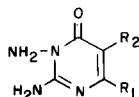


Table I [a]

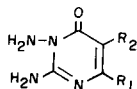


	$\text{R}_1$	$\text{R}_2$	mp °C	C	H	Elemental Analysis		F
						Calcd.	(Found)	
<b>4a</b>	$-\text{CF}_3$	H	217-219	30.94 (30.90)	2.60 (2.49)	28.86 (29.24)		29.36 (29.50)
<b>4b</b>	$-\text{C}(\text{CH}_3)_3$	H	165-167	52.73 (52.86)	7.74 (7.78)	30.75 (30.86)		
<b>4c</b>	$-\text{C}_6\text{H}_5$	H	125-128	59.40 (59.16)	4.98 (4.98)	27.71 (28.00)		
<b>4d</b>	$-\text{C}_6\text{H}_5$	Br	280-282	42.73 (42.50)	3.23 (3.21)	19.93 (19.90)	28.43 (28.01)	
<b>4e</b>	$-\text{C}_6\text{H}_5$	Et	180-183	62.59 (62.35)	6.13 (6.13)	24.33 (24.10)		
<b>4f</b>	$-\text{C}_6\text{H}_5$	$-\text{N}=\text{N}-\text{C}_6\text{H}_5$	241 Dec	62.74 (62.52)	4.61 (4.77)	27.43 (27.03)		
<b>4g</b>	$-\text{C}_6\text{H}_5$	$\text{NH}_2$	185-190	55.29 (55.81)	5.10 (5.01)	32.24 (32.28)		
<b>4h</b>	$-\text{C}_6\text{H}_4\text{F}(p)$	H	160-162	54.54 (54.30)	4.12 (4.14)	25.44 (25.76)		8.63 (8.69)
<b>4j</b>	$-\text{C}_6\text{H}_4\text{Cl}(p)$	H	247-250	50.75 (51.07)	3.82 (3.98)	23.67 (23.31)	14.98 (14.90)	

<b>4k</b>	-C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> ( <i>p</i> )	H	261-264	48.59 (48.27)	3.67 (3.81)	28.33 (28.52)		
<b>4l</b>	-C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> ( <i>p</i> )	H	244-246	61.10 (61.10)	5.59 (5.47)	25.91 (26.01)		
<b>4m</b>	-C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> ( <i>m</i> )	H	193-195	56.89 (56.86)	5.21 (5.00)	24.12 (24.34)		
<b>4n</b>	Adamantyl	H	230-236	64.59 (64.84)	7.74 (7.73)	21.52 (21.71)		
<b>4o</b>	CH <sub>3</sub>	CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> C <sub>2</sub> C <sub>5</sub>	92-95	49.99 (49.94)	6.71 (6.52)	23.32 (22.98)		
<b>4p</b>	CH <sub>3</sub>	Cl	302-305	34.40 (34.51)	4.04 (4.06)	32.09 (32.07)	20.31 (20.16)	
<b>4q</b>	CH <sub>3</sub>	CH <sub>2</sub> CH <sub>2</sub> COOH	121-122	45.28 (45.58)	5.70 (5.59)	26.0 (26.02)		
<b>4r</b>	CH <sub>3</sub>	CH <sub>2</sub> CH <sub>2</sub> OH	109-111	45.65 (45.38)	6.57 (6.40)	30.42 (30.21)		
<b>4s</b>	CF <sub>3</sub>	Br	225-228	21.99 (21.89)	1.48 (1.39)	20.52 (20.44)	29.2 (29.07)	20.73 (20.77)
<b>4t</b>	CH <sub>3</sub>	H	282-285	42.85 (42.84)	5.75 (5.69)	39.88 (40.36)		

[a] Compounds **4d**, **4p** and **4s** were prepared by Experimental Procedure B. Compounds **4a**, **4o** and **4r** were prepared by Experimental Procedure A. Compound **4q** was prepared by hydrolysis of **4p** (see Experimental for details). All other compounds in the Table were prepared by Experimental Procedure C.

