

Experimental Section

Instrumentation. Spectra were measured with Bruker AMX-300 NMR and Perkin-Elmer 1600 series FTIR spectrometers. Gas chromatography was performed on a Hewlett-Packard 5790A apparatus with a flame ionization detector using a Spectra Physics SP 4400 work station and a 30 m SE-30 "Econo-Cap" column (Alltech) with ID = 0.25 mm and a film thickness of 0.25 μm .

Sodium 2-Pyridine Diazotate (1a). Using the method of Baker, *et al.*,¹ a suspension of sodium amide (0.82 g, 10.5 mmol) (in a toluene suspension, 50/50, w/w) was added to a solution of 2-aminopyridine (1.00 g, 10.5 mmol) in 13 mL of THF under nitrogen with stirring at 25 °C. After 35 min, a solution of butyl nitrite (1.23 mL, 1.08 g, 10.5 mmol) in 1.5 mL of THF was added dropwise; the reaction mixture became yellow in color. After 15 min, a light yellow precipitate formed. The mixture was stirred for 15 h at 25 °C, then filtered and the precipitate was washed with THF (3 x 10 mL) to give 1.10 g of product. It was washed with excess ether and dried at 0.1 Torr to give 0.58 g (4.0 mmol, 38%) of diazotate **1a**. In a parallel run, the crude diazotate (1.01 g) was added to 17 ml of DMF with stirring. After 20 min, half of it had dissolved. The mixture was filtered and to the filtrate was added 18 mL of ether at 25 °C. A precipitate was formed when the solution was cooled to 0 °C. This solid was filtered, washed with 1 x 3 mL of ether and dried at 0.1 Torr to produce 225 mg (1.55 mmol, 16%) of compound (**1a**): mp 170 °C dec; ¹H NMR (DMSO-*d*₆) δ 8.23 (d, *J* = 4.0 Hz, 1H), 7.51 (t, *J* = 7.0 Hz, 1H), 7.35 (d, *J* = 7.0 Hz, 1H), 6.86 (t, *J* = 6.0 Hz, 1H). The recrystallized sample contains 2% of DMF [¹H NMR (DMSO-*d*₆) δ 7.95 (s, 1H), 2.92 (s, 3H), 2.76 (s, 3H)]; IR (KBr) 1590, 1570, 1431, 1345, 1295, 1255 cm^{-1} ; *R*_f = 0.1 (Alumina, CH₃OH) (a yellow color was produced at that *R*_f when the plate was sprayed with phenol and heated to 80 °C).

Sodium Pyrazine Diazotate (1b). Using the method of Baker, *et al.*,¹ a suspension of sodium amide (1.6 g, 21 mmol) (in a toluene suspension, 50/50, w/w) was added to a stirred solution of 2-aminopyrazine (2.0 g, 21 mmol) in 25 mL of THF under

nitrogen at 25 °C. After 35 min, a solution of butyl nitrite (2.46 ml, 2.13 g, 21 mmol) in 5 mL of THF was added dropwise and stirring was continued for 15 h at 25 °C. The yellow precipitate that formed was filtered, washed with ether (3 x 10 mL) and dried at 0.1 Torr to give 2.4 g (83%) of crude diazotate. The crude material (494 mg) was mixed with 13 mL of absolute methanol at 25 °C, the mixture was heated to 40 °C, then filtered to remove a small amount of solid. Ether (11 mL) was added slowly and the resulting precipitate was filtered. The solid was washed with ether (3 x 3 mL), then dried at 0.1 Torr (40 °C) to produce diazotate **1b** as a yellow solid (260 mg, 1.78 mmol, 43%): mp 235 °C dec; ¹H NMR (DMSO-*d*₆) δ 8.60 (d, *J* = 1.5 Hz, 1H), 8.22 (dd, *J* = 2.7 Hz, *J* = 1.5 Hz, 1H), 8.04 (d, *J* = 2.6 Hz, 1H) [lit.¹ 8.60 (d, *J* = 1.4 Hz), 8.23 (dd, *J* = 2.5 Hz), 8.06 (d, *J* = 2.5 Hz)]; IR (KBr) 1470, 1350, 1275, 1231, 875 cm⁻¹; *R*_f = 0.7 (silica gel, CH₃OH; the TLC plate was sprayed with phenol, then heated for 2 min to 80 °C to produce a brown color at *R*_f = 0.7). The diazotate, following recrystallization from MeOH, produced 96-97% of the theoretical amount of nitrogen when treated with an excess of acetic acid.

Sodium 2-Pyrimidine Diazotate (1c). Using the method of Baker, *et al.*,¹ a suspension of sodium amide (1.56 g, 20.0 mmol) (in a toluene suspension, 50/50, w/w) was added to a solution of 2-aminopyrimidine (1.90 g, 20.0 mmol) in 25 mL of THF under nitrogen with stirring. The mixture turned milky with some precipitate, and then butyl nitrite (2.26 g, 2.56 mL, 22.0 mmol) was added. After 15 h at 25 °C, the yellow precipitate that formed was filtered, washed, and dried at 0.1 Torr to give 2.28 g of product. To 1.03 g of this crude product was added 27 mL of ethanol and the mixture was heated to 40 °C. A small amount of solid remained, which was removed by filtration and a few drops of methanol were added to the filtrate to achieve a clear solution. Ether (25 mL) was added; the precipitate that formed was filtered, washed with ether (2 x 3 mL) and dried at 0.1 Torr to give 296 mg (2.00 mmol, 22%) of compound **1c** as a yellow solid: mp >250 °C; ¹H NMR (DMSO-*d*₆) δ 8.49 (d, *J* = 4.7 Hz, 2H), 6.94 (t, *J* = 4.7 Hz, 1H); IR (KBr) 1652, 1417, 1357, 1281, 1251, 812 cm⁻¹; *R*_f = 0.7 (silica gel, CH₃OH; the TLC plate

was sprayed with phenol and heated at 80 °C for 2 min to produce a pink color at $R_f = 0.7$); Anal. Calcd for $C_4H_3N_4ONa \cdot 0.60 NaHCO_3$: C, 28.11; H, 1.83. Found: C 28.33, H, 2.01. This diazotate produced 69-75% of the theoretical amount of nitrogen when it was treated with an excess of acetic acid. A sample of the diazotate, after recrystallization (as described above) produced 87-91% of the theoretical amount of nitrogen when treated with an excess of acetic acid.

