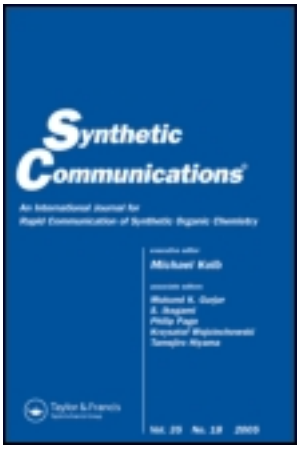

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Synthesis of Heterocyclic Compounds Using Amidines as Their Ene-1,1-diamine Tautomers, IV: Synthesis of N-Bridged Heterocycles 1,2,3,4-Tetrahydropyrido[1,2-a]pyrimidin-6-ones and Methyl 1,2,3,4-Tetrahydropyrrolo[1,2-a]pyrimidin-7-ylideneacetates

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SYNTHESIS OF HETEROCYCLIC COMPOUNDS USING AMIDINES AS THEIR ENE-1,1-DIAMINE TAUTOMERS, IV: SYNTHESIS OF *N*-BRIDGED HETEROCYCLES 1,2,3,4-TETRAHYDROPYRIDO[1,2-*a*]PYRIMIDIN-6-ONES AND METHYL 1,2,3,4-TETRAHYDROPYRROLO-[1,2-*a*]PYRIMIDIN-7-YLIDENEACETATES

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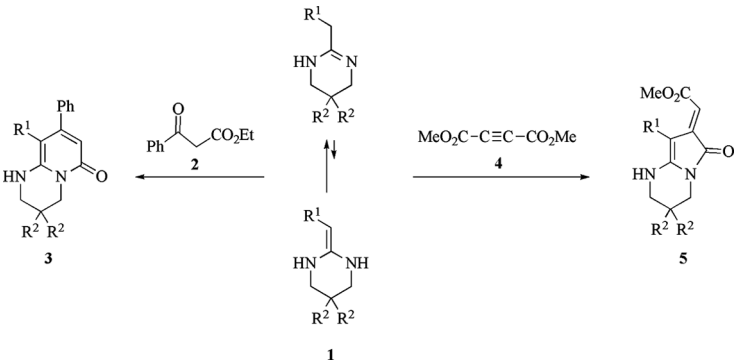
GRAPHICAL ABSTRACT



Abstract *2-Benzyl-1,4,5,6-tetrahydropyrimidines **1** (as ene-1,1-diamine* N,C*-tautomers) in diglyme reacted with ethyl benzoylacetate at 160°C in an oil bath to give 1,2,3,4-tetrahydropyrido[1,2-*a*]pyrimidin-6-ones **3** and with dimethyl acetylenedicarboxylate in methanol at room temperature, leading to methyl 1,2,3,4-tetrahydropyrrolo[1,2-*a*]pyrimidin-7-ylideneacetates **5**, respectively.*

Keywords Cyclic ene-1,1-diamine; dimethyl acetylenedicarboxylate; ethyl benzoylacetate; 1,2,3,4-tetrahydropyrido[1,2-*a*]pyrimidin-6-one,methyl; *N*-bridged heterocycles; 1,2,3,4-tetrahydropyrrolo[1,2-*a*]pyrimidin-7-ylideneacetate; α,β-unsaturated carbonyl compound

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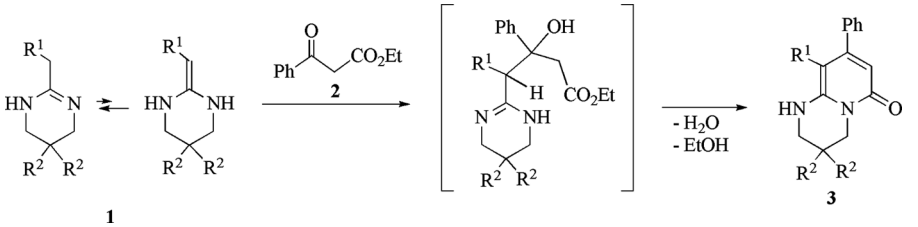
INTRODUCTION