Table II [a]

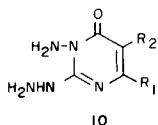


[R<sub>1</sub> and R<sub>2</sub> are connected in this Table]

	R <sub>1</sub> R <sub>2</sub>	mp °C	Elemental Analysis			
			C	H	N	X(Cl, Br, I) S
<b>12</b>	-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> -	246-248	50.59 (50.59)	6.07 (6.02)	33.71 (34.09)	
<b>14</b>	-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> -	215-218	53.32 (53.04)	6.71 (6.71)	31.09 (30.80)	
<b>28</b>	-CH <sub>2</sub> N(CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> CH <sub>2</sub> -	200-202	61.98 (61.59)	6.32 (6.21)	25.81 (25.66)	
<b>29</b>	1,4-piperidyl	300 dec	52.16 (51.98)	6.32 (6.39)	33.79 (33.61)	
<b>19</b>	-CH <sub>2</sub> S-CH <sub>2</sub> -	285-287	39.12 (38.84)	4.38 (4.03)	30.41 (30.25)	17.41 (17.44)
<b>22</b>	-CH <sub>2</sub> CH <sub>2</sub> NHCH <sub>2</sub> -	262.5-263.5	46.40 (46.0)	6.12 (6.19)	38.65 (38.20)	
<b>17</b>	-CH=CH-CH=CH-	175-176	54.54 (54.17)	4.58 (4.41)	31.80 (31.95)	
<b>15</b>	-CH(Br)-CH <sub>2</sub> CH <sub>2</sub> -CH <sub>2</sub> -	155-157	34.31 (34.52)	3.70 (4.01)	22.86 (22.52)	32.60 (32.30)
<b>13</b>	-CH(Br)-CH <sub>2</sub> -CH <sub>2</sub> -	88-90	34.31 (34.31)	3.70 (3.66)	22.86 (22.95)	32.6 (32.40)

[a] Compounds **14**, **19**, **17**, and **22** were prepared by Experimental Procedure A, compounds **13** and **15** were prepared by Experimental Procedure B and **12**, **28**, and **29** by Experimental Procedure C.

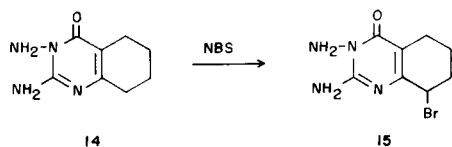
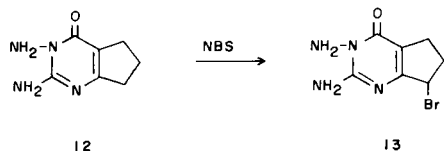
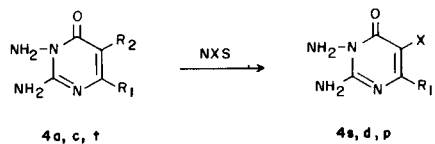
Table III [a]



	R <sub>1</sub>	R <sub>2</sub>	mp °C	C	Elemental Analysis	
					Calcd. (Found)	H
<b>10a</b>	CH <sub>3</sub>	H	207-210	38.71 (38.46)	5.85 (5.62)	45.11 (45.42)
<b>10b</b>	CH <sub>3</sub>	CH <sub>3</sub>	137-140	42.60 (42.44)	6.55 (6.17)	41.39 (41.73)
<b>10c</b>	Pr	H	155-157	45.89 (45.61)	7.15 (7.11)	38.22 (38.57)
<b>10d</b>	Et	H	144-145	42.60 (42.30)	6.55 (6.31)	41.39 (41.68)
<b>10e</b>	CH <sub>3</sub>	-CH <sub>2</sub> CH <sub>2</sub> COOEt	107-109	47.05 (47.01)	6.71 (6.59)	27.43 (27.59)
<b>10f</b>	C <sub>6</sub> H <sub>5</sub>	H	192-Dec	55.29 (55.65)	5.10 (5.20)	32.24 (32.19)
<b>10g</b>	C <sub>6</sub> H <sub>4</sub> Cl( <i>p</i> )	H	235-238	47.72 (48.12)	4.01 (4.20)	27.83 (27.78)
<b>10h</b>	C <sub>6</sub> H <sub>2</sub> (OCH <sub>3</sub> ) <sub>3</sub> (3,4,5)	H	200-201	50.81 (50.67)	5.58 (5.29)	22.79 (22.85)
<b>10h</b>	CH <sub>3</sub>	CH <sub>3</sub>	172-174	58.76 (58.57)	6.16 (6.26)	28.55 (28.35)
<b>10i</b>	CH <sub>3</sub>	Et	175-177	45.89 (45.69)	7.15 (7.15)	38.22 (38.24)
<b>10j</b>	C <sub>6</sub> H <sub>5</sub>	Et	176-177	58.76 (58.49)	6.16 (6.01)	28.55 (28.85)
<b>10k</b>	<i>t</i> -Bu	H	228-230	48.72 (48.35)	7.67 (7.28)	35.51 (35.80)
<b>10l</b>	CH <sub>3</sub>	Pr	166-168	48.72 (48.88)	7.67 (7.41)	35.51 (35.86)

