(t), 26.3 (t); GC/MS (70 eV), *m/e* (relative intensity) 159.0 (2.3), 158.0 (molecular ion – [CO], 18.5), 145.1 (10.9), 144.1 (molecular ion – [H_2C=C=O], 100.0), 129.1 (79.2), 115.1 (39.1); high-resolution mass spectrometry, calcd for $C_{13}H_{14}O$ M_r 186.1045, found M_r 186.1034.

2-Oxa-3-tetramethylenebicyclo[3.2.0]heptan-7-one (9b). A 117-mg (50% yield) portion of **9b** was obtained from 338 mg of **9a** as a pale yellow oil: IR (neat) 1786 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.10 (m, 1 H), 3.50 (m, 2 H), 2.44–0.92 (m, 11 H); ^{13}C NMR ($CDCl_3$) δ 212.1 (s), 96.5 (s), 93.7 (d), 50.0 (t), 42.3 (d), 39.4 (t, 2 C), 31.5 (t), 24.8 (t), 23.7 (t); GC/MS (70 eV), *m/e* (relative intensity) 139.00 (0.5), 138.10 (molecular ion – [CO], 5.1), 124.00 (molecular ion – [H_2C=C=O], 23.9), 120.10 (10.6), 109.10 (16.0), 95.00 (21.1), 81.00 (23.9), 67.00 (100.0), 55.00 (22.5), 41.00 (39.5), 39.00 (43.0); high-resolution mass spectrometry, calcd for $C_{10}H_{14}O_2$ M_r 166.0994, found M_r 166.0993.

Acknowledgment. We are grateful to the Robert A. Welch Foundation for support of this work.

Registry No. 1 (acid), 6839-30-1; **1a**, 6839-43-6; **1b**, 99477-39-1; 2 (acid), 99477-30-2; **2a**, 107770-73-0; **2b**, 99477-37-9; 3 (acid), 997477-28-8; **3a**, 107770-74-1; **3b**, 99477-35-7; 4 (acid), 6627-85-6; **4a**, 107770-75-2; **4b**, 107770-80-9; 5 (acid), 107770-68-3; **5a**, 107770-76-3; **5b**, 107770-81-0; **6a**, 107770-72-9; **6b**, 107770-82-1; 7 (acid), 107770-69-4; **7a**, 107770-77-4; **7b**, 107770-83-2; 8 (acid), 39764-82-4; **8a**, 107770-78-5; **8b**, 39764-85-7; 9 (acid), 107770-71-8; **9a**, 107770-79-6; **9b**, 107770-84-3; $Cl(CH_2)_2CO_2H$, 107-94-8; 2-$HOC_6H_4CH_2CH$=CH_2, 1745-81-9; $Br(CH_2)_4Br$, 110-52-1; 2-H_2C=$CHCH_2C_6H_4O(DcH_2)_4Br$, 107770-70-7; $BrCH_2CH$=CH_2, 106-95-6; $BrCH_2CO_2H$, 79-08-3; Et_2NH, 109-89-7; Cl-$(CH_2)_3CONEt_2$, 56794-28-6; cyclopentanone, 120-92-3; 1-allylcyclopentanol, 36399-21-0.

Cyclocondensation Reactions of 3-Amino-2-hydrazino-4(3*H*)-pyrimidinones.[1,2] Formation of 1,2,4-Triazolo[4,3-*a*]pyrimidines and Pyrimido[1,2-*b*][1,2,4,5]tetrazines