Ene-1,1-diamines analogs of enamines are versatile reagents in the synthesis of heterocyclic compounds. Additionally, cyclic ene-1,1-diamines lead to construction of fused heterocyclic compounds by the reaction with bifunctional electrophiles,[1] although ene-1,1-diamines having electron-withdrawing group at the β-carbon reacts. For the *C*-alkylation of amidines (as ene-1,1-diamine *N,C*-tautomers), the reaction of *N*-monosubstituted arylacetamidines with arylidenemalononitrile,[2] tri-substituted amidines (2-alkylimino-*N*-methylpyrrolidines) with methyl acrylate,[3] 2-alkyl-4,5-dihydroimidazole with acetoacetate,[4] and arylacetamidines with α,β-unsaturated esters[5] were reported, respectively. In a previous article, we reported a facile synthesis for heterocycles by the reaction of amidines (via ene-1,1-diamines) with α,β-unsaturated carbonyl compounds.[6] In the course of our investigation of amidines (as ene-1,1-diamine *N,C*-tautomers), here we report the *C*-alkylation of 2-benzyl-1,4,5,6-tetrahydropyrimidines (**1**) with ethyl benzoylacetate (**2**) and dimethyl acetylenedicarboxylate (**4**), leading to 1,2,3,4-tetrahydropyrido[1,2-*a*] pyrimidin-6-ones (**3**) and methyl 1,2,3,4-tetrahydropyrrolo[1,2-*a*]pyrimidin-7-ylideneacetates (**5**), respectively.

RESULTS AND DISCUSSION

The synthesis of 1,2,3,4-tetrahydropyrido[1,2-*a*]pyrimidin-6-ones **3** was carried out at 160 °C in an oil bath by the reaction of 2-benzyl-1,4,5,6-tetrahydropyrimidines **1** with ethyl benzoylacetate **2** in diglyme. As shown in Scheme 1, cyclic amidines (as the ene-1,1-diamine *N,C*-tautomers) **1** reacted with **2** followed by elimination of water and ethanol to give condensed heterocycles **3** in 51–78% yields. The results are listed in Table 1. The structure of **3** was confirmed by elemental analysis, ^{1}H NMR, and ^{13}C NMR spectroscopic measurements. The ^{1}H NMR spectra showed signals corresponding to 1,2,3,4-tetrahydropyrido[1,2-*a*]pyrimidin-6-ones **3**. For **3a**–**f**, the ^{13}C NMR signals at δ 161.3, 161.7, 161.4, 161.5, 161.4, and 161.6 correspond to the carbonyl carbon of the amide group. These signals are revealed that amidines, 1,4,5,6-tetrahydropyrimidines **1** (as the ene-1,1-diamine *N,C*-tautomers), added to the β-carbonyl carbon of **2** followed by elimination of ethanol and water afford condensed heterocycles 1,2,3,4-tetrahydropyrido[1,2-*a*]pyrimidin-6-ones **3**.

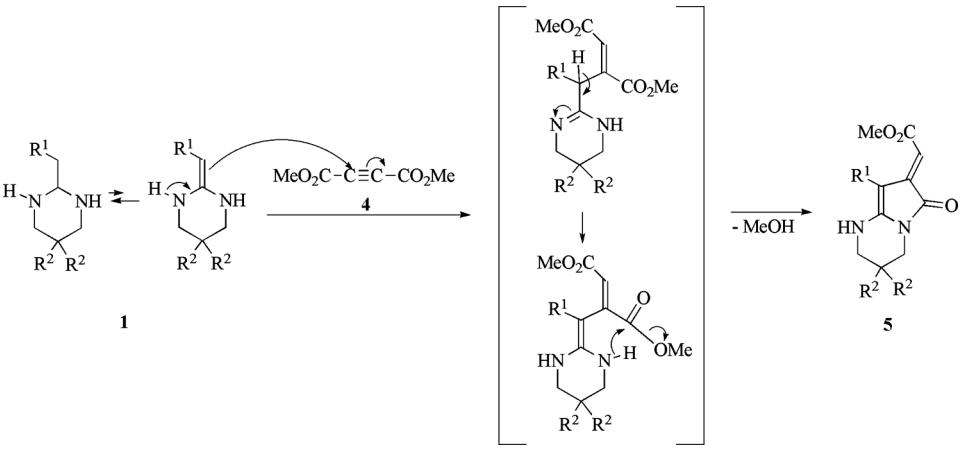
The methyl 1,2,3,4-tetrahydropyrrolo[1,2-a]pyrimidin-7-ylideneacetates **5** were prepared by the reaction of **1** with dimethyl acetylenedicarboxylate **4** in methanol at room temperature (Scheme 2, Table 2). The structures of **5** were confirmed on



Scheme 1.