[a] All compounds in Table III were prepared by Experimental Procedure D.

with *N*-bromosuccinimide (Procedure B in Experimental), allylic bromination occurred to yield **13** or **15**.



## EXPERIMENTAL

All melting points were taken on a Mel-Temp apparatus. Samples for elemental analysis were dried at 50-60° for 1-24 hours under high vacuum. The <sup>1</sup>H nmr measurements were obtained on a Varian Model HA-100 spectrometer, and chemical shift values are reported in δ downfield from tetramethylsilane internal standard.

### 2,3-Diamino-6-(trifluoromethyl)-4(3H)-pyrimidinone, **4a**. Procedure A.

A suspension of 40.8 g (0.30 mole) of aminoguanidine bicarbonate and 55.2 g (0.30 mole) of ethyl 4,4,4-trifluoroacetoacetate in 250 ml of normal butanol was refluxed for 5 hours and then cooled to ice bath temperature. Crystalline precipitate was collected, washed with 1-butanol, then with water and dried to give 26 g (45%) of **4a** as white crystals.

### 2,3-Diamino-5-bromo-6-(trifluoromethyl)-4(3H)-pyrimidinone (**4s**). Procedure B.

Typical Example for 5-Halopyrimidinones.

A solution of 3.0 g (0.0154 mole) of 2,3-diamino-6-(trifluoromethyl)-4(3H)-pyrimidinone (**4a**) and 2.74 g (0.0154 mole) of *N*-bromosuccinimide in 50 ml of glacial acetic acid was stirred at room temperature for 30 minutes (to one hour). The crystalline precipitate was collected, washed

with water and then recrystallized from hot water to give 2.37 g (56%) of **4s** as white crystals.

2,3-Diamino-6-methyl-4(3H)-pyrimidinone, (**4t**). Procedure C. Typical Example of 6-Alkyl (other than CF<sub>3</sub>)pyrimidinones.

To a suspension of 11.0 g (0.1 mole) of aminoguanidine hydrochloride in 100 ml absolute ethanol was added 5.4 g (0.1 mole) of sodium methoxide. Suspension was stirred for 30 minutes at room temperature and filtered. The ethyl acetoacetate (6.5 g, 0.05 mole) was added to the filtrate and solution stirred at room temperature for 3 hours (to 24 hours depending on the ester). Crystalline precipitate was collected, washed with ethanol and dried to give 2.83 g (40%) of **4t**.

3-Amino-2-hydrazino-6-methyl-4(3H)-pyrimidinone, (**10a**). Procedure D. Typical Example of the 2-Hydrazino Series.

To a suspension of 13.22 g (0.1 mole) of 95% *N,N'*-diaminoguanidine hydrochloride in 100 ml of absolute alcohol was added 5.4 g (0.1 mole) of sodium methoxide. Suspension stirred at room temperature for 30 minutes and filtered. To the filtrate was added 6.5 g (0.05 mole) of ethyl acetoacetate and the reaction mixture was stirred at room temperature for 30 minutes (to 24 hours depending on the ester). Crystalline precipitate was collected, washed with ethanol and dried to give 2.58 g (37%) of **10a**.

2,3-Diamino-6-phenyl-4(3H)-pyrimidinone, **4c** and **5a**. Typical example of aryl pyrimidinones.