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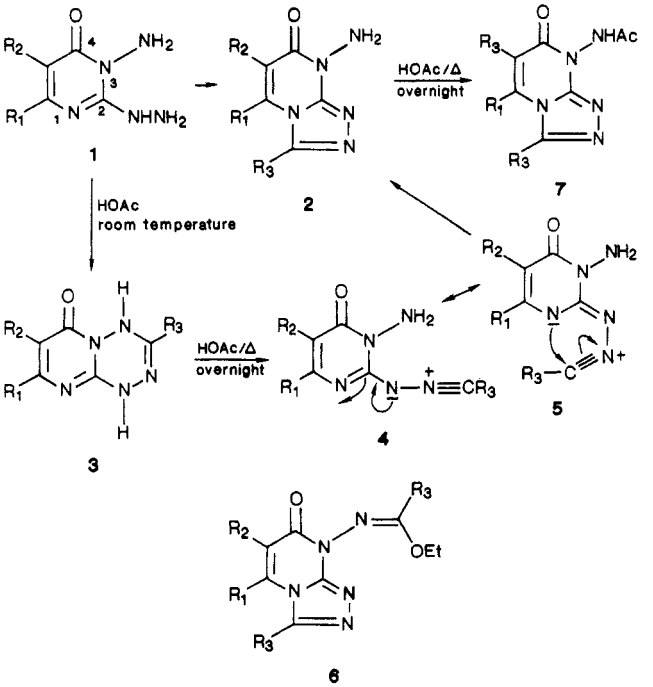
3-Amino-2-hydrazino-4(3*H*)-pyrimidinones **1**, derived from diaminoguanidine and β-keto esters,[1,2] react readily with ortho esters in hot acetic acid or butanol to give 1,2,4-triazolo[4,3-*a*]pyrimidin-7(8*H*)-ones **2**. In acetic acid at room temperature, **1** reacts with ortho esters, dimethylformamide dimethyl acetal, and diethoxymethyl acetate to form **2** and 6*H*-pyrimido[1,2-*b*][1,2,4,5]tetrazin-6-ones **3**. The latter ring system undergoes a thermal, acid-catalyzed, rearrangement to **2**.

Adjacent amino and hydrazino functional groups in a heterocyclic system provide many opportunities for the elaboration of additional ring systems. This synthetic strategy provides a route to ring-fused systems containing nitrogen at the ring-junction when an *N*-amino group is utilized. We now wish to describe our results utilizing 3-amino-2-hydrazino-4(3*H*)-pyrimidinones **1**, previously prepared[1,2] in our laboratory from diaminoguanidine and substituted β-keto esters, as a route to 1,2,4-triazolo[4,3-*a*]pyrimidin-7(8*H*)-ones **2** and 6*H*-pyrimido[1,2-*b*]-[1,2,4,5]tetrazin-6-ones **3**, which can now be readily prepared with a variety of substituents.

Reaction of **1** with ortho esters may occur in three ways: reaction with the *N*-NH_2 group or the $NHNH_2$ group to give the corresponding imino ethers, cyclocondensation at N-1 to give a 1,2,4-triazole system, or cyclocondensation between the *N*-NH_2 and the $NHNH_2$ groups to afford a 1,4-dihydrotetrazine derivative. Reaction of **1** with ortho esters in boiling butanol overnight or glacial acetic acid for 30 min gave only one product, identified as an 8-amino-1,2,4-triazolo[4,3-*a*]pyrimidin-7(8*H*)-one derivative **2**, in 50–75% yields. When the refluxing in acetic acid continued overnight, the acetamido derivative **7** was obtained.

Although the ^1H NMR data (Table I) were consistent with the assigned structure, they could not be considered conclusive. The structure **2c** (R_1 = R_3 = CH_3, R_2 = H) was finally determined by a single-crystal X-ray analysis[3] (supplementary material). Reaction of **1** with ortho esters, dimethylformamide dimethyl acetal, or diethoxymethyl acetate in glacial acetic acid at room temperature led to a mixture, readily separable by crystallization, of **2** and a second product **3** identified as a pyrimido[1,2-*b*][1,2,4,5]-tetrazin-6-one derivative (supplementary material) (Scheme I). The NMR spectra of the ring-fused tetrazines **3** show two NH signals at δ 9.3–9.8 (Table II), and they

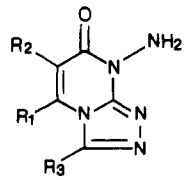
Scheme I



(1) Hlavka, J. J.; Bitha, P.; Lin, Y.-i.; Strohmeyer, T. *J. Heterocycl. Chem.* **1984**, *21*, 1537.
(2) Hlavka, J. J.; Bitha, P.; Lin Y.-i.; Strohmeyer, T. *J. Heterocycl. Chem.* **1985**, *22*, 1317.
(3) X-ray work was performed by the crystallographic staff of Molecular Structure Corporation: Dr. M. W. Extine, R. A. Meisner, Dr. J. M. Troup, and B. B. Warrington, College Station, TX.