Sodium 9-Propyl-6-purine Diazotate (10a). The method of Bunton, *et al.*,² was followed with modifications (incremental addition of the sodium amide, doubling its quantity and halving the reaction time). Sodium amide (0.22 g, 5.6 mmol obtained from a 50% by wt. suspension in toluene, which was evaporated to dryness in a nitrogen stream) was added as a powder to a stirred solution of 9-propyladenine (1.0 g, 5.6 mmol) in 160 mL of dry THF at 25 °C. After 60 min, butyl nitrite (1.16 g, 11.2 mmol) was added. The mixture was stirred at room temperature under nitrogen. Residual 9-propyladenine ($R_f = 0.18$) in the reaction mixture was detected *via* TLC [silica gel, ethanol/ $CHCl_3$ (1/9, v/v)]. After a reaction time of 96 h, additional $NaNH_2$ (0.11g, 2.8 mmol) was added. The mixture was stirred for 30 min, then a further 0.58 g (5.6 mmol) of butyl nitrite was added and the mixture was stirred as before. After 8 days (TLC still showed trace amounts of 9-propyladenine in the reaction mixture) a yellow/green flocculent precipitate was collected by centrifugation; after washing with THF and drying at 0.1 Torr, 1.08 g of a yellow/green solid was obtained. The solid was mixed with 2.0 mL of DMF and 200 mg of a white insoluble material [sodium carbonate: mp >300 °C; IR (KBr) 1443 (br) cm^{-1} (lit.³ 1450-1410) the IR spectrum matched that of an authentic (Baker Analyzed) sample] was removed by filtration. Ether (5.0 mL) was added to the liquid phase, resulting in the formation of a yellow/brown precipitate. After storage at -25 °C for 3 h, the mother liquor was decanted and the precipitate was washed with dry THF. After decanting the solvent, the solid was dried at 0.1 Torr to afford 0.64 g (2.8 mmol, 50%) of sodium 9-propyl-6-purine diazotate (**10a**): $R_f = 0.74$ [Al_2O_3 , EtOH/ NH_4OH (8/2, v/v); yellow spot stained brick red with 5%

phenol in ether]; mp 149-151 °C dec; ^1H NMR ($\text{DMSO-}d_6$), δ 8.46 (s, 1H, H-2), 8.25 (s, 1H, H-8), 4.18 (t, $J = 7.1$ Hz, 2H), 1.84 (m, 2H), 0.86 (t, $J = 7.3$ Hz, 3H). The ^1H NMR spectrum of a CDCl_3 solution at 25 °C showed a series of unresolved broad peaks at the expected chemical shifts, possibly due to aggregation. Changing such spectrometer parameters as the pulse width and the acquisition time failed to sharpen the peaks. The addition of EDTA (disodium salt, dihydrate) to the NMR sample also failed in this regard. A usable spectrum was obtained when data was acquired at 65 °C: ^1H NMR (CDCl_3 , at 65 °C) δ 8.04 (s, 1H, H-2), 7.82 (s, 1H, H-8), 3.70 (br s, 2H), 1.49 (br s, 2H), 0.61 (br s, 3H); UV (0.1M formate buffer, pH 7.38) λ_{max} 304 nm (lit.² 304); IR (KBr) 3420, 2966, 1598, 1384, 1245, 918, 842, 807, 647 cm^{-1} . The diazotate produced 73-75% of the theoretical amount of nitrogen when treated with an excess of acetic acid.

2-Phenylpyridine (7a) and 2-Acetoxypyridine (6a). Acetic acid (11.4 μL , 12 mg, 0.20 mmol) was added to a stirred suspension of sodium 2-pyridine diazotate (14.5 mg, 0.100 mmol) in 0.5 mL of benzene. After 5 min, bubbling ceased. The mixture was evaporated to dryness at 0.1 Torr and the products were separated by TLC [silica gel, ether/trichloroethylene (1/1, v/v)] and eluted with ether from the plate to give: (A) **2-phenylpyridine (7a)**, with $R_f = 0.54$; ^1H NMR (CDCl_3) δ 8.70 (d, $J = 4.5$ Hz, 1H), 7.99 (d, $J = 8.1$ Hz, 2H), 7.79-7.71 (m, 2H), 7.51-7.41 (m, 3H), 7.26-7.22 (m, 1H), [lit.⁴ δ 8.8-8.6 (m, 1H), 8.1-7.9 (m, 2H), 7.8-7.6 (m, 2H), 7.6-7.1 (m, 4H) in CDCl_3]; ^1H NMR (C_6D_6) δ 8.61 (d, $J = 4.8$ Hz, 1H), 8.14 (d, $J = 8.4$ Hz, 2H), 7.32-7.06 (m, 4H), 6.63 (t, $J = 5.9$ Hz, 1H), (B) **2-Acetoxypyridine (6a)**, with $R_f = 0.40$; ^1H NMR (CDCl_3) δ 8.42 (d, $J = 4.9$ Hz, 1H), 7.80 (td, $J = 7.4$ Hz, $J = 2.4$ Hz, 1H), 7.24 (m, 1H), 7.10 (dd, $J_1 = 8.2$ Hz, $J_2 = 0.8$ Hz, 1H), 2.35 (s, 3H) [lit.⁵ 8.44 (m, $J = 5$ Hz, $J = 2$ Hz, 1H), 7.81 (m, $J_1 = 8$ Hz, $J_2 = 2$ Hz, 1H), 7.29 (m, $J_1 = 5$ Hz, $J_2 = 2$ Hz, 1H), 7.10 (d, $J = 8$ Hz, 1H), 2.31 (s, 3H)]; ^1H NMR (C_6D_6) δ 8.14 (d, $J = 4.7$ Hz, 1H), 6.97 (t, $J = 6.1$ Hz, 1H), 6.69 (d, $J = 8.1$ Hz, 1H), 6.46 (t, $J = 4.9$ Hz, 1H), 1.67 (s, 3H).

2-Hydroxypyridine (5a) (Aldrich Chemical Company): ^1H NMR (CDCl_3) 7.52-7.46 (m, 1H), 7.41-7.38 (m, 1 H), 6.60 (d, $J = 8.0$ Hz, 1H), 6.30 (td, $J_1 = 6.5$ Hz, $J_2 = 1.1$ Hz, 1H)]; ^1H NMR (C_6D_6) δ 6.71-6.65 (m, 2H), 6.47 (dd, $J_1 = 10$ Hz, $J_2 = 1.1$ Hz, 1H), 5.42 (td, $J_1 = 6.5$ Hz, $J_2 = 1.1$ Hz, 1H).

