Studies on Pyrimidine-Annulated Heterocycles: A Short Synthesis of Novel 6,9-Disubstituted Cyclohepta[*b*]pyrimido[5,4-*d*]pyrrole-8(6*H*),10(9*H*)-diones

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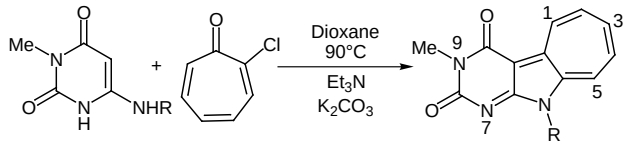
Abstract: A number of 6,9-disubstituted cyclohepta[*b*]pyrimido[5,4-*d*]pyrrole-8(6*H*),10(9*H*)-dione derivatives have been synthesized in good to moderate yields by the reaction of 6-amino-3-methyluracil derivatives with 2-chlorotropone in an enamine-alkylation process, subsequent condensation of the amino group with the carbonyl function, dehydrochlorination, and dehydration.

Key words: cyclohepta[*b*]pyrimido[5,4-*d*]pyrrole, 1-azaazulene, 2-chlorotropone, 6-amino-3-methyluracil, enamine-alkylation

The importance of fused pyrimidines, which are common sources for the development of new potential therapeutic agents,[1,2] is well known. Among these, 5-deazaflavins (5-deazaalloxazines and 5-deazaisoalloxazines) have been studied extensively in both enzymatic[3] and model systems[4,5] in the hopes of providing mechanistic insight into flavin-catalyzed reactions. Several routes for the preparation of 5-deaza-flavins have been previously described.[5-9] We have been interested recently in exploiting the unique reactivity afforded by the vinyliminophosphoranes[10,11] and related compounds[12,13] in developing efficient strategies for the preparation of fused heterocycles. In most cases, a few easy reaction steps enable the synthesis of novel and highly interesting types of condensed heterocycles, which are difficult to obtain by other synthetic means. Since 1-azaazulene derivatives have also attracted much attention in view of their pharmacological activities,[14,15] we have previously reported a methodology to synthesize 7,9-dialkylcyclohepta[*b*]pyrimido[5,4-*d*]pyrrole-8(7*H*),10(9*H*)-dione derivatives (structural isomer of 5-deazaalloxazine).[16] In this context, as well as to pursue our interest in enzymatic or catalytic functionalities, we now report a new facile synthesis of novel cyclohepta[*b*]pyrimido[5,4-*d*]pyrrole-8(6*H*),10(9*H*)-dione derivatives (structural isomer of 5-deazaisoalloxazine), by the reaction of 6-amino-3-methyluracil derivatives with 2-chlorotropone.

The starting 6-amino-3-methyluracil derivatives **1a, b**[17] and **1g–i**[18,19] are prepared easily as described in the literature. The new 6-amino-3-methyluracils **1c–f**, also used in this study, are prepared by a similar procedure.[17-19] The physical data of **1c–f** are satisfactory and are summarized in Tables 1 and 2. The reaction of uracils **1a–i** with 2-chlorotropone (**2**) in dioxane in the presence of Et_3N and K_2CO_3 at 90 °C leads directly to the 6,9-disubstituted cyclohepta[*b*]pyrimido[5,4-*d*]pyrrole-8(6*H*),10(9*H*)-dione derivatives **3a–i**, respectively (Scheme 1). The yields of the products **3a–i** are also summarized in Table 1. The structures of the new compounds **3a–i** were unequivocally assigned on the basis of the microanalyses and the spectral data (Tables 1, 2). The mass spectra showed the expected molecular ion peaks, and the IR spectra showed two absorption bands in the region of ν = 1685–1683 and 1637–1635 cm^{-1} due to the two carbonyl groups (Table 2). In the ^1H NMR spectra, the characteristic chemical shifts of H-1 were found at a low field of δ = 9.26–9.37 as a doublet, owing to the deshielding effect of the C-10 carbonyl group.[16,20] Meanwhile, the ^{13}C NMR spectra showed two signals at δ = 159.75–161.45 and 164.24–165.15 due to the two carbonyl groups (Table 2). The UV–VIS spectra of compounds **3a–i** (Table 1) appeared at longer wavelengths as compared to those of 7,9-dialkylcyclohepta[*b*]pyrimido[5,4-*d*]pyrrole-8(7*H*),10(9*H*)diones.[16]



1a-i **2** **3a-i**

1, 3	R	Reaction Time / h	1, 