0022-3263/87/1952-2220$01.50/0

Table I. Substituted 8-Amino-1,2,4-triazolo[4,3-*a*]pyrimidin-7(8*H*)-ones

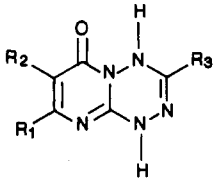


2

compd	R_1	R_2	R_3	yield, %	mp, °C	formula[c]	^{1}H NMR measurements (δ)			
							R_1	R_2	R_3	NH_2
2a	CH_3	H	H	47[a]	263–266 dec	$C_6H_7N_5O$	CH_3 (2.5)	H (6.2)	H (8.92)	(5.7)
2b	CH_3	CH_3	H	67[b]	276–278	$C_7H_9N_5O$	CH_3 (2.5)	CH_3 (2.0)	H (8.96)	(5.77)
2c	CH_3	H	CH_3	56[b]	275–278 dec	$C_7H_9N_5O$	CH_3 (2.66)	H (6.1)	CH_3 (2.55)	(5.65)
2d	CH_3	H	C_6H_5	29[b]	210 dec	$C_{12}H_{11}N_5O$	CH_3 (2.0)	H (6.2)	Ph (7.6;m)	(7.81)
2e	C_6H_5	H	H	31[a]	260–266	$C_{11}H_9N_5O$	Ph (7.7; m)	H (6.43)	H (8.76)	(5.86)

[a] Prepared with ortho ester in acetic acid at room temperature. [b] Prepared with ortho ester in butanol at reflux. [c] Satisfactory analyses were reported.

Table II. Substituted 1,4-Dihydro-6*H*-pyrimido[1,2-*b*]-1,2,4,5-tetrazin-6-ones

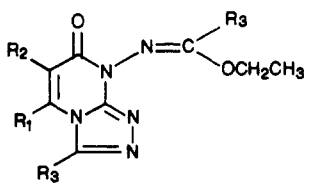


3

compd	R_1	R_2	R_3	yield, %	mp, °C	formula[c]	^{1}H NMR measurements (δ)			
							R_1	R_2	R_3	NH
3a	CH_3	H	H	23[a]	215–220 dec	$C_6H_7N_5O$	CH_3 (2.06)	H (5.86)	H (6.97) (7.01)	(9.51, 9.75)
3b	CH_3	CH_3	H	15[b]	255–258 dec	$C_7H_9N_5O$	CH_3 (2.06)	CH_3 (1.86)	H (7.0)	(9.48, 9.56)
3c	CH_3	H	CH_3	51[a]	239–241	$C_7H_9N_5O$	CH_3 (2.06)	H (5.78)	CH_3 (1.9)	(9.3, 9.6)
3d	C_6H_5	H	CH_3	31[a]	220–224 dec	$C_{12}H_{11}N_5O$	Ph (7.5, 8.0; m)	H (6.5)	CH_3 (1.94)	(9.45, 9.78)
3e	C_6H_5	H	H	30[a]	200 dec	$C_{11}H_9N_5O$	Ph (7.7, 7.9; m)	H (7.05)	H (6.58)	(9.8)

[a] Prepared with ortho ester in acetic acid at room temperature. [b] Prepared with dimethylformamide dimethyl acetal in acetic acid at room temperature. [c] Satisfactory analyses were reported.

Table III. Schiff Bases of 8-Amino-1,2,4-triazolo[4,3-*a*]pyrimidin-7(8*H*)-ones



6

compd	R_1	R_2	R_3	yield, %	mp, °C	formula[a]	^{1}H NMR measurements (δ)					
							R_1	R_2	R_3	R_4	CH_3	CH_2
6a	CH_3	H	H	70	200–204	$C_9H_{11}N_5O_2$	CH_3 (2.5)	H (6.2)	H (8.5)	H (8.86)	(1.4; t)	(4.4; q)
6b	CH_3	H	CH_3	71	188–190	$C_{11}H_{15}N_5O_2$	CH_3 (2.7)	H (6.15)	CH_3 (2.63)	CH_3 (1.75)	(1.4; t)	(4.4; q)
6c	C_6H_5	H	H	88	148–150	$C_{14}H_{13}N_5O_2$	Ph (7.7; m)	H (6.42)	H (8.6)	H (8.77)	(1.44; t)	(4.45; q)

[a] Satisfactory analyses were reported.