2-Phenylpyrazine (7b). Acetic acid (17.8 μL , 0.309 mmol) was added to sodium 2-pyridine diazotate (15.0 mg, 0.103 mmol) in 1 ml of benzene at 25 °C with stirring. Gas evolution was observed for 30 min. The mixture was evaporated to dryness at 0.1 Torr. TLC separation of the reaction products [silica gel, hexane/ethyl acetate, 1/1 (v/v)] and extracting the band at $R_f = 0.33$ with ether afforded 2-phenylpyrazine: ^1H NMR (CDCl_3) δ 9.04 (d, $J = 1.5$ Hz, 1H), 8.64 (dd, $J = 2.5$ Hz, $J = 1.5$ Hz, 1H), 8.52 (d, $J = 2.5$ Hz, 1H), 8.04-8.00 (m, 2H), 7.53 - 7.50 (m, 3 H) [lit.⁶ ^1H NMR (CDCl_3) δ 9.10-9.00 (d, $J = 1.4$ Hz, 1H), 8.65 (dd, $J = 2.4$ Hz, $J = 1.4$ Hz, 1H), 8.50 (d, $J = 2.4$ Hz, 1H), 8.25-7.90 (m, 2H), 7.65-7.35 (m, 3H)]; ^1H NMR (C_6D_6) δ 8.82 (t, 1H), 8.09 (m, 1H), 8.03 (m, 1H), 7.94-7.90 (m, 2H), 7.16 (m, 3H); MS m/z (rel intensity) 156 (M^+ , 100), 129 (7), 103 (53) [lit.⁶ 156 (M^+ , 100), 129 (8), 103 (75)].

2-Phenylpyrimidine (7c). A literature procedure⁷ was used. Butyl nitrite (3.99 ml, 3.46 g, 33.6 mmol) was added to a solution of 2-aminopyrimidine (951 mg, 10.0 mmol) in 40 mL of benzene at 70 °C with stirring. A precipitate formed and the mixture turned orange in color. It was then stirred for 4 h at 70 °C; a black tar formed and the solution became red in color. The mixture was treated with 20 mL of 1N sodium hydroxide with stirring for 30 min; the aqueous phase became dark in color. The aqueous layer was separated and extracted with 10 mL of benzene. The organic layers were combined, dried with Na_2SO_4 , evaporated, and dried at 0.1 Torr to produce 472 mg (30%) of crude product as a yellow oil. It was purified by distillation at 60 °C and 0.2 Torr to produce a colorless oil (82 mg, 0.50 mmol, 5%): ^1H NMR (CDCl_3) δ 8.81 (d, $J = 4.9$ Hz, 2H), 8.45-8.42 (m, 2H), 7.51-7.49 (m, 3H), 7.18 (t, $J = 4.9$ Hz, 1H) [lit.⁸ (CDCl_3) δ 8.78 (d, 2H), 8.52 (m, 2H), 7.52 (m, 3H), 7.10 (t, 1 H)]; ^1H NMR (C_6D_6) δ 8.92-8.89 (m, 2H), 8.25 (d, J

= 4.8 Hz, 2H), 7.32-7.16 (m, 3H), 6.17 (t, $J = 4.8$ Hz, 1H); IR (KBr) 1566, 1555, 1417, 825, 809, 744, 688 cm^{-1} .

2-Acetoxypyrimidine (6c). The title compound was prepared as described by Krchnak, *et al.*⁹ Sodium nitrite (0.276 g, 4.00 mmol) was added to a solution of 2-aminopyrimidine (190 mg, 2.00 mmol) in glacial acetic acid (6 mL) portionwise over 30 min at 15 °C with stirring. The mixture, after being stirred for 15 min, was cooled to 0 °C and diluted with 60 mL of dichloromethane. Saturated aqueous potassium carbonate (30 mL) was added to pH ~ 10. The organic layer was separated, dried with Na_2SO_4 , filtered, concentrated, and the product was dried at 0.1 Torr to give 157 mg (0.114 mmol, 57%) of compound **6c** as a yellow oil: ^1H NMR (CDCl_3) δ 8.76 (d, $J = 4.8$ Hz, 2H), 7.30 (t, $J = 4.8$ Hz, 1H), 2.39 (s, 3H); ^1H NMR (C_6D_6) δ 7.99 (d, $J = 4.8$ Hz, 2H), 6.04 (t, $J = 4.8$, 1H), 1.70 (s, 3H); IR (neat) 1753, 1713, 1581, 1412, 1375, 1181, 925 cm^{-1} (Only the bp was reported in the lit.; 75-80 °C/0.4 Torr).⁹

2-Hydroxypyrimidine (5c). The title compound was obtained from the diazotization of 2-aminopyrimidine following the procedure of 2-amino-4-*tert*-butylpyrimidine¹⁰: ^1H NMR (CDCl_3) δ 8.30 (d, $J = 4.6$ Hz, 2H), 6.47 (t, $J = 4.6$ Hz, 1H); ^1H NMR ($\text{DMSO}-d_6$) δ 8.24 (d, 2H), 6.34 (t, 1 H) [lit.¹¹ 8.29 (d, 2H), 6.40 (t, 1H)]; IR (KBr) 1553, 1477, 1344, 1222, 801 cm^{-1} ; ^1H NMR (C_6D_6) δ 7.96 (d, $J = 4.8$ Hz, 2H), 5.92 (t, $J = 4.8$ Hz, 1H) [the addition of acetic acid (6.0 mg, 0.1 mmol) shifted δ values to 7.56 (d, $J = 4.6$ Hz), 7.26 (d, $J = 4.6$ Hz), 5.58 (t, $J = 4.6$ Hz) and 5.12 (t, $J = 4.6$ Hz)].

9-Propylhypoxanthine (10b). Following the suggestion of Bunton, *et al.*,² a stirred solution of 9-propyladenine (1.0 g, 5.6 mmol) and 34.5 mL of 4 M NaNO_2 (138 mmol) in 173 mL of an acetate buffer (3 M) was stirred for 16 h at 25 °C. The reaction mixture was evaporated to dryness (20 Torr and 80 °C) and extracted with 2-butanone (4 x 25 mL). The solvent was evaporated at 20 Torr to afford 1.43 g of a yellowish-white solid. Recrystallization from acetone afforded 0.58 g (3.3 mmol, 59%) of compound **10b** in the

form of white plates, mp 254-255 °C (lit.² 255-260 °C); ¹H NMR (CDCl₃) δ 8.10 (s, 1H, H-2), 7.81 (s, 1H, H-8), 4.16 (t, *J* = 7.1 Hz, 2H), 1.93 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H); IR (KBr) 3053, 2961, 1688, 1589, 1547, 1520, 1474, 1413, 1343, 1202 cm⁻¹; (lit.¹² (KBr) 3050, 2960, 1680, 1590, 1545, 1520, 1470, 1410, 1340 cm⁻¹); *R_f* = 0.11 (silica gel, ethanol/CHCl₃ (1/9,v/v)).

