

Norimitsu Hamamichi\* [1] and Tadashi Miyasaka\*

School of Pharmaceutical Sciences, Showa University, Hatanodai 1-5-8, Shinagawa-ku,  
Tokyo 142 Japan

6-Cyanomethylene (**2**), which was prepared *via* **1** by substitution with malononitrile, has been catalytically hydrogenated to the  $\alpha$ -(aminomethylene)-9-(methoxymethyl)-9*H*-purine-6-acetonitrile (**3**) in good yield using *N,N*-dimethylformamide-benzene as solvent over Pd-C under medium pressure. Intermediate **3** was derived to aldehyde **5** by hydrolysis with acid or base. Substitution of **3** with amines gave the corresponding alkylamines **6** and **7**. Reaction of **3** with hydrazine and acetamidine hydrochloride gave pyrazole derivative **8** and pyrimidine derivative **9**, respectively.

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6-*N*-Substituted purine derivatives and 9-alkylpurine derivatives exhibit a number of interesting biological [2] and antiviral activities [3]. Therefore, in recent years much attention has been focused on the 6-*C*-substituted purine derivatives.

It is well known that cyanomethylene systems can be easily prepared in high yield by heteroarylation of the sodium salt of an active methylene containing cyano group with halogenated or methylsulfonated purine derivatives [4]. However, studies on the conversion of the cyano groups of cyanomethylene compounds into amino methylene functionalities have not been described because the solubility of these is limited.

As part of our studies on the synthesis of 6-*C*-substituted purine derivatives [5], in this report we describe a new convenient synthetic method of  $\alpha$ -(aminomethylene)-9-(methoxymethyl)-9*H*-purine-6-acetonitrile (**3**) *via* 6-cyanomethyl-

enepurine (**2**) using catalytic hydrogenation in a *N,N*-dimethylformamide-benzene solvent system and synthesis of purine derivatives *via* **3**.

The synthesis of 6-substituted enamionitrile purine **3** and its derivatives is summarized in Scheme 1. Substitution of 6-chloro-9-(methoxymethyl)purine (**1**) [6] with malononitrile in sodium hydride/*N,N*-dimethylformamide gave **2** in 90% yield, which was catalytically hydrogenated over 5% Pd-C in *N,N*-dimethylformamide-benzene under medium pressure (4.0 atm) to give **3** in 65% yield. When *N,N*-dimethylformamide only was used as reaction solvent, mainly starting material **3** was recovered. However, when **2** was subjected to catalytic hydrogenation over 5% Pd-C in methanol under ordinary pressure or medium hydrogen pressure, **3** was obtained in 8-30% yield. In this reaction the main products were over reduced. Therefore, it was found that benzene was necessary in the catalytic hy-