Table 1. 1,2,3,4-Tetrahydropyrido[1,2-*a*]pyrimidin-6-ones **3**

Compd.	R1	R2	Temp. (°C)/Time (h)	Yield (%)
3a	Ph	H	160/5	63
3b	Ph	Me	160/5	78
3c	4-MePh	H	160/4	53
3d	4-MePh	Me	160/4	72
3e	4-MeOPh	H	160/5	51
3f	4-MeOPh	Me	160/5	69



Scheme 2.

Table 2. Methyl 1,2,3,4-tetrahydropyrrolo[1,2-*a*]pyrimidin-7-ylidene) acetates **5**

Compd.	R1	R2	Temp. (°C)/Time (h)	Yield (%)
5a	Ph	H	rt/0.5	43
5b	Ph	Me	rt/0.5	55
5c	4-MePh	H	rt/0.5	44
5d	4-MePh	Me	rt/0.5	60
5e	4-MeOPh	H	rt/1	37
5f	4-MeOPh	Me	rt/1	41

the basis of their elemental analysis and spectral data. The result of heteronuclear Overhauser effect spectroscopic (HOESY) analysis of **5c** provided the evidence that a proton at the α -position of the ester group was close to the carbon atom of amide group. On the basis of this information, compound **5c** was decided as the *E*-configuration for the ester group of the acrylate moiety, and also **5a,b** and **5d–f** were assigned to the same configuration as **5c**.

EXPERIMENTAL

All melting points are uncorrected. Infrared (IR) spectra were recorded on a Horiba FT-720 spectrometer as potassium bromide pellets. ^{1}H and ^{13}C NMR data were obtained using a Jeol JNM-ECX500 M (500-MHz) spectrometer in $CDCl_3$ with tetramethylsilane (0.03%) as an internal standard. Mass spectra of compounds **1a**–**f** were measured using a Shimadzu GC/MS-QP5050A spectrometer at 70 eV ionization energy using a direct-inlet system. For compounds **3** and **5**, matrix-assisted laser desorption/ionization time-of-flight mass spectroscopic (MALDI-TOF-MS) spectra were recorded on a Bruker AutoFlex II TOF/TOF mass spectrometer equipped with a nitrogen laser ($\lambda = 337$ nm), a pulsed ion extraction, and a reflector. The operation was performed at an accelerating potential of 20 kV for a reflector in positive ion mode. Samples for the MALDI analysis were prepared by mixing volumes of the matrix solution (*trans*-2-(2-methyl-3-phenyl-2-propylidene)malononitrile, called MPPM, 10 mg/mL in THF), sample solution (2 mg/mL in $CHCl_3$), and cationization reagent solution (2 mg/mL in THF) to obtain a 20:1:8 ratio (matrix/sample/TFANa) v/v. Elemental analysis was performed using a Perkin-Elmer 2400 II CHN Analyzer. *trans*-2-(2-Methyl-3-phenyl-2-propylidene)malononitrile (MPPM) as matrix for MALDI-TOF-MS analysis was synthesized by Knoevenagel reaction with α-methyl-*trans*-cinnamaldehyde and malononitrile at 65 °C for 1 h in ion-exchanged water under an argon atmosphere. ^{1}H NMR δ 2.41 (2H, d, $J = 1.2$ Hz), 7.14 (1H, br s), 7.46 (1H, d, $J = 0.9$ Hz), 7.39–7.49 (5H, m); ^{13}C NMR: δ 14.9, 81.0, 112.8, 114.4, 128.8, 130.1, 130.3, 133.4, 134.5, 149.6, 164.4. Anal. calcd. for $C_{17}H_{18}N_2O_3$: C, 80.39; H, 5.19; N, 14.42. Found: C, 80.67; H, 5.21; N, 14.56.

Starting Materials

2-Benzyl-1,4,5,6-tetrahydropyrimidines **1a**–**f** were prepared from the corresponding 1,3-diamines and ethyl 2-arylacetimidates[7] according to literature[8] by gently refluxing in diglyme.