9-Propyl-6-acetoxypurine (10c) From 9-Propylhypoxanthine (10b). A literature¹³ procedure was used except for the following modifications: the use of 25 °C instead of reflux, and also dimethylaniline was not used. Acetyl chloride (0.88 μL, 0.015 mmol) was added to a suspension of 9-propylhypoxanthine (2.1 mg, 0.012 mmol) in 0.4 mL of CDCl₃ in a 5 mm NMR tube. After 6 min, the ¹H NMR spectrum of the mixture indicated the following products: 9-propyl-6-acetoxypurine (**10c**) (10%) [δ 8.78 (s, 1H, H-2), 8.08 (s, 1H, H-8), 4.28 (t, *J* = 7.1 Hz, 2H), 2.50 (s, 3H), 1.97 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H)] and 9-propylhypoxanthine (**10b**) (90%) [8.07 (br s, 1H, H-2), 7.82 (br s, 1H, H-8), 4.16 (t, *J* = 7.2 Hz, 2H), 1.94 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H)]. Note: The signals for protons at C-11 and C-12 of **10c** and **10b** overlap. After 5.5 h, the product distribution was as follows: 9-propyl-6-acetoxypurine (**10c**) (24%), 9-propylhypoxanthine (**10b**) (72%) and a compound [δ 8.66 (s, 1H, H-2), 7.79 (s, 1H, H-8), 4.16 (t, *J* = 7.6 Hz, 2H), 2.90 (s, 3H), 1.93 (m, 2H), 0.97 (t, *J* = 7.6 Hz, 3H)] (4%) that probably was 9-propyl-N-acetylhypoxanthine on the basis of the chemical shift of the acetyl group, which at δ 2.90 is 0.4 ppm downfield from the chemical shift of the O-isomer (**10c**) [the chemical shifts (in CDCl₃) of 2-acetoxypyridine,¹⁴ 4-acetoxypyridine¹⁵ and 2-acetoxyquinoline¹⁵ exhibit methyl signals at 2.29, 2.29 and 2.36 ppm, while those of the corresponding N-isomers are at 2.76, 2.55 and 2.64, respectively]. The acetate (**10c**) could not be isolated; evaporation of the reaction mixture *in vacuo* (0.1 Torr and 25 °C, 1 h) led to total conversion of **10c** into **10b**, storage of the reaction mixture (in CDCl₃) at 25 °C for 24 h, and at -25 °C for 7 h had the same results. A rearrangement¹⁴ of the O-isomer (**10c**) into the N-isomer (9-propyl-N-acetylhypoxanthine) appears not to be

involved since there was not a commensurate increase in the integral of the latter compound during the loss of the O-isomer (**10c**).

From the Sodium salt of 9-Propylhypoxanthine. The method of Taylor, *et al.*,¹⁴ was followed (except that the sodium salt was used instead of the thallium salt). Acetyl chloride (1.00 μ L, 0.014 mmol) was added to a suspension of the sodium salt of 9-propylhypoxanthine (3.1 mg, 0.017 mmol) in 0.4 mL of CDCl₃ in a 5 mm NMR tube. After 5 min, the ¹H NMR spectrum (CDCl₃) indicated the following products: 9-propyl-6-acetoxypurine (**10c**) (9%) [δ 8.79 (s, 1 H, H-2), 8.08 (s, 1 H, H-8), 4.26 (t, J = 7 Hz, 2-H), 2.50 (s, 3H), 1.91 (m, 2 H), 0.97 (t, J = 7 Hz, 3 H)], 9-propyl-N-acetoxypurine (71%) [δ 8.65 (s, 1H, H-2), 7.79 (s, 1H, H-8), 4.14 (t, J = 7.6 Hz, 2H), 2.90 (s, 3H), 1.91 (m, 2H), 0.97 (t, J = 7.6 Hz, 3H)] and hypoxanthine **10b** (20%) (the signals for protons at C-11 and C-12 of the various products overlap).

9-Propyl-6-phenylpurine (10d). The method of Mc Kenzie, *et al.*,¹⁶ for the synthesis of 9-methyl-6-phenylpurine, a homolog, was followed. A solution of 9-propyladenine (0.05 g, 0.28 mmol) and *n*-butyl nitrite (0.04 g, 0.39 mmol) in 5 mL of benzene was refluxed for 20 h. An additional 0.04 g of *n*-butyl nitrite was added and the mixture was heated for an additional 26 h. TLC [silica gel, ethanol/CHCl₃ (1/9,v/v)] indicated two products at R_f = 0.10 and 0.55. Filtration yielded a pale yellow solid which was recrystallized from a benzene/CHCl₃ mixture (20/1,v/v), to afford 0.018 g, (0.10 mmol, 36%) of 9-propylhypoxanthine (**10b**), mp 252-253 °C (lit.² 255-260 °C). The remainder of the reaction mixture was chromatographed on silica gel. Elution with ethyl acetate gave a pale yellow solid which was recrystallized from pentane/CHCl₃ (20/1,v/v) to afford 0.018 g (0.076 mmol, 27%) of a cream-colored amorphous solid: mp 82-83 °C. Subsequent recrystallization from ethanol produced a pale yellow crystalline solid: mp 82-82.5 °C; ¹H NMR (CDCl₃) δ 9.04 (s, 1H, H-2), 8.77 (d J = 8.3 Hz, 2H), 8.14 (s, 1H, H-8), 7.56 (m, 3H), 4.30 (t, J = 7.2 Hz, 2H), 1.99 (m, 2H), 1.01 (t, J = 7.4 Hz, 3H); GC t_R = 45.5 min (180 °C, 15 psi). The ¹H NMR data¹⁶ for the 9-methyl-6-phenylpurine

analog is similar [^1H NMR (CDCl_3 , 300MHz) δ 9.00 (s, 1H, H-2), 8.77 (d 2H), 8.03 (s, 1H, H-8), 7.53 (m, 3H), 3.83 (s, 3H)].