Scheme 1

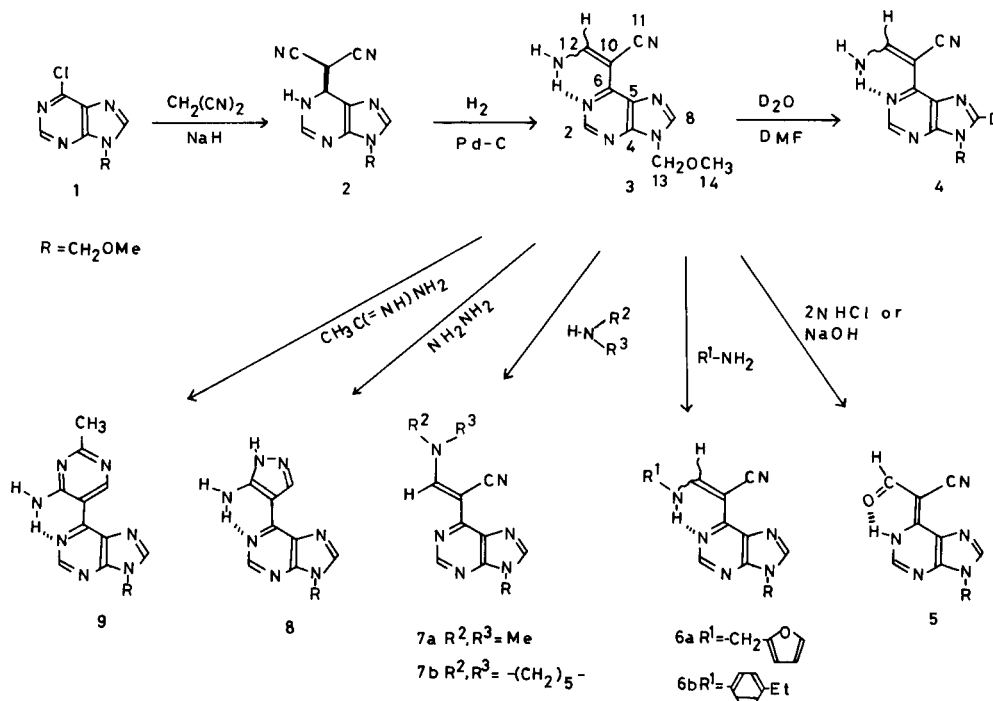


Table 1  
<sup>13</sup>C-NMR Data for **3** in DMSO-d<sub>6</sub>

Carbon	Chemical Shifts(ppm)	<sup>13</sup> C-H Coupling Constant (Hz)				
		C <sub>2</sub> H	C <sub>8</sub> H	C <sub>12</sub> H	CH <sub>2</sub>	CH <sub>3</sub>
2	151.4 ( <i>E</i> )	<sup>1</sup> J = 203.9				
	152.1 ( <i>Z</i> )	<sup>1</sup> J = 201.4				
4	150.0 ( <i>Z</i> )	*	*			
	150.4 ( <i>E</i> )	*	*			
5	126.1		<sup>3</sup> J = 12.2			
6	153.6 ( <i>Z</i> )	<sup>3</sup> J = 12.2		<sup>3</sup> J = 3.7		
	153.7 ( <i>E</i> )	<sup>3</sup> J = 12.2		*		
8	143.1 ( <i>E</i> )		<sup>1</sup> J = 212.4			<sup>3</sup> J = 4.9
	144.0 ( <i>Z</i> )		<sup>1</sup> J = 213.6			<sup>3</sup> J = 4.9
10	75.3 ( <i>E</i> )			<sup>2</sup> J = 3.7		
	78.9 ( <i>Z</i> )			<sup>2</sup> J = 3.7		
11	116.8 ( <i>Z</i> )			<sup>3</sup> J = 11.0		
	121.2 ( <i>E</i> )			<sup>3</sup> J = 4.9		
12	156.3 ( <i>E</i> )			<sup>1</sup> J = 169.6		
	157.7 ( <i>Z</i> )			<sup>1</sup> J = 168.4		
13	73.5		<sup>3</sup> J = 4.9			<sup>1</sup> J = 161.1
14	56.4					<sup>3</sup> J = 6.1
						<sup>1</sup> J = 142.8

[\*]: Data not clear.

drogenation of **2** in order to afford good yield of **3**. Structural confirmation of **3** was established by <sup>1</sup>H-nmr and <sup>13</sup>C-nmr spectroscopy. The <sup>1</sup>H-nmr spectrum of **3** showed two sets of vinyl proton signals ( $\delta$  7.71 and  $\delta$  9.28) as a doublet of doublets which collapsed to a singlet with deuterium oxide. The <sup>13</sup>C-nmr spectrum of **3** also showed the presence of two nitrile signals at  $\delta$  116.8 (<sup>3</sup>J<sub>CN,H</sub> = 11.0 Hz, *Z*) [7] as the major and at  $\delta$  121.2 (<sup>3</sup>J<sub>CN,H</sub> = 4.9 Hz, *E*) as the minor signal (Table I). In the <sup>1</sup>H-nmr spectrum of **3**, the C<sub>2</sub> and C<sub>8</sub> protons of the purine ring were distinguished by comparison with 8-deuterated **4** which was prepared by reaction of **3** with deuterium oxide. The deuterated position at C<sub>8</sub> was confirmed by long-range coupling in the <sup>13</sup>C-nmr spectrum with methylene of the methoxymethyl group at position 9. Generally, it is known that geometrical isomers (*E/Z*) are present in enaminoacetic acid derivatives [8]. Therefore, on the basis of these results the geometrical isomers of **3** exist in an enamino nitrile tautomeric equilibrium rather than the imino nitrile equilibrium. The ratio of geometrical isomers (*E/Z*) in deuterio-dimethyl sulfoxide (DMSO-d<sub>6</sub>) is 14:86 by comparing the integration of C<sub>2</sub>, C<sub>8</sub> and vinyl protons of each isomer in the <sup>1</sup>H-nmr spectrum.