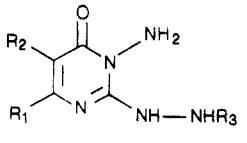
are lacking the *N*-NH_2 signal at δ 5.6–5.9 (Table I) which is characteristic of product **2**. The yields of the ring-fused tetrazines **3** (R_3 = H) varied from 15–55% when triethyl orthoformate was used as the cyclocondensation agent. With dimethylformamide dimethyl acetal yields of **3** were slightly less (10–42%), and with diethoxymethyl acetate the yields were 15–20%.

Refluxing of **3** in acetic acid overnight resulted in isomerization to **2** in 52% yield, isolated as crystalline acetamido derivative **7** (R_1 = CH_3, R_2 = R_3 = H). When **3** was refluxed in butanol overnight, no isomerization occurred. Although 1,2- and 1,4-dihydrotetrazines undergo ready acid-catalyzed isomerization to 4-amino-1,2,4-triazoles,[4] this is the first recorded example of such an isomerization of a ring-fused tetrazine derivative to a ring-fused 1,2,4-triazole.

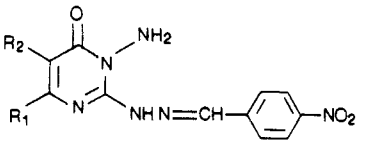
The mechanism of this isomerization may be rationalized in terms of an intermediate 1,5-dipolar species **5** obtained from **3** by initial protonation at N-4 in **3** followed

(4) Neunhoeffer, H. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Rees, C. W., Eds.; Pergamon: Oxford, 1984; Vol. 3, p 531.

Table IV. Substituted 3-Amino-2-hydrazino-4(3*H*)-pyrimidinones



8

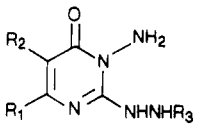


9

compd	R_1	R_2	R_3	yield, %	mp, °C	formula[a]
8a	CH_3	H	CH_3CO	89	226–228	$C_7H_{11}N_5O_2$
8b	CH_3	CH_3CH_2	p-$CH_3C_6H_4CO$	98	228–230	$C_{15}H_{19}N_5O_2$
8c	CH_3	H	p-$CH_3C_6H_4CO$	95	228–230	$C_{13}H_{15}N_5O_2 \cdot {}^1/_2H_2O$
8d	p-ClC_6H_4	H	CH_3CO	91	275 dec	$C_{12}H_{12}N_5O_2Cl$
8e	p-ClC_6H_4	H	p-$CH_3C_6H_4SO_2$	98	235 dec	$C_{17}H_{16}N_5O_3SCl$
9a	CH_3	CH_3CH_2		85	245 dec	$C_{14}H_{16}N_6O_3$
9b	C_6H_5	H		43	266–268 dec	$C_{17}H_{14}N_6O_3$
9c	p-ClC_6H_4	H		91	235 dec	$C_{17}H_{13}N_6O_3Cl$

[a] Satisfactory analyses were reported.

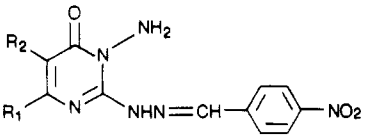
Table V



8

	^1H NMR measurements (δ)				
compd	R_1	R_2	R_3	NH_2	NH
8a	CH_3 (2.14)	H (5.76)	$COCH_3$ (1.94)	(5.45)	(9.0, 9.85)
8b	CH_3 (2.05)	CH_3CH_2(1.0; t) (2.35; q)	p-$CH_3C_6H_4CO$ (2.4; s) (7.3–7.8; q)	(5.5)	(8.9, 10.3)
8c	CH_3 (2.0)	H (5.7)	p-$CH_3C_6H_4CO$ (2.36; s) (7.3, 7.85; q)	(5.45)	(9.15, 10.36)
8d	p-ClC_6H_4 (7.5–8.05; q)	H (6.45)	$COCH_3$ (1.96)	(5.5)	(9.25, 9.9)
8e	p-ClC_6H_4 (7.45–7.85; q)	H (6.3)	p-$CH_3C_6H_4SO_2$ (2.1, s) (7.05–7.65; q)	(5.5)	(9.4, 9.9)