9-Propylpurine (10e) and 9-Propyl-6-chloropurine (10f). The method of Nair, *et al.*,¹⁷ for the synthesis of 9-ethyl-6-chloropurine, a homolog, was followed: however, CHCl_3 was used as the solvent instead of CCl_4 . A mixture of 9-propyladenine (0.10 g, 0.56 mmol) and *n*-butyl nitrite (0.08 g, 0.78 mmol) in 20 mL of chloroform in a reaction vessel flushed with nitrogen and fitted with a condenser and a CaCl_2 filled drying tube was heated to reflux. After a reaction time of 24 h, an additional 0.08 g (0.78 mmol) of *n*-butyl nitrite was added to the reaction mixture. After a reaction time of 96 h, the solvent was removed at 20 Torr and the residue was dried at 0.1 Torr. The solid was separated by chromatography on silica gel and developed with ethyl acetate; the band at $R_f = 0.14$ gave 0.03 g (0.17 mmol, 30%) of a white solid identified as propylhypoxanthine (**10b**): mp 252-253 °C (lit.² 255-260). The band at $R_f = 0.31$ produced starting material (0.03 g, 0.16 mmol, 29%). The band at $R_f = 0.52$ produced a pale yellow oil (0.03 g, 0.18 mmol, 33%): ^1H NMR (CDCl_3) δ 9.16 (s, 1H, H-6), 9.00 (s, 1H, H-2) 8.11 (s, 1H, H-8), 4.28 (t, $J = 7.2$ Hz, 2H), 2.05-1.93 (m, 2H), 0.99 (t, $J = 7.4$ Hz, 3H); $R_f = 0.51$ (silica gel, ethanol/ CHCl_3 (1/9,v/v); GC $t_R = 7.7$ min (180 °C, 15 psi). The compound was identified as 9-propylpurine (**10e**) based on the ^1H NMR spectrum reported (CDCl_3 , 60 MHz) for compound **10e**:¹² δ 9.26 (s, 1H, H-6), 9.10 (s, 1H, H-2), 8.23 (s, 1H, H-8), 4.33 (t, 2H), 2.33-1.83 (m, 2H), 1.00 (t, 3H). The band at $R_f = 0.63$ produced a pale yellow oil (0.02 g, 0.01 mmol, 18%): ^1H NMR (CDCl_3) δ 8.76 (s, 1H, H-2), 8.14 (s, 1H, H-8), 4.28 (t, $J = 7.2$ Hz, 2H, CH_2), 1.99 (m, 2H, CH_2), 0.99 (t, $J = 7.4$ Hz, 3H, CH_3); IR (KBr) 2963, 2932, 2875, 1726, 1594, 1559, 1334, 1205, 942, 801, 647 cm^{-1} ; $R_f = 0.7$ (silica gel, ethanol/ CHCl_3 (1/9,v/v); GC $t_R = 8.1$ min (180 °C, 15 psi) (95% pure by GC analysis). This compound gave a positive *Beilstein* test¹⁸ for halogen. The product 9-propyl-6-chloropurine (**10f**), exhibited similar chemical shifts to a homolog, 9-ethyl-6-chloropurine¹⁷ (purine aromatic singlets at 8.76 and 8.14 (CDCl_3))

versus 8.76 and 8.17 for the homolog). The melting point of the hydrochloride salt was the only physical data reported in the literature¹⁹ for 9-propyl-6-chloropurine (**10f**). The same material prior to chromatography was obtained from a deamination run in CCl₄. Anhydrous HCl gas was bubbled for 2 min through a solution of 0.20g (0.10 mmol) of this product in 5 mL of CCl₄. A cream-colored precipitate was formed instantly. The precipitate was collected and dried *in vacuo* (0.1 Torr, 25 °C) to afford 0.18 mg of an orange/yellow solid: mp 160-177 °C. This was recrystallized from acetonitrile to afford a yellow, crystalline solid (0.14 g, 0.06 mmol, 60 %): mp 175-177 °C (unchanged after two additional recrystallizations) [lit.¹⁹ 193-195 °C (sic) (acetonitrile)]; ¹H NMR (D₂O) δ 8.63 (s, 1H, H-2), 8.57 (s, 1H, H-8), 4.26 (t, *J* = 7.1 Hz, 2H), 1.86 (m, 2H), 0.85 (t, *J* = 7.4 Hz, 3H).

The Reaction of Sodium 2-Pyridine Diazotate (1a) with Acetic Acid. In CDCl₃. Acetic acid (11.4 μL, 12 mg, 0.20 mmol) was added to a mixture of compound **1a** (14.5 mg, 0.0100 mmol) and 0.5 mL of CDCl₃ at 24 °C with manual shaking. The mixture became yellow in color and gas evolution was observed for 20 min. The ¹H NMR (CDCl₃) spectrum showed that the products were 2-acetoxypyridine (71 ± 3%) [δ 8.42 (d, *J* = 4.9 Hz, 1H), 7.80 (td, *J* = 7.4 Hz, *J* = 2.4 Hz, 1H), 7.24 (m, 1H), 7.10 (dd, *J* = 8.2 Hz, *J* = 0.8 Hz, 1H), 2.35 (s, 3H)], 2-hydroxypyridine (14 ± 3%) [δ 7.46-7.52 (m), 7.35-7.33 (m), 6.65 (d, *J* = 7.1 Hz, 1H), 6.30 (td, *J* = 6.5 Hz, *J* = 1.1 Hz, 1H)] and 2-chloropyridine (15%) [δ 7.68 (td, *J* = 8.0 Hz, *J* = 2.0 Hz)]. When the NMR sample was spiked with 2-chloropyridine, that signal (δ 7.68) was enhanced as well as signals at δ 8.42 (d, *J* = 5.1 Hz) and 7.23 (m) which coincide with signals from 2-acetoxypyridine, and δ 7.34 (dt, *J* = 8.0 Hz, *J* = 0.9 Hz) which overlaps with a signal from 2-hydroxypyridine. The sum of the absolute yields of the three products (nitromethane calibration) was 78%.

In Benzene-*d*₆. Acetic acid (12 mg, 11.4 μL, 0.20 mmol) was added to a mixture of sodium 2-pyridine diazotate (**1a**) (14.5 mg, 0.010 mmol) and 0.5 mL of C₆D₆ with manual shaking at 24 °C. The mixture bubbled vigorously for ~ 1 min. After 20 min the ¹H NMR

(C₆D₆) spectrum showed that the reaction afforded 2-phenylpyridine (22%) [δ 8.62 (d, J = 4.6 Hz, 1H), 7.29 (d, J = 6.6 Hz, 1H), 7.10 (d, 1H), 6.62 (m, overlapped with 2-hydroxypyridine)], 2-acetoxypyridine (67%) [δ 8.15 (d, J = 4.5 Hz, 1H), 6.98 (td), 6.69 (d), 6.46 (t, J = 4.9 Hz, 1H), 1.73 (s, 3H)], and 2-hydroxypyridine (11%) [δ 6.69-6.58 (m, overlapped with 2-acetoxypyridine), 6.48-6.37 (m, overlapped with 2-acetoxypyridine), 5.40 (t, J = 6.7 Hz, 1H)]. The other run afforded 2-phenylpyridine (22%), 2-acetoxypyridine (64%), and 2-hydroxypyridine (13%).