Hydrolysis of **3** with acid or base gave aldehyde **5** in good yield. Substitution of **3** with furfuryl amine and *p*-ethylaniline by heating gave the corresponding *N*-substituted amine (**6a** and **6b**) in 91% yields. The <sup>1</sup>H-nmr spectrum of **6a** showed the presence of two sets of vinyl protons at  $\delta$  7.92 (*E*), and at  $\delta$  9.33 (*Z*). The ratio of geometrical isomer (*E/Z*) in DMSO-d<sub>6</sub> was 29:71. Also, the ratio (*E/Z*) of

**6b** in DMSO-d<sub>6</sub> was 19:81. Substitution of **3** with secondary amines gave **7a** in 83% yield and **7b** in 87% yield, respectively. The <sup>1</sup>H-nmr spectrum of **7a** showed vinyl proton at  $\delta$  9.24 (s, 1H). The vinyl proton in **7b** was at  $\delta$  9.25 and was a singlet as well. This indicates that the geometrical isomer of the enamine moiety was *Z* form only. Reaction of **3** with hydrazine or acetamidine hydrochloride gave the pyrazole (**8**) in 73% yield, and the pyrimidine (**9**) in 63% yield, respectively.

In conclusion, the present work demonstrates that catalytic hydrogenation of 6-cyanomethylenepurine (**2**) to enamino nitrile purine (**3**) in *N,N*-dimethylformamide-benzene is highly chemoselective because the enamine moiety and purine ring are unaffected. Enamino nitrile purine **3** is also shown to be a versatile compound for the preparation of 6-*C*-substituted purine alkyl side chains, pyrazole and pyrimidine rings.

## EXPERIMENTAL

All melting points were determined on a Yamato capillary melting point apparatus, MP-21, and are uncorrected. The ir spectra (potassium bromide) were taken on a JASCO Model A-102 spectrometer. The uv spectra were measured using a Hitachi Model EPS-3T spectrometer. The <sup>1</sup>H-nmr and <sup>13</sup>C-nmr spectra were recorded on JEOL JNM-FX100 and JEOL-GX spectrometers using tetramethylsilane as an internal standard. For the resonance signals the following abbreviations are used: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad; and dd, doublet of doublets. The mass spectra (ms) were measured by a JEOL JMS-D300 spectrometer using a direct inlet system; ionizing potential at 70 eV. Column chromatography was performed on sili-

ca gel (Merck 60) or neutral alumina (Woelm).

[9-(Methoxymethyl)-9H-purin-6-yl]propanedinitrile (**2**).

To a cold (0-5°) stirred suspension of 60% sodium hydride (3.44 g, 0.086 mole) in dry *N,N*-dimethylformamide (50 ml) was added dropwise a solution of malononitrile (6.070 g, 0.09 mole) in dry *N,N*-dimethylformamide (7 ml) over a period of 30 minutes, and the solution was stirred for 30 minutes at room temperature under argon. After this time, a solution of **1** (3.970 g, 0.02 mole) in dry *N,N*-dimethylformamide (26 ml) was added to the solution and the solution was stirred for 18 hours at the same temperature. After cooling, the solution was diluted with water (70 ml) and acidified to pH 3 with 10% hydrochloric acid. The precipitate was filtered and recrystallized from *N,N*-dimethylformamide-ethanol to give **2** (4.350 g, 90%) as colorless needles, mp 270-273° dec; ir: 3230 (NH), 3100 (NH), 2200 (CN), 2180 (CN)  $\text{cm}^{-1}$ ; uv (methanol):  $\lambda$  max ( $\epsilon$ ) 211 (16900), 235 (10200), 335 (34600) nm;  $^1\text{H-nmr}$  (DMSO- $d_6$ ):  $\delta$  3.29 (s, 3H, OMe), 5.54 (s, 2H, CH<sub>2</sub>), 8.23 (s, 1H, C<sub>2</sub>H), 8.53 (s, 1H, C<sub>8</sub>H); ms: *m/z* 228 ( $M^+$ ), 198.

