/z 348(M^+, 75%); ^{1}H-nmr (deuteriochloroform): δ 5.0 (s, 1H, NH, exchangeable with D_2O), 5.7(broad s, 2H, NH_2, exchangeable with D_2O), 7.2-8.0 (m, 9H, aromatic-H).

Anal. Calcd. for $C_{17}H_{12}N_6OS$: C, 58.62; H, 3.49; N, 24.13. Found C, 58.60; H, 3.45; N, 24.10.

Synthesis of **5n** from **5k** Using Hydrazine Hydrate.

A mixture of 0.22 g (0.5 mmoles) of **5k**, 0.2 ml of hydrazine hydrate (80%) and 2 ml of methanol was refluxed for 2 hours, the separated solid was collected by filtration and recrystallized from ethanol to give 0.035 g (20%) of **5n**, mp 272-274 °C

3-Hydrazino-4-oxo-2(2'-benzothiazolyl)pyrazolo[3',4':4,5]-pyrimido[2,1-*b*]benzothiazole (**5o**).

This compound (0.155 g, 0.38 mmole) was prepared from **3c** (0.39 g, 1 mmole) in 38% yield in a manner similar to that described for **5m**, mp 290-295 °C; ir (potassium bromide): ν max cm-$^{-1}$ 3350, 3240(NH_2), 3180(NH), 1730(C=O); ms: m/z 405(M^+, 70%); ^{1}H-nmr (deuteriochloroform): δ 4.7 (s, 1H, NH, exchangeable with D_2O), 5.7 (broad s, 2H, NH_2, exchangeable with D_2O), 7.3-8.1 (m, 8H, aromatic-H).

Anal. Calcd. for $C_{18}H_8N_5OS_2Br$: C,53.33; H, 2.71; N, 24.19. Found C, 53.30; H, 2.70; N, 24.17.

Synthesis of **5o** from **5l** Using Hydrazine Hydrate.

A mixture of 0.25 g (0.5 mmoles) of **5l**, 0.2 ml of hydrazine hydrate (80%) and 2 ml of methanol was refluxed for 4 hours, the separated solid was collected by filtration and recrystallized from ethanol to give 0.05 g (25%) of **5o**, mp 290-292 °C

Acknowledgment.

Authors are grateful to Dr. B. S. Dhengle, Principal, Yeshwant College, Nanded (India) for providing laboratory facilities and Director, Indian Institute of Chemical Technology, Hyderabad (India) for providing spectra.

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