In N-Methylpyrrole. Acetic acid (11.4 μ L, 12 mg, 0.20 mmol) was added with stirring to a mixture of sodium 2-pyridine diazotate (14.5 mg, 0.10 mmol) and 0.5 mL of N-methylpyrrole at 24 °C. After 10 min, the bubbling that occurred was essentially over and the mixture became light yellow in color. The ¹H NMR (CDCl₃) spectrum gave a ratio of 2-acetoxypyridine to 2-(N-methylpyrrol-2-yl)pyridine of 1.5. The mixture was then evaporated to dryness (some 2-acetoxypyridine may be lost at this point) at 0.1 Torr to remove the interfering N-methylpyrrole. From a new ¹H NMR spectrum in CDCl₃ and the above ratio, the following product distribution was calculated (based on three runs): 14 \pm 2 % of 2-hydroxypyridine (**5a**) [7.65 - 7.30 (m, 2H), 6.60 (m, 1H), δ 6.30 (t, 1H)], 30 \pm 5% of 2-acetoxypyridine (**6a**) [δ 8.42 (d, 1H), 7.80 (t, 1H), 7.36-7.22 (m, 1H), 7.10 (m, 1H)], 20 \pm 1% of 2-(N-methylpyrrol-2-yl)pyridine (**8**) [δ 8.56 (d, 1H), 7.65-7.40 (m), 2H, overlapped with **9**], 7.10-7.00 (m, 1H, overlapped with **6a**, **9**), 6.70-6.50 (m, 2H, overlapped with **5a**, **9**), 6.18 (t, 1H), 3.99 (s, 3H); lit.²⁰ for **8** (CDCl₃) δ 8.48 (m, 1H), 7.47 (m, 2H), 6.95 (m, 1H), 6.67 (m, 1H), 6.53 (m, 1H), 6.14 (m, 1H), 3.95 (s, 3H)], and 36 \pm 3% of 2-(N-methylpyrrol-3-yl)pyridine (**9**) [δ 8.50 (d, 1H), 7.65-7.40 (m, 2H, overlapped with **8**), 7.10-7.00 (m, 2H, overlapped with **6a**, **8**), 6.65-6.60 (m, 2H, overlapped with **5a**, **8**), 3.71 (s, 3H)]²¹.

A Search for Pyridine in the Products from the Reaction of Sodium 2-Pyridine Diazotate with Acetic Acid in a Mixture of Benzene/Chloroform (1/1 molar ratio). Acetic acid (6.0 mg, 0.10 mmol) was added to a mixture of sodium 2-

pyridine diazotate (7.3 mg, 0.050 mmol) and 0.5 mL of chloroform/benzene (1/1 mol ratio) with stirring at 25 °C. The bubbling of nitrogen that was observed stopped after 10 min. The mixture was analyzed by GC; 10 μ L of the sample was injected onto a SE-30 column (100 °C and 5 psi). No peak was observed in the region $t_R = 7.25$ -7.35 min, while injection of pyridine produced a peak at $t_R = 7.30$ min. A sample (10 μ L) of a solution of pyridine (10^{-3} M) in 1/1 benzene/chloroform (mol ratio) [prepared by adding pyridine (0.4 mg, 0.005 mmol) to 5 mL of the benzene/chloroform mixture] was injected onto the same column; the 10 μ L contains an amount of pyridine equivalent to a 1% yield in the diazotate reaction above. From the integral of the peak seen at $t_R = 7.30$ min, it can be estimated that the maximum yield of pyridine in the diazotate reaction was less than 0.5%. TLC (silica gel, ether) of the products showed the formation of 2-hydroxypyridine with $R_f = 0.1$, 2-acetoxypyridine with $R_f = 0.4$, and 2-phenylpyridine with $R_f = 0.6$.

The Reaction of Sodium Pyrazine Diazotate (1b) with Acetic Acid. In CDCl_3 . Acetic acid (27.1 μ L, 6.0 mg, 0.50 mmol) was added with manual shaking to a mixture of sodium 2-pyrazine diazotate (**1b**) (7.5 mg, 0.051 mmol) and 0.5 mL of CDCl_3 at 25 °C; gas evolution was observed (lasting ~ 15 min) and a light yellow color developed. The ^1H NMR (CDCl_3) spectrum showed the products were 2-acetoxypyrazine ($80 \pm 5\%$) [δ 8.52 (m, 2H), 8.41 (m, 1H), 2.40 (s, 3H); lit.²² ^1H NMR (CDCl_3) δ 8.5 (m, 2H), 8.4 (dd, $J = 2.5$ Hz, $J = 1.5$ Hz, 1H), 2.4 (s, 3H)]; 2-hydroxypyrazine ($20 \pm 5\%$) [δ 8.30 (s, 1H), 7.56 (d, 1H), 7.24 (d, 1H) in CDCl_3 and δ 7.95 (s, 1H), 7.45-7.35 (m, 2H) in $\text{DMSO-}d_6$; lit.¹ ^1H NMR ($\text{DMSO-}d_6$) δ 7.95 (s, 1H), 7.39 (m, 2H)]; the absolute yield of the two products (spectrum calibrated with p-nitrotoluene) was 94-96%, based on two runs. The mixture was evaporated to dryness (20 Torr). A new ^1H NMR spectrum showed: 2-hydroxypyrazine (**5b**) [^1H NMR (C_6D_6) δ 8.14 (s, 1H), 6.88 (d, 1H), 5.82 (d, 1H)]; 2-acetoxypyrazine (**6b**): [^1H NMR (C_6D_6) δ 8.26 (d, 1H), 7.85 (d, $J = 1.8$ Hz, 1H), 7.69 (dd, $J = 1.8$ Hz, $J = 0.9$ Hz, 1H), 1.65 (s, 3H)].

In a separate series of three runs, the reaction of **1b** with 2.0 mol equivalents of acetic acid over 45 min resulted in an absolute yield of products of 64-74%. The relative yield of products (**5b**, **6b**) was essentially unchanged from the data listed above.