*Anal.* Calcd. for C<sub>10</sub>H<sub>9</sub>N<sub>5</sub>O: C, 52.63; H, 3.53; N, 36.83. Found: C, 52.55; H, 3.58; N, 36.88.

$\alpha$ -(Aminomethylene)-9-(methoxymethyl)-9H-purine-6-acetonitrile (**3**).

A solution of **2** (2.0 g, 8.76 mmoles) in *N,N*-dimethylformamide-benzene (1:1 v/v, 240 ml) was hydrogenated over 5% Pd-C (1.0 g) at room temperature for 40 hours at 4 atm. The catalyst was filtered off, and the solvent was evaporated *in vacuo*. The residue was dissolved in methanol-dichloromethane (1:9 v/v, 300 ml), and the solution passed through a column of neutral alumina (60 g) and evaporated *in vacuo*. The residue was recrystallized from methanol-chloroform to give **3** (1.30 g, 65%) as colorless needles, mp 201-203° dec; ir: 3360 (NH), 3100 (NH), 2148 (CN)  $\text{cm}^{-1}$ ; uv (methanol):  $\lambda$  max ( $\epsilon$ ) 232 (15100), 239 (14700), 256 (6910), 331 (27500), 342 (23900) nm;  $^1\text{H-nmr}$  (DMSO- $d_6$ ):  $\delta$  3.29 (s, 3H, OMe), 5.57 (s, 2H, CH<sub>2</sub>), 7.71 (dd, 0.14H, *J* = 15 Hz, *J* = 8 Hz, C=CH, *E*), 8.00-8.42 (m, 1.70H, NH, *Z*, exchangeable with deuterium oxide), 8.56 (s, 0.86H, C<sub>8</sub>H, *Z*), 8.63 (s, 1H, C<sub>2</sub>H, *Z* and C<sub>8</sub>H, *E*), 8.72 (s, 0.14H, C<sub>2</sub>H, *E*), 9.28 (dd, 0.86H, *J* = 15 Hz, *J* = 8 Hz, C=CH, *Z*), 10.63 (d, 0.14H, *J* = 15 Hz, NH, *E*, exchangeable with deuterium oxide); ms: *m/z* 230 ( $M^+$ ), 200.

*Anal.* Calcd. for C<sub>10</sub>H<sub>10</sub>N<sub>6</sub>O: C, 52.17; H, 4.38; N, 36.51. Found: C, 52.45; H, 4.29; N, 36.61.

$\alpha$ -(Aminomethylene)-8-deuterio-9-(methoxymethyl)-9H-purine-6-acetonitrile (**4**).

A solution of **3** (0.2 g, 0.86 mmole) in deuterium oxide-*N,N*-dimethylformamide (6:1 v/v, 7 ml) was heated at 100° for 14 hours with stirring. After cooling, the precipitate was recrystallized from methanol-hexane to give **4** (0.170 g, 85%) as colorless needles, mp 195-198° dec; ir: 3375 (NH), 2200 (CN), 1672  $\text{cm}^{-1}$ ;  $^1\text{H-nmr}$  (DMSO- $d_6$ ):  $\delta$  3.29 (s, 3H, OMe), 5.57 (s, 2H, CH<sub>2</sub>), 7.71 (dd, 0.14H, C=CH, *E*), 8.00-8.42 (m, 1.7H, NH), 8.63 (s, 0.86H, C<sub>2</sub>H, *Z*), 8.72 (s, 0.14H, C<sub>2</sub>H, *E*), 9.28 (dd, 0.86H, C=CH, *Z*), 10.65 (m, 0.14H, NH, *E*); ms: *m/z* 231.0998 ( $M^+$ , Calcd: C<sub>10</sub>H<sub>9</sub>N<sub>6</sub>O<sub>1</sub>D<sub>1</sub>, 231.0978).