2-Benzyl-1,4,5,6-tetrahydropyrimidine (1a)

This compound was obtained as white powder, 70% yield, mp 110–113 °C [lit.[8] mp 112–114 °C]; ^{1}H NMR: δ 1.74 (2H, quin, $J = 5.7$ Hz, CH_2), 3.30 (4H, br s, $2 \times NCH_2$), 3.46 (2H, s, CH_2), 4.11 (1H, br s, N*H*), 7.23–7.28 (3H, m, Ar-*H*), 7.32 (2H, t, $J = 7.5$ Hz, Ar-*H*); MS: (CI) m/z 175 (MH^+).

2-Benzyl-5,5-dimethyl-1,4,5,6-tetrahydropyrimidine (1b)

This compound was obtained as white prisms, 80% yield, mp 94–95 °C [lit.[9] mp 95–96 °C]; ^{1}H NMR: δ 0.91 (6H, s, $2 \times CH_3$), 2.93 (4H, br s, $2 \times CH_2$), 3.47 (2H, s, CH_2), 3.61 (1H, br s, N*H*), 7.24–7.29 (3H, m, Ar-*H*), 7.32 (2H, t, $J = 7.5$ Hz, Hz, Ar-*H*); MS: (CI) m/z 203 (MH^+).

2-(4-Methylbenzyl)-1,4,5,6-tetrahydropyrimidine (1c)

This compound was obtained as white powder, 65% yield, mp 114–116 °C; ^{1}H NMR: δ 1.73 (2H, quin, $J = 5.7$ Hz, CH_2), 2.33 (3H, s, Ar-CH_3), 3.29 (4H, br s,

$2 \times CH_2$), 3.42 (2H, s, CH_2), 7.13 and 7.16 (each 2H, d, $J = 8.0$ Hz, Ar-*H*), N*H* not observed; MS: (CI) m/z 189 (MH^+).

5,5-Dimethyl-2-(4-methylbenzyl)-1,4,5,6-tetrahydropyrimidine (1d)

This compound was obtained as white needles, 66% yield, mp 131–133 °C; ^{1}H NMR: δ 0.91 (6H, s, $2 \times CH_3$), 2.33 (3H, s, Ar-CH_3), 2.94 (4H, br s, $2 \times NCH_2$), 3.44 (2H, s, CH_2), 4.36 (1H, br s, N*H*), 7.13 and 7.17 (each 2H, d, $J = 8.0$ Hz, Ar-*H*); MS: (CI) m/z 217 (MH^+).

2-(4-Methoxybenzyl)-1,4,5,6-tetrahydropyrimidine (1e)

This compound was obtained as white powder, 54% yield, mp 118–121 °C; ^{1}H NMR: δ 1.73 (2H, quin, $J = 5.7$ Hz, CH_2), 3.29 (4H, br s, $2 \times NCH_2$), 3.41 (2H, s, CH_2), 3.80 (3H, s, OCH_3), 6.86 and 7.19 (each 2H, d, $J = 8.6$ Hz, Ar-*H*), N*H* not observed; MS: (CI) m/z 205 (MH^+).

2-(4-Methoxybenzyl)-5,5-dimethyl-1,4,5,6-tetrahdropyrimidine (1f)

This compound was obtained as white plates, 66% yield, mp 126–127 °C;^{1}H NMR: δ 0.91 (6H, s, $2 \times CH_3$), 2.92 (4H, br s, $2 \times NCH_2$), 3.42 (2H, s, CH_2), 3.80 (3H, s, OCH_3), 4.18 (1H, br s, N*H*) 6.86 and 7.19 (each 2H, d, $J = 8.6$ Hz, Ar-*H*); MS: (CI) m/z 233 (MH^+).

Ethyl benzoylacetate **2** and dimethyl acetylenedicarboxylate **4** purchased from Tokyo Chemical Industry Co. Ltd. were used without further purification. Other chemicals were purchased from commercial sources.