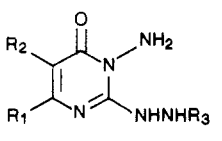
Table VI



9

	^1H NMR measurements (δ)					
compd	R_1	R_2	NO_2-C_6H_4	N=CH	NH_2	NH
9a	CH_3 (2.2)	CH_3CH_2(1.0; t) (2.35; q)	(7.95–8.35; q)	(8.55)	(5.55)	(11.14)
9b	C_6H_5 (7.5–8.05; m)	H (6.56)	(7.95–8.35; q)	(8.70)	(5.6)	(11.38)
9c	p-ClC_6H_4 (7.55–8.15; q)	H (6.6)	(7.95–8.35; q)	(8.70)	(5.65)	(11.4)

by generation of nitrile imine **4**. This nitrile imine undergoes ready electrocyclization to **2**. The primary amino function of the hydrazino substituent of **1** was found to be more reactive than the N-NH_2 group. As indicated earlier, refluxing of **1** with ortho esters in butanol overnight yielded **2**. In the absence of solvent, however, and when excess of the ortho ester was used, the triazolo[4,3-*a*]pyrimidinones **6**, in which the amino group had been converted into an imino ether, was obtained (Table III). Heating of **6** in acetic acid gave **2**. Other electrophilic reagents reacted with the hydrazino group of **1** in preference to the N-NH_2 group. Thus, sulfonyl chlorides in pyridine at room temperature gave the corresponding sulfonamides **8** (R_3 = SO_2R_4) (Table IV). Acyl halides under analogous conditions (or acetic anhydride) gave the corresponding amides **8** (R_3 = COR_4) and with *p*-nitrobenzaldehyde the corresponding benzal derivative **9** was obtained. NMR spectra of products **8** and **9** showed the characteristic N-NH_2 signal at δ 5.5–5.7 (Tables V and VI).



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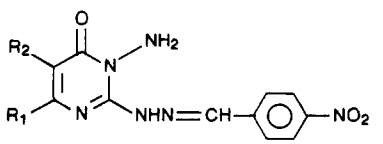

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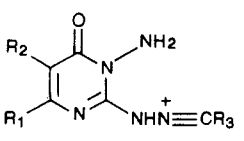

10

The structure **8a** was confirmed by nuclear Overhauser difference spectroscopy.[5] Oxidative ring closure of **9** with *N*-bromosuccinimide gave **3** (R_3 = C_6H_4-*p*-NO_2). These reactions suggest that in the formation of the ring-fused tetrazine **3** from **1**, initial reaction with the ortho ester occurs at the primary amino function of the hydrazine group to give an initial imino ether which then forms a nitrilium salt **10**. Cyclization of the *N*-NH_2 group onto the nitrilium salt to give **3** is a favored 6-endo dig process.[6]

Experimental Section

All melting points were taken on a Mel-Temp apparatus. Samples for elemental analysis were dried for 1–24 h under high vacuum. The ^1H NMR measurements were obtained on a Varian Model FT-80 spectrometer and chemical shift values are reported in δ downfield from tetramethylsilane internal standard. All spectra were taken in deuteriated dimethyl sulfoxide.

Crystallography. The colorless needlelike crystals of **2c** were obtained from the 1-butanol reaction solution and **3d** was recrystallized from tetrahydrofuran in pale needlelike crystals. Preliminary examination and data collection were performed with Cu Kα radiation on an Enraf-Nonius CAD4 computer controlled κ axis diffractometer equipped with a graphite crystal, incident beam monochromator. The structure **3d** consists of two crystallographyically independent (yet chemically identical) molecules. Both structures were solved by direct methods; all calculations were performed on a PDP-11/60 based TEXRAY[7] system (supplementary material).