9-(Methoxymethyl)-9H-purine-6-malonaldehydonitrile (**5**).

[Method A] A solution of **3** (0.5 g, 2.17 mmoles) in 2*N* hydrochloric acid (5 ml) was stirred for 48 hours at room temperature. The solution was adjusted to pH 3 with saturated sodium bicar-

bonate, and the solution was allowed to stand overnight in an ice-bath. The precipitate was filtered and recrystallized from *N,N*-dimethylformamide-methanol to give **5** (0.395 g, 79%) as colorless needles, mp 209-210°; ir: 3160 (NH), 2200 (CN), 1620  $\text{cm}^{-1}$ ;  $^1\text{H-nmr}$  (DMSO- $d_6$ ):  $\delta$  3.35 (s, 3H, OMe), 5.61 (s, 2H, CH<sub>2</sub>), 8.66 (s, 2H, C<sub>2</sub>H, and C<sub>8</sub>H), 9.33 (broad s, 1H, CHO); ms: *m/z* 231 ( $M^+$ ), 203.

*Anal.* Calcd. for C<sub>10</sub>H<sub>9</sub>N<sub>5</sub>O<sub>2</sub>: C, 51.94; H, 3.92; N, 30.29. Found: C, 52.04; H, 3.78; N, 30.20.

[Method B] To a solution of **3** (0.1 g, 0.43 mmole) in dimethyl sulfoxide (1 ml) was added dropwise a solution of sodium hydroxide (78.3 mg) in water (1 ml) over a period of 5 minutes and the solution was stirred for 24 hours. The solution was adjusted to pH 2 with 2*N* hydrochloric acid and allowed to stand overnight. The precipitate was filtered and recrystallized from *N,N*-dimethylformamide-ethanol to give **5** (70 mg, 70%). The compound was identical (mp, ir, and  $^1\text{H-nmr}$ ) with an authentic sample described above.

$\alpha$ -(Furfurylaminomethylene)-9-(methoxymethyl)-9H-purine-6-acetonitrile (**6a**).

A solution of **3** (0.30 g, 1.30 mmoles) and furfurylamine (0.378 g, 3.89 mmoles) in ethanol (8 ml) was refluxed for 1.5 hours. After cooling, the precipitate was filtered and recrystallized from methanol-hexane to give **6a** (0.368 g, 91%) as colorless needles, mp 167-168° dec; ir: 3280 (NH), 3232 (NH), 220 (CN)  $\text{cm}^{-1}$ ; uv (methanol):  $\lambda$  max ( $\epsilon$ ) 235 (15400), 258 (8510), 341 (31600), 351 (30100) nm;  $^1\text{H-nmr}$  (DMSO- $d_6$ ):  $\delta$  3.28 (s, 3H, OMe), 4.56-4.74 (m, 2H, CH<sub>2</sub>), 5.57 (s, 2H, CH<sub>2</sub>O), 6.45 (d, 2H, *J* = 2 Hz), 7.66 (s, 1H), 7.92 (d, 0.29H, *J* = 13 Hz, C=CH, *E*), 8.56 (s, 0.71H, C<sub>8</sub>H, *Z*), 8.62 (s, 1H, C<sub>8</sub>H, *E*, and C<sub>2</sub>H, *Z*), 8.71 (s, 0.29H, C<sub>2</sub>H, *E*), 9.33 (s, 0.71H, C=CH, *Z*), 11.18-11.42 (m, 0.29H, NH, *E*, exchangeable with deuterium oxide); ms: *m/z* 310 ( $M^+$ ).

*Anal.* Calcd. for C<sub>15</sub>H<sub>14</sub>N<sub>6</sub>O<sub>2</sub>: C, 58.05; H, 4.55; N, 27.09. Found: C, 58.26; H, 4.47; N, 27.22.

$\alpha$ -(*p*-Ethylphenylaminomethylene)-9-(methoxymethyl)-9H-purine-6-acetonitrile (**6b**).