General Procedure for the Preparation of 1,2,3,4-Tetrahydropyrido-[1,2-*a*]pyrimidin-6-ones 3

In a flask equipped with a reflux condenser, a solution of 2-benzyl-1,4,5,6-tetrahydropyrimidines **1** (30 mmol) in diglyme (15 mL) was stirred at 160 °C in an oil bath. A solution of ethyl benzoylacetate **2** was added dropwise during a period of 1 h through a dropping funnel on the top of reflux condenser and then refluxed for 4 or 5 h (Table 1). After removal of solvent and low boiling materials in vacuo, residual products were filtered, washed with ethyl acetate, and recrystallized from ethyl acetate to give **3**.

Selected Data for 3a–3f

8,9-Diphenyl-1,2,3,4-tetrahydropyrido[1,2-*a*]pyrimidin-6-one (3a). This compound was obtained as pale yellow powder, mp 210–211 °C; IR: 3411, 1651 cm^{-1}; ^{1}H NMR: δ 2.08 (2H, quin, $J = 6.0$ Hz, CH_2), 3.31 (2H, td, $J = 6.0$, 2.5 Hz, $NHCH_2$), 4.15 (2H, t, $J = 6.0$ Hz, NCH_2), 4.83 (1H, br s, N*H*), 5.93 (1H, s, C*H*), 7.01 and 7.05 (each 2H, d, $J = 8.0$ Hz, Ar-*H*), 7.08–7.12 (3H, m, Ar-*H*), 7.18 (1H, t, $J = 7.4$ Hz, Ar-*H*), 7.23–7.27 (2H, m, Ar-*H*); ^{13}C NMR: δ 20.4, 39.4, 39.9, 100.5, 103.3, 127.1, 127.5, 128.6, 128.9, 132.1, 135.3, 139.8, 147.1, 153.5, 161.3;

MS: (MALDI) m/z 302.1 (M^+). Anal. calcd. for $C_{20}H_{18}N_2O$: C, 79.44; H, 6.00; N, 9.26. Found: C, 79.52; H, 6.12; N, 9.31.

3,3-Dimethyl-8,9-diphenyl-1,2,3,4-tetrahydropyrido[1,2-*a*]pyrimidin-6-one (3b). This compound was obtained as pale yellow powder, mp 221–223 °C; IR: 3307, 1649 cm^{-1}; ^1H NMR: δ 1.13 (6H, s, $2 \times CH_3$), 2.97 (2H, d, $J = 2.6$ Hz, $NHCH_2$), 3.86 (2H, s, NCH_2), 4.81 (1H, br s, NH), 5.95 (1H, s, CH), 7.02–7.06 (4H, m, Ar-H), 7.09–7.13 (3H, m, Ar-H), 7.21 (1H, t, $J = 7.5$ Hz, Ar-H), 7.26 (2H, t, $J = 7.5$ Hz, Ar-H); ^{13}C NMR: δ 24.4, 27.4, 51.0, 51.1, 100.2, 103.6, 127.3, 127.6, 128.8, 129.1, 132.2, 135.5, 139.8, 146.2,153.6, 161.7; MS: (MALDI) m/z 330.2 (M^+). Anal. calcd. for $C_{22}H_{22}N_2O$: C, 79.97; H, 6.71; N, 8.48. Found: C, 79.98; H, 6.80; N, 8.52.

8-Phenyl-9-(4-methylphenyl)-1,2,3,4-tetrahydropyrido[1,2-*a*]pyrimidin-6-one (3c). This compound was obtained as pale yellow powder, mp 218–220 °C; IR: 3278, 1653 cm^{-1}; ^1H NMR: δ 2.08 (2H, quin, $J = 6.0$ Hz, CH_2), 2.28 (3H, s, Ar-CH_3), 3.31 (2H, td, $J = 6.0$, 2.5 Hz, $NHCH_2$), 4.15 (2H, t, $J = 6.0$ Hz, NCH_2), 4.81 (1H, br s, NH), 5.93 (1H, s, CH), 6.93 (2H, d, $J = 8.0$ Hz, Ar-H), 7.02–7.06 (4H, m, Ar-H), 7.11–7.13 (3H, m, Ar-H); ^{13}C NMR: δ 20.5, 21.2, 39.5, 40.0, 100.5, 103.4, 127.2, 127.6, 128.7, 129.8, 131.9, 132.1, 136.9, 140.0, 147.3, 153.6, 161.4; MS: (MALDI) m/z 316.2 (M^+). Anal. calcd. for $C_{21}H_{20}N_2O$: C, 79.72; H, 6.37; N, 8.85. Found: C, 79.44; H, 6.54; N, 8.86.