(b) **In Benzene-d₆**. Acetic acid (5.7 μ L, 6.0 mg, 0.10 mmol) was added to compound **1b** (7.3 mg, 0.050 mmol) mixed with 0.5 mL of C₆D₆ at 25 °C with manual shaking. After 2 min, the ¹H NMR (C₆D₆) spectrum showed an intermediate [δ 8.95 (1H), 7.85 (1H), 7.60 (1H)] (coupling not resolved) with a half-life of ~10 min. Gas evolution was observed and the mixture became yellow in color. The ¹H NMR (C₆D₆) spectrum showed that the reaction afforded 16 \pm 3% of 2-phenylpyrazine [δ 8.82 (d, *J* = 1.2 Hz, 1H), 8.09 (m, 1H), 8.03 (d, *J* = 2.4 Hz, 1H)]; 60 \pm 5% of 2-acetoxypyrazine (**2b**) [δ 8.25 (m, 1H), 7.84 (d, *J* = 2.1 Hz, 1H), 7.70 (dd, *J* = 1.8 Hz, *J* = 0.9 Hz, 1H)] and 24 \pm 8% of 2-hydroxypyrazine (**3b**) [δ 8.14 (t, 1H), 6.88 (d, 1H), 5.82 (d, *J* = 3 Hz, 1H)].

(c) **In CDCl₃/Benzene-d₆**. Acetic acid (5.7 μ L, 6.0 mg, 0.10 mmol) was added to a mixture of sodium 2-pyrazine diazotate (7.3 mg, 0.050 mmol) and 0.5 mL of an equimolar mixture of CDCl₃ and C₆D₆ at 24 °C. Gas evolution was observed for 30 min and the mixture became yellow in color. The ¹H NMR spectrum showed the reaction afforded 4% of 2-phenylpyrazine [δ 8.82 (d)], 68% of 2-acetoxypyrazine [δ 8.28 (m)] and 28% of 2-hydroxypyrazine [δ 7.08 (d)]. The maximum yield of pyrazine was less than 1% (based on the singlet at δ 8.18).

The Reaction of Sodium 2-Pyrimidine Diazotate (1c) with Acetic Acid with Detection of an Intermediate. In CDCl₃. Acetic acid (4.0 μ L, 4.2 mg, 0.070 mmol) was added to a suspension of sodium 2-pyrimidine diazotate (10 mg, 0.070 mmol) in 0.5 mL of CDCl₃ at 0 °C. The mixture was shaken; a few bubbles were observed and the liquid phase turned light yellow in color. A ¹H NMR spectrum was taken after 10 min and showed an intermediate with signals at δ 8.78 (d, 2H, *J* = 4.8 Hz), 7.32 (t, 1H, *J* = 4.8 Hz). The sample was filtered, and the filtrate was evaporated at 0 °C (0.1 Torr) to produce a light yellow residue: ¹H NMR (CDCl₃) (same as above); ¹H NMR (C₆D₆) δ

7.89 (d, $J = 4.8$ Hz, 2H), 5.97 (t, $J = 4.8$ Hz, 1H); IR (KBr) 1572, 1521, 1477, 1422, 1390, 1287, 1130 cm^{-1} . Similar results were obtained with a $\text{CH}_3\text{COOH}/\mathbf{1c}$ ratio of 2. After 3 h at 25 °C the intermediate decomposed to give 2-acetoxypyrimidine (68%) [δ 8.76 (d, $J = 4.8$ Hz, 2H), 7.30 (t, $J = 4.8$ Hz, 1H), 2.39 (s, 3H)] and 2-hydroxypyrimidine (32%) [δ 8.30 (d, $J = 4.6$ Hz, 2H), 6.47 (t, $J = 4.6$ Hz, 1H)].

In Benzene- d_6 . Acetic acid (5.7 μL , 6.0 mg, 0.10 mmol) was added to a suspension of sodium 2-pyrimidine diazotate (14.6 mg, 0.10 mmol) in 1 mL of C_6D_6 with stirring at 25 °C. After 3 h, the ^1H NMR (C_6D_6) spectrum showed an intermediate with δ 7.91 (d, $J = 4.8$ Hz, 2H), 5.98 (t, $J = 4.8$ Hz, 1H). The benzene solution of the neutral compound was centrifuged. The liquid phase was removed and treated with acetic acid (5.7 μL , 6.0 mg, 0.10 mmol). After 4.5 h reaction time, the ^1H NMR of the mixture showed that the protonated product of the diazotate (**2c**) had fully reacted and that the products were 2-phenylpyrimidine (14%) [δ 8.29 (d, $J = 4.8$ Hz), 6.17 (t, $J = 4.8$ Hz)], 2-acetoxypyrimidine (54%) [δ 8.00 (d, $J = 4.8$ Hz), 6.00 (t, $J = 4.8$ Hz)], 1.73 (s, 3H) and 2-hydroxypyrimidine (32%) [δ 7.55 (d, $J = 4.8$ Hz), 7.20 (m), 5.57 (t, $J = 4.8$ Hz), 5.08 (d, $J = 4.8$ Hz)]; see synthesis of **5c**. In a second run, the ^1H NMR spectrum showed the formation of 13% of 2-phenylpyrimidine, 48% of 2-acetoxypyrimidine and 39% of 2-hydroxypyrimidine.

The Reaction of Sodium 2-Pyridine Diazotate with Acetic Acid in the Presence of 2-Aminopyridine. In CDCl_3 . Acetic acid (11.4 μL , 12.0 mg, 0.20 mmol) was added with shaking to a solution of 2-aminopyridine (47 mg, 0.50 mmol) in 0.5 mL of CDCl_3 ; sodium 2-pyridine diazotate (14.5 mg, 0.10 mmol) was then added. Vigorous gas evolution was observed for about 10 min. After 1h, the ^1H NMR (CDCl_3) spectrum showed that the reaction produced 2-acetoxypyridine (47%) [δ 8.39 (m, 1H), 7.77 (t, 1H)], 7.21 (d, 1H), 7.09 (d, 1H), 2.32 (s, 3H)], 2,2'-dipyridylamine (19%) [δ 8.23 (m, 2H), 7.5-7.6 (m, 4H), 6.82 (m, 2H)] and 2-hydroxypyridine (34%) [δ 7.4-7.5 (m, 1H), 7.30 (d, 1H), 6.47 - 6.61(m, 1H), 6.27 (t, 1H)]. The sample was heated to 60

°C and 0.1 Torr to remove the solvent and excess 2-aminopyridine: the ^1H NMR (CDCl_3) spectrum showed the presence of 2-hydroxypyridine (as above) and δ for 2,2'-dipyridylamine [δ 8.26 (d, 2H), 7.62-7.60 (m, 4H), 6.87-6.83 (m, 2H); lit.²³ (CDCl_3) 8.28 (m, 2H), 7.65-7.55 (m, 4H), 6.84 (m, 2H)].