A solution of **3** (0.230 g, 0.001 mole) and *p*-ethylaniline (0.363 g, 0.003 mole) in ethanol (6 ml) was refluxed with stirring for 7 hours. After cooling, the precipitate was filtered and recrystallized from chloroform-ethanol to give **6b** (0.304 g, 91%) as yellow needles, mp 188-189°; ir: 2205 (CN), 1632  $\text{cm}^{-1}$ ; uv (methanol):  $\lambda$  max ( $\epsilon$ ) 241 (16900), 263 (15100), 296 (2950), 374 (36300);  $^1\text{H-nmr}$  (DMSO- $d_6$ ):  $\delta$  1.19 (t, 3H, *J* = 7 Hz), 2.64 (q, 2H, *J* = 7 Hz), 3.30 (s, 3H, OMe), 5.60, 5.65 (2s, H, CH<sub>2</sub>), 7.28-7.49 (m, 4H, phenyl-H), 8.44 (d, 0.19H, *J* = 13 Hz, C=CH, *E*), 8.65 (s, 0.81H, C<sub>8</sub>H, *E*), 8.71 (s, 0.81H, C<sub>2</sub>H, *Z*), 8.75 (s, 0.19H, C<sub>8</sub>H, *E*), 8.89 (s, 0.19H, C<sub>2</sub>H, *E*), 9.86 (s, 0.81H, C=CH, *Z*), 10.67 (broad s, 0.81H, NH, *Z*), 13.18 (d, 0.19H, *J* = 13 Hz, NH, *E*); ms: *m/z* 334 ( $M^+$ ).

*Anal.* Calcd. for C<sub>18</sub>H<sub>18</sub>N<sub>6</sub>O: C, 64.65; H, 5.43; N, 25.14. Found: C, 64.63; H, 5.42; N, 25.10.

(*Z*)- $\alpha$ -(Dimethylaminomethylene)-9-(methoxymethyl)-9H-purine-6-acetonitrile (**7a**).

A solution of **3** (0.30 g, 1.3 mmoles) in 10% w/w ethanolic dimethylamine (8 ml) was heated at 85° for 2 hours in a sealed tube. After cooling, the precipitate was filtered and recrystallized from ethyl acetate-hexane to give **7a** (0.198 g, 83%) as colorless needles, mp 182-183°; ir: 2188 (CN), 1630  $\text{cm}^{-1}$ ; uv (methanol):  $\lambda$  max ( $\epsilon$ ) 242 (16500), 261 (9550), 270 (8310), 342.5 (46700), 350

(43600) nm;  $^1\text{H-nmr}$  ( $\text{DMSO-d}_6$ ):  $\delta$  3.29 (s, 3H, OMe), 3.34 (s, 6H, 2  $\times$  Me), 5.58 (s, 2H,  $\text{CH}_2$ ), 8.57 (s, 1H,  $\text{C}_8\text{H}$ ), 8.63 (s, 1H,  $\text{C}_2\text{H}$ ), 9.24 (s, 1H, C=CH); ms:  $m/z$  258 ( $\text{M}^+$ ).

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{14}\text{N}_6\text{O}\cdot\frac{1}{2}\text{H}_2\text{O}$ : C, 55.42; H, 5.38; N, 32.31. Found: C, 55.54; H, 5.48; N, 32.19.

(*Z*)- $\alpha$ -(Piperidinoaminomethylene)-9-(methoxymethyl)-9*H*-purine-6-acetonitrile (**7b**).

A solution of **3** (0.30 g, 1.3 mmole) and piperidine (0.332 g, 3.90 mmole) in ethanol (8 ml) was refluxed for 2 hours. After cooling, the precipitate was filtered and recrystallized from methanol-hexane to give **7b** (0.388 g, 87%) as colorless needles, mp 205-206 $^\circ$ ; ir: 2200 (CN), 1630  $\text{cm}^{-1}$ ; uv (methanol):  $\lambda$  max ( $\epsilon$ ) 242 (16200), 263 (9120), 271 (7940), 345 (36300), 350 (35400) nm;  $^1\text{H-nmr}$  ( $\text{DMSO-d}_6$ ):  $\delta$  1.70 (broad s, 6H), 3.28 (s, 3H, OMe), 3.57-4.25 (m, 4H), 5.58 (s, 2H,  $\text{CH}_2$ ), 8.57 (s, 1H,  $\text{C}_8\text{H}$ ), 8.62 (s, 1H,  $\text{C}_2\text{H}$ ), 9.25 (s, 1H, C=CH); ms:  $m/z$  298 ( $\text{M}^+$ ).