A suspension of 40.8 g (0.30 mole) of aminoguanidine bicarbonate and 57.6 g (0.3 mole) of ethyl benzoylacetate in 250 ml normal butanol was refluxed for 5 hours and then cooled to room temperature. It was stored in the refrigerator overnight. Crystals filtered, washed with butanol, water and dried to give 13 g (22%) of white crystals; mp 195-198°.

*Anal.* Calcd. for C<sub>10</sub>H<sub>10</sub>N<sub>4</sub>O: C, 59.40; H, 4.98; N, 27.71. Found: C, 59.39; H, 5.02; N, 27.89.

The 3-aminotriazole **5a** was isolated pure from the above mixture by suspending 5 g of it in 50 ml of *N,N*-dimethylformamide and stirring for 30 minutes at room temperature. The white crystals filtered, washed with dimethylformamide and dried to give 1.75 g of the pure product **5a** (37%)

The *R<sub>f</sub>* values for the 2,3-diamino derivative, **4c**, and the triazole, **5a**, isomers were 0.4 and 0.06, respectively, using silica gel plates and chloroform/methanol (95:5) as the elution solvent.

3-Amino-5-(*o*-methylthiobenzoylmethyl)-1,2,3-triazole (**5b**).

Using the procedure described above, 7.0 g (0.051 moles) of aminoguanidine bicarbonate was reacted with 12.25 g (0.051 mole) of ethyl (*o*-methylthiobenzoyl)acetate. The solid that crystallized on cooling weighed 2.7 g, mp 205-207°. The structure was confirmed by mass spec-

trometry (*m/e* = 248).

*Anal.* Calcd. for C<sub>11</sub>H<sub>12</sub>N<sub>4</sub>SO: C, 53.21; H, 4.87; N, 22.56; S, 12.91. Found: C, 52.89; H, 4.62; N, 22.33; S, 12.59.

2-Methyl-5-(trifluoromethyl)-1,2,4-triazolo[1,5-*a*]pyrimidine-7-ol (**8**).

A solution of 2,2-diamino-6-(trifluoromethyl)-4(3H)-pyrimidinone (**4a**) (2.91 g), triethyl orthoacetate (10 ml) and glacial acetic acid (20 ml) was refluxed for 15-20 hours. Solution cooled to room temperature and white crystalline solid filtered, washed with acetic acid, ether and dried to afford 1.2 g of 2-methyl-5-(trifluoromethyl)-1,2,4-triazolo[1,5-*a*]pyrimidine-7-ol (**8**) (56%), mp 346-348°.

*Anal.* Calcd. for C<sub>7</sub>H<sub>5</sub>F<sub>3</sub>N<sub>4</sub>O: C, 38.54; H, 2.31; N, 25.68; F, 26.13. Found: C, 38.23; H, 2.29; N, 25.60; F, 26.08.

1,2-Diamino-1,6-dihydro-4-methyl-6-oxo-5-pyrimidinepropanoic Acid (**27**).

A solution of 2.8 g (0.01 mole) of 1,2-diamino-1,6-dihydro-4-methyl-6-oxo-5-pyrimidinepropanoic acid ethyl ester in 80 ml of 1*N* sodium hydroxide was stored at room temperature overnight. The pH of the solution was adjusted to 6.8 with 6*N* hydrochloric acid with cooling. A solid crystallized, yield 1.5 g, mp 121-122°.

*Anal.* Calcd. for C<sub>8</sub>H<sub>12</sub>N<sub>4</sub>O<sub>3</sub>: C, 45.28; H, 5.7; N, 26.4. Found: C, 45.58; H, 5.59; N, 26.0.

2,3,7,8-Tetraamino-3,5,8,10-tetrahydropyrimidine[4,5-*g*]quinazoline-4,9-dione (**26**).

A mixture of 12.8 g (0.05 mole) of diethyl 1,4-cyclohexanedione-2,5-dicarboxylate and 13.6 g (0.1 mole) of aminoguanidine bicarbonate in 100 ml of 1-butanol was heated at reflux for nine hours. The resulting solution was cooled to room temperature and a solid crystallized, yield, 17 g, mp, 152-155°.

*Anal.* Calcd. for C<sub>10</sub>H<sub>12</sub>N<sub>8</sub>O<sub>2</sub>: C, 43.38; H, 4.38; N, 40.56. Found: C, 42.99; H, 4.21; N, 40.32.

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