3,3-Dimethyl-8-phenyl-9-(4-methylphenyl)-1,2,3,4-tetrahydropyrido[1,2-a]pyrimidin-6-one (3d). This compound was obtained as pale yellow powder, mp 223–225 °C; IR: 3248, 1655 cm^{-1}; ^1H NMR: δ 1.12 (6H, s, $2 \times CH_3$), 2.29 (3H, s, Ar-CH_3), 2.96 (2H, d, $J = 2.6$ Hz, $NHCH_2$), 3.84 (2H, s, NCH_2), 4.84 (1H, br s, NH), 5.93 (1H, s, CH), 6.93 (2H, d, $J = 8.0$ Hz, Ar-H), 7.03–7.06 (4H, m, Ar-H), 7.09–7.12 (3H, m, Ar-H); ^{13}C NMR: δ 21.2, 24.3, 27.3, 51.0, 100.1, 103.3, 127.2, 127.6, 128.7, 129.8, 131.9, 132.2, 136.9, 139.9, 146.3, 153.5, 161.5; MS: (MALDI) m/z 344.2 (M^+). Anal. calcd. for $C_{23}H_{24}N_2O$: C, 80.20; H, 7.02; N, 8.13. Found: C, 80.31; H, 7.20; N, 8.19.

9-(4-Methoxyphenyl)-8-phenyl-1,2,3,4-tetrahydropyrido[1,2-*a*]pyrimidin-6-one (3e). This compound was obtained as yellow powder, mp 214–216 °C; IR: 3264, 1649 cm^{-1}; ^1H NMR: δ 2.08 (2H, quin, $J = 6.0$ Hz, CH_2), 3.32 (2H, td, $J = 6.0$, 2.5 Hz, $NHCH_2$), 3.76 (3H, s, OCH_3), 4.16 (2H, t, $J = 6.0$ Hz, NCH_2), 4.77 (1H, br s, NH), 5.93 (1H, s, CH), 6.78 and 6.96 (each 2H, d, $J = 8.6$ Hz, Ar-H), 7.02–7.04 (2H, m, Ar-H), 7.11–7.13 (3H, m, Ar-H); ^{13}C NMR: δ 20.6, 39.5, 40.0, 55.2, 100.2, 103.4, 114.5, 127.2, 127.7, 128.7, 133.3, 140.0, 147.4, 153.8, 158.7, 161.4; MS: (MALDI) m/z 332.2 (M^+). Anal. calcd. for $C_{21}H_{20}N_2O_2$: C, 75.88; H, 6.06; N, 8.43. Found: C, 75.80; H, 6.21; N, 8.46.

9-(4-Methoxyphenyl)-3,3-dimethyl-8-phenyl-1,2,3,4-tetrahydropyrido[1,2-*a*]pyrimidin-6-one (3f). This compound was obtained as yellow powder, mp 217–218 °C; IR: 3234, 1653 cm^{-1}; ^1H NMR: δ 1.12 (6H, s, $2 \times CH_3$), 2.97 (2H, d, $J = 2.3$ Hz, $NHCH_2$), 3.76 (3H, s, OCH_3), 3.85 (2H, s, $NHCH_2$), 4.80 (1H, br s, NH), 5.93 (1H, s, CH), 6.79 and 6.96 (each 2H, d, $J = 8.6$ Hz, Ar-H), 7.03–7.05 (2H, m, Ar-H), 7.10–7.13 (3H, m, Ar-H); ^{13}C NMR: δ 24.3, 27.4, 51.0 (overlapped

two carbon atoms), 55.2, 99.8, 103.3, 114.5, 127.2, 127.3, 127.6, 153.7, 158.6, 161.6; MS: (MALDI) m/z 360.2 (M^+). Anal. calcd. for $C_{23}H_{24}N_2O_2$: C, 76.64; H, 6.71; N, 7.77. Found: C, 76.74; H, 6.89; N, 7.82.