*Anal.* Calcd. for  $\text{C}_{15}\text{H}_{18}\text{N}_6\text{O}$ : C, 60.38; H, 6.08; N, 28.17. Found: C, 60.48; H, 6.13; N, 27.88.

9-(Methoxymethyl)-9*H*-6-(3-amino-4-pyrazolyl)purine (**8**).

A solution of **3** (0.10 g, 0.43 mmole) and hydrazine hydrate (65 mg, 1.30 mmole) in ethanol (3 ml) was refluxed for 5 hours. After cooling, the solution was evaporated *in vacuo*. The residue was recrystallized from methanol-hexane to give **8** (78 mg, 73%) as colorless needles, mp 178-179 $^\circ$ ; ir: 3380, 3255 (NH), 1620  $\text{cm}^{-1}$ ; uv (methanol):  $\lambda$  max ( $\epsilon$ ) 205 (14100), 216 (12800), 360 (3460), 329 (17300) nm;  $^1\text{H-nmr}$  ( $\text{DMSO-d}_6$ ):  $\delta$  3.31 (s, 3H, OMe), 5.59 (s, 2H,  $\text{CH}_2$ ), 6.70 (s, 2H, NH, exchangeable with deuterium oxide), 8.40 (s, 1H), 8.58 (s, 1H), 8.71 (s, 1H), 12.03 (broad s, 1H, exchangeable with deuterium oxide); ms:  $m/z$  245 ( $\text{M}^+$ ), 215.

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_{11}\text{N}_7\text{O}$ : C, 48.97; H, 4.53; N, 39.98. Found: C, 49.21; H, 4.66; N, 39.88.

9-(Methoxymethyl)-9*H*-6-(4-amino-2-methyl-5-pyrimidinyl)purine (**9**).

To a solution of sodium propoxide in 1-propanol [prepared from sodium (0.138 g, 4.0 mg-atom) and absolute 1-propanol (3.5 ml)] was added acetamidine hydrochloride (0.378 g, 4.0 mmole) at room temperature under argon. The solution was stirred for 30 minutes at the same temperature. After this time a solution of **3** (0.186 g, 0.8 mmole) in *N,N*-dimethylformamide (7 ml) was added to the solution, and heated at 120 $^\circ$  for 5.5 hours. After cooling, the solution was diluted with water (20 ml) and allowed to stand overnight. The precipitate was filtered and recrystallized from methanol to give **9** (0.138 g, 63%) as colorless needles, mp 232-233 $^\circ$  dec; ir: 3268 (NH), 1625, 1570  $\text{cm}^{-1}$ ; uv (methanol):  $\lambda$  max ( $\epsilon$ ) 212 (31600), 264 (8910), 272 (8310), 282 (6760), 336 (16500), 348 (15100) nm;  $^1\text{H-nmr}$  ( $\text{DMSO-d}_6$ ):  $\delta$  2.44 (s, 3H, Me), 3.33 (s, 3H, OMe), 5.67 (s, 2H,  $\text{CH}_2$ ), 7.94 (broad s, 1H, NH, exchangeable with deuterium oxide), 8.83 (s, 1H,  $\text{C}_8\text{H}$ ), 9.01 (s, 1H,  $\text{C}_2\text{H}$ ), 9.92 (broad s, 1H, NH, exchangeable with deuterium oxide), 10.05 (s, 1H, pyridine-H); ms:  $m/z$  271 ( $\text{M}^+$ ).

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{13}\text{N}_7\text{O}$ : C, 53.14; H, 4.83; N, 36.14. Found: C, 53.01; H, 4.79; N, 36.44.

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