General Procedures for the Synthesis of 8-Amino-1,2,4-triazolo[4,3-*a*]pyrimidin-7(8*H*)-ones (2). Method A. A suspension of 3-amino-2-hydrazino-5,6-dimethyl-4(3*H*)-pyrimidinone (**1**; R_1 = R_2 = CH_3) (1.94 g) in butanol (60 mL) and triethyl orthoformate (20 mL) was refluxed overnight and the resulting suspension cooled to room temperature. The crystalline product **2b** was collected, washed with butanol, and dried to give 1.37 g (67%) of colorless needles, mp 276–278 °C.

Method B. A solution of **1** (R_1 = R_2 = CH_3) (1.3 g; 0.0077 mol) and triethyl orthoformate (1.3 mL; 0.0077 mol) in glacial acetic acid (30 mL) was refluxed for 30 min and then kept at room temperature overnight. The solution was evaporated to dryness and the residue was recrystallized from methanol to give 1.04 g (76%) of **2b** as colorless needles, mp 276–278 °C.

General Procedures for the Synthesis of 1,4-Dihydro-6*H*-pyrimido[1,2-*b*][1,2,4,5]tetrazin-6-ones (3). Method A. A solution of 3-amino-2-hydrazino-6-methyl-4(3*H*)-pyrimidinone **1** (R_1 = CH_3, R_2 = H) (1.55 g; 0.01 mol) and triethyl orthoformate (1.48 g; 0.01 mol) in glacial acetic acid (10 mL) was kept at room temperature for 1 h. The crystalline precipitate was collected, washed with acetic acid and ether, and dried to give 0.37 g (23%) of **3a**: mp 215–220 °C. Dilution of the filtrate with ether gave 0.78 g (47%) of **2a**, mp 263–266 °C.

Method B. A solution of **1** (R_1 = CH_3, R_2 = H) (4.6 g; 0.03 mol) and dimethylformamide dimethyl acetal (3.5 g; 0.03 mol) in glacial acetic acid (30 mL) was kept at room temperature for 3 h. The crystalline precipitate was collected, washed with acetic acid and ether, and dried to give 0.49 g (10%) of **3a**: mp 215–220 °C. The filtrate was diluted with ether to give 2.19 g (45%) of **2a** as colorless crystals, mp 263–266 °C.

Method C. A solution of **1** (R_1 = CH_3, R_2 = H) (3.1 g; 0.02 mol) and diethoxymethyl acetate (3.24 g; 0.02 mol) in glacial acetic acid (20 mL was kept at room temperature for 1 h. The crystalline precipitate was collected, washed with acetic acid, ether and dried to give 0.5 g (15%) of **3a**, mp 215–220 °C. The filtrate was diluted with ether to give 1.5 g (45%) of **2a** as colorless crystals, mp 263–266 °C.

***N*-(3,5-Dimethyl-7-oxo-1,2,4-triazolo[4,3-*a*]pyrimidin-8-(7*H*)-yl)ethanimidic Acid Ethyl Ester (6b).** A suspension of **1** (R_1 = CH_3, R_2 = H) (1.82 g; 0.012 mol) in triethyl orthoacetate (60 mL) was refluxed overnight and the resulting solution cooled to room temperature. The crystalline precipitate was collected and dried to give 2.13 g (71%) of **6b**, mp 188–190 °C.

2′-(1-Amino-1,6-dihydro-4-methyl-6-oxo-2-pyrimidinyl)-acetohydrazide (8a). Acetic anhydride (1.88 mL; 0.02 mol) was added to a suspension of **1** (R_1 = CH_3, R_2 = H) (3.1 g; 0.02 mol) in anhydrous tetrahydrofuran (200 mL). The resulting solution was kept at room temperature overnight. The precipitated product was collected, washed with tetrahydrofuran, and dried to give 3.5 g (89%) of **8a**, mp 226–228 °C.