General Procedure for the Preparation of Methyl 1,2,3,4-Tetrahydropyrrolo[1,2-*a*]pyrimidin-7-ylideneacetates 5

A solution of dimethyl acetylenedicarboxylate **4** (45 mmol) in methanol (15 mL) was added dropwise to a stirred solution of 2-benzyl-1,4,5,6-tetrahydropyrimidines **1** (30 mmol) in methanol (15 mL) at rt over 30 min. After stirring the reaction mixture at rt for 1 h the precipitated material was collected by filtration, then washed with ethyl acetate. The desired products **5** (Table 2) were of satisfactory purity, as determined by ^{1}H NMR spectroscopy. Samples for analysis were recrystallized from ethyl acetate.

Selected Data for 5a–5f

Methyl (*E*)-(6-oxo-8-phenyl-1,2,3,4-tetrahydropyrrolo[1,2-*a*]pyrimidin-7-ylidene)acetate (5a). This compound was obtained as orange powder, mp 193–195 °C; IR: 3350, 1710, 1670 cm^{-1}; ^{1}H NMR: δ 2.07 (2H, quin, $J = 6.0$ Hz, CH_2), 3.41 (2H, td, $J = 6.0$, 2.9 Hz, NHCH_2), 3.75 (3H, s, OCH_3), 4.06 (2H, t, $J = 6.0$ Hz, NCH_2), 5.97 (1H, s, C*H*), 6.57 (1H, br s, N*H*), 7.12 (1H, t, $J = 7.4$ Hz, Ar-*H*), 7.31 (2H, t, $J = 8.0$ Hz, Ar-*H*), 7.36 (2H, d, $J = 8.3$ Hz, Ar-*H*); ^{13}C NMR: δ 21.5, 39.2, 43.1, 51.6, 92.9, 95.8, 125.3, 127.2, 128.8, 131.5, 145.0, 162.9, 166.5, 176.6; MS: (MALDI) m/z 284.1 (MH^+). Anal. calcd. for $C_{16}H_{16}N_2O_3$: C, 67.59; H, 5.67; N, 9.85. Found: C, 67.80; H, 5.71; N, 9.96.

Methyl (*E*)-(3,3-dimethyl-6-oxo-8-phenyl-1,2,3,4-tetrahydropyrrolo[1,2-*a*]-pyrimidin-7-ylidene)acetate (5b). This compound was obtained as orange powder, mp 233–235 °C; IR: 3330, 1705, 1668 cm^{-1}; ^{1}H NMR: δ 1.14 (6H, s, 2 × CH_3), 3.15 (2H, d, $J = 3.2$ Hz, NHCH_2), 3.76 (3H, s, OCH_3), 3.82 (2H, s, NCH_2), 6.05 (1H, s, C*H*), 6.21 (1H, br s, N*H*), 7.16 (1H, t, $J = 7.4$ Hz, Ar-*H*), 7.36 and 7.43 (each 2H, d, $J = 8.3$ Hz, Ar-*H*); ^{13}C NMR: δ 24.4, 29.6, 50.8, 51.8, 54.6, 92.7, 96.0, 125.4, 127.2, 129.1, 131.7, 145.4, 162.2, 166.6, 177.0; MS: (MALDI) m/z 312.2 (MH^+). Anal. calcd. for $C_{18}H_{20}N_2O_3$: C, 69.21; H, 6.45; N, 8.97. Found: C, 69.39; H, 6.58; N, 8.92.

Methyl (*E*)-(6-oxo-8-(4-methylphenyl)-1,2,3,4-tetrahydropyrrolo[1,2-*a*]-pyrimidin-7-ylidene)acetate (5c). This compound was obtained as orange powder, mp 202–203 °C; IR: 3359, 1709, 1662 cm^{-1}; ^{1}H NMR: δ 2.11 (2H, quin, $J = 6.0$ Hz, CH_2), 2.31 (3H, s, Ar-CH_3), 3.44 (2H, td, $J = 6.0$, 2.9 Hz, NHCH_2), 3.75 (3H, s, OCH_3), 4.09 (2H, t, $J = 6.0$ Hz, NCH_2), 6.01 (1H, s, C*H*), 6.30 (1H, br s, N*H*), 7.15 and 7.28 (each 2H, d, $J = 8.2$ Hz, Ar-*H*); ^{13}C NMR: δ 21.2, 21.6, 39.2, 43.1, 51.7, 93.1, 95.6, 127.4, 128.5, 129.5, 134.9, 145.3, 163.0, 166.8, 176.6; MS: (MALDI) m/z 298.1 (MH^+). Anal. calcd. for $C_{17}H_{18}N_2O_3$: C, 68.44; H, 6.08; N, 9.39. Found: C, 68.63; H, 6.09; N, 9.39.