In Aqueous Solution. Sodium 2-pyridine diazotate (29 mg, 0.20 mmol) was added to a solution of 2-aminopyridine (1.03 g, 10.9 mmol) in 1 mL of distilled water and acetic acid (24 mg, 0.40 mmol) was added. After 30 min nitrogen evolution had essentially stopped. The volatiles were removed from the mixture at 60 °C (0.1 Torr). The ^1H NMR spectrum (CDCl_3) of the residue showed the presence of 2,2'-dipyridylamine (12%) [δ 8.26 (d); lit.²³ 8.28 (m)], 2-hydroxypyridine [δ 7.48 (m), 63%] and unknown compounds [δ 8.50-8.70 (m), ~25%] (possibly products from pyridine ring alkylation of 2-aminopyridine based on the chemical shifts of a model compound, 2,2'-bipyridyl [lit.²⁴ δ 8.70 (H₆ of the pyridine ring)]; TLC R_f = 0.57 for 2,2'-dipyridylamine (Alumina, ether) (an authentic sample of 2,2'-dipyridylamine gave the same R_f); GC t_R = 12.3 min for 2,2'-dipyridylamine (160 °C, 15 psi) (an authentic sample gave the same t_R).

The Reaction of Sodium 9-Propyl-6-purine Diazotate (10a) with Acetic Acid. In CHCl_3 . Acetic acid (4.5 μL , 0.080 mmol) was added to a solution of sodium 9-propyl-6-purine diazotate (**10a**) (9.0 mg, 0.040 mmol) in 0.5 mL of CDCl_3 in a 5 mm NMR tube at 25 °C. After 6 min, ^1H NMR spectrum revealed the protonated diazotate [δ 8.89 (s, 1H, H-2), 8.25 (s, 1H, H-8), 4.34 (t, J = 6.5 Hz, 2H), 2.04 (m, 2H), 1.02 (t, J = 7.4 Hz, 3H)]. After 7 h, the reaction was over as indicated by the disappearance of those ^1H NMR signals. The ^1H NMR spectrum of the reaction mixture (CDCl_3) indicated the following compounds: 9-propylpurine (**10e**) (2 %) [δ 9.04 (s, 1H, H-2), 8.11 (s, 1H, H-8); R_f = 0.51 (silica gel, ethanol/ CHCl_3 (1/9,v/v); GC t_R = 7.7 min (180 °C, 15 psi)], 9-propyl-6-acetoxypurine (**10c**) (12 %) [δ 8.80 (s, 1H, H-2), 8.15 (s, 1H, H-8), 2.50 (s, 3H CH_3)], 9-propyl-6-chloropurine (**10f**) (8 %) [δ 8.80 (s, 1H, H-2), 8.19 (s, 1H, H-8); R_f = 0.7 (silica gel, ethanol/ CHCl_3 (1/9,v/v); GC t_R = 8.1 min (180 °C, 15 psi)] and 9-

propylhypoxanthine (**10b**) (78 %) [δ 8.13 (br s, 1H, H-2), 7.84 (br s, 1H, H-8); R_f = 0.11 (silica gel, ethanol/ CHCl_3 (1/9,v/v)]. Due to extensive overlap of signals in the aliphatic region of the ^1H NMR spectrum, signals for the protons at C-2 and C-8 of the products formed, which are clearly resolved, was used to determine the ratio of products. The R_f values for compounds **10b**, **10e** and **10f**, as well as the t_R values for **10e** and **10f**, matched those for the authentic compounds listed earlier. Note: 9-Propyl-6-acetoxypurine (**10c**) decomposes to 9-propylhypoxanthine (**10b**) upon evaporation of the reaction mixture to dryness (0.1 Torr, 25 °C, 2 h), or on standing for 24 h at 25 °C.

In Benzene. Acetic acid (3.76 μL , 0.066 mmol) was added to a suspension of sodium 9-propyl-6-purine diazotate (**10a**) (5.0 mg, 0.022 mmol) in 0.5 mL of C_6D_6 at 25 °C in a 5 mm NMR tube. As above, product analysis was carried out *via* the resolved aromatic signals. After 6 min, ^1H NMR (C_6D_6) spectrum indicated the protonated diazotate with δ 8.88 (s, 1H, H-2), 7.49 (s, 1H, H-8), 3.37 (t, J = 7.2 Hz, 2H), 1.30 (m, 2H), 0.48 (t, J = 7.4 Hz, 3H). After 3.5 h, the reaction was over as indicated by the absence of those signals. The ^1H NMR spectrum of the reaction mixture (C_6D_6) indicated the following compounds: 9-propyl-6-phenylpurine (**10d**) [δ 9.20(s, 1H, H-2), 7.45 (s, 1H, H-8); R_f = 0.55 (silica gel, ethanol/ CHCl_3 (1/9,v/v)] and 9-propyl-6-acetoxypurine (**10c**) [δ 8.61 (s, 1H, H-2), 7.79 (s, 1H, H-8)] in a ratio of 2:1. A pale yellow precipitate of 9-propylhypoxanthine (**10b**) was also formed. The reaction mixture was evaporated *in vacuo* (0.1 Torr) (which led to the hydrolysis of the acetate **10c** to **10b**), and dissolved in CDCl_3 in which the hypoxanthine is more soluble. The ^1H NMR (CDCl_3) spectrum indicated the following composition: 9-propyl-6-phenylpurine (**10d**) [δ 9.04 (s, 1H, H-2), 8.79 (d 2H), 8.14 (s, 1H, H-8), 7.57 (m, 3H); R_f = 0.55 (silica gel, ethanol/ CHCl_3 , 1/9,v/v)] and 9-propylhypoxanthine (**10b**) [δ 8.08 (s, 1H, H-2), 7.80 (s, 1H, H-8); R_f = 0.11 (silica gel, ethanol/ CHCl_3 , 1/9,v/v)]. The ratio of **10b** to **10d** was 5.4:1.0. Combining the two ratios (and correcting for the hydrolysis of the acetate **10c**) gave a product ratio of

4.9:0.5:1.0 or, 76, 8, and 16 %, respectively. The *R_f* values for compounds **10b** and **10d** matched those for the authentic compounds listed earlier.

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