2′-(1-Amino-5-ethyl-1,6-dihydro-4-methyl-6-oxo-2-pyrimidinyl)-4-methylbenzohydrazide (8b). *p*-Toluoyl chloride (1.32 mL; 0.01 mol) was added to a suspension of **1** (R_1 = CH_3, R_2 = CH_3CH_2) (1.83 g; 0.01 mol) in anhydrous tetrahydrofuran containing triethylamine (1.4 mL; 0.01 mol). The reaction mixture was stirred at room temperature for 1 h and then evaporated to dryness. The residue was slurried in water (30 mL), stirred for 30 min, and filtered to give 2.96 g (98%) of **8b**, mp 228–230 °C.

2-[1-Amino-4-(4-chlorophenyl)-1,6-dihydro-6-oxo-2-pyrimidinyl]-4-methylbenzenesulfonohydrazide (8e). *p*-Toluenesulfonyl chloride (0.572 g; 0.0003 mol) was added to a suspension of **1** (R_1 = *p*-ClC_6H_4, R_2 = H) (0.755 g; 0.003 mol) in anhydrous pyridine (15 mL). The resulting solution was kept at room temperature overnight and then evaporated to dryness. The residue was slurred in water and filtered to give 1.2 g (89%) of **8e**, mp 235 °C dec. **4-Nitrobenzaldehyde (1-Amino-5-ethyl-6-oxo-4-methyl-2(1*H*)-pyrimidinyl)hydrazone (9a).** *p*-Nitrobenzaldehyde (0.825 g; 0.0055 mol) was added to the suspension of **1** (R_1 = CH_3; R_2 = CH_3CH_2) (1 g; 0.0055 mol) in ethanol (100 mL) containing a catalytic amount (3 drops) of acetic acid. The resulting solution was stirred at room temperature for 2 h and the orange suspension filtered to give 1.46 g (85%) of **9a**, mp 245 °C dec.

Isomerization of 3a. A suspension of **3a** (1 g) in glacial acetic acid (10 mL) was refluxed overnight and cooled to room temperature. The solution was evaporated to an oily residue. The oil was diluted with methanol (10 mL), and ether was added until crystals precipitated out and collected by filtration to give **7a** (52%), which is the acetyl derivative of **2a**.

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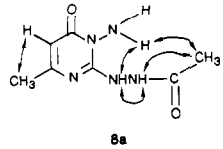
Registry No. **1**(R_1 = CH_3, R_2 = H), 95095-47-9; **1**(R_1 = R_2 = CH_3), 95095-48-0; **1**(R_1 = C_6H_5,R_2 = H), 95095-52-6; **1**(R_1 = CH_3, R_2 = Et), 95095-55-9; **1**(R_1 = *p*-C_6H_4Cl,R_2 = H), 95095-53-7; **2a**, 107769-19-7; **2b**, 107769-20-0; **2c**, 107769-21-1; **2d**, 107769-22-2; **2e**, 107769-23-3; **3a**, 107769-24-4; **3b**, 107769-25-5; **3c**, 107769-26-6; **3d**, 107769-27-7; **3e**, 107769-28-8; **6a**, 107769-29-9; **6b**, 107769-30-2; **6c**, 107769-31-3; **7a**, 107769-40-4; **8a**, 107769-32-4; **8b**, 107769-33-5; **8c**, 107769-34-6; **8d**, 107769-35-7; **8e**, 107769-36-8; **9a**, 107769-37-9; **9b**, 107769-38-0; **9c**, 107769-39-1; $CH(OEt)_3$, 122-51-0; $H_3CC(OEt)_3$, 78-39-7; 4-$O_2NC_6H_4CHO$, 555-16-8; $(H_3C)_2NCH(OCH_3)_2$, 4637-24-5; $H_3CO_2CCH(OEt)_2$, 14036-06-7; 4-$H_3CC_6H_4COCl$, 874-60-2.

Supplementary Material Available: Tables of crystal data, intensity measurements, structure solution and refinement, thermal parameters and standard deviation, temperature factor expressions, torsion angles, bond distances, bond angles, intermolecular constants and weighted least-square planes for compounds **2c** and **3d** (29 pages). Ordering information is given on any current masthead page.

(5) Dunne, T., unpublished work. The observed NOE's of **8a** are indicated by the double headed arrows.



8a

(6) Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734.

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