Methyl (*E*)-(3,3-dimethyl-6-oxo-8-(methylphenyl)-1,2,3,4-tetrahydropyrrolo[1,2-*a*]pyrimidin-7-ylidene)acetate (5d). This compound was obtained as orange powder, mp 241–242 °C; IR: 3327, 1713, 1664 cm^{-1}; ^1H NMR: δ 1.13 (6H, s, $2 \times CH_3$), 2.32 (3H, s, Ar-CH_3), 3.13 (2H, d, $J = 2.6$ Hz, $NHCH_2$), 3.75 (3H, s, OCH_3), 3.80 (2H, s, NCH_2), 6.03 (1H, s, CH), 6.18 (1H, br s, NH), 7.18 and 7.31 (each 2H, d, $J = 8.2$ Hz, Ar-H); ^{13}C NMR: δ 21.3, 24.4, 29.6, 50.9, 51.8, 54.6, 92.6, 95.9, 127.2, 128.6, 129.7, 135.1, 145.5, 162.2, 166.7, 177.1; MS: (MALDI) m/z 326.2 (MH^+). Anal. calcd. for $C_{19}H_{22}N_2O_3$: C, 69.92; H, 6.79; N, 8.58. Found: C, 70.02; H, 6.82; N, 8.51.

Methyl (*E*)-(8-(4-methoxyphenyl)-6-oxo-1,2,3,4-tetrahydropyrrolo[1,2-*a*]pyrimidin-7-ylidene)acetate (5e). This compound was obtained as orange powder, mp 172–174 °C; IR: 1701, 1664 cm^{-1}; ^1H NMR: δ 2.12 (2H, quin, $J = 6.0$ Hz, CH_2), 3.45 (2H, td, $J = 6.0$, 2.9 Hz, $NHCH_2$), 3.75 and 3.78 (each 3H, s, OCH_3), 4.10 (2H, t, $J = 6.0$ Hz, NCH_2), 6.01 (1H, s, CH), 6.23 (1H, br s, NH), 6.90 and 7.30 (each 2H, d, $J = 8.9$ Hz, Ar-H); ^{13}C NMR: δ 21.7, 39.3, 43.1, 51.7, 55.4, 92.8, 95.8, 114.5, 123.8, 128.9, 145.3, 157.5, 163.1, 166.7, 176.7; MS: (MALDI) m/z 314.1 (MH^+). Anal. calcd. for $C_{17}H_{18}N_2O_4$: C, 64.96; H, 5.77; N, 8.9. Found: C, 64.91; H, 5.86; N, 8.87.

Methyl (*E*)-(8-(4-methoxyphenyl)-3,3-dimethyl-6-oxo-1,2,3,4-tetrahydropyrrolo[1,2-*a*]pyrimidin-7-ylidene)acetate (5f). This compound was obtained as orange powder, mp 214–215 °C; IR: 1701, 1664 cm^{-1}; ^1H NMR: δ 1.09 (6H, s, $2 \times CH_3$), 3.07 (2H, s, $NHCH_2$), 3.74 (3H, s, OCH_3), 3.76 (2H, s, NCH_2), 3.77 (3H, s, OCH_3), 5.94 (1H, s, CH), 6.55 (1H, br s, NH), 6.87 and 7.29 (each 2H, d, $J = 8.8$ Hz, Ar-H); ^{13}C NMR: δ 24.3, 29.5, 50.7, 51.7, 54.4, 55.3, 92.6, 95.5, 114.4, 123.8, 128.9, 145.7, 157.5, 162.3, 166.6, 176.7; MS: (MALDI) m/z 342.2 (MH^+), 342.09. Anal. calcd. for $C_{19}H_{22}N_2O_4$: C, 66.65; H, 6.48; N, 8.18. Found: C, 66.73; H, 6.45; N, 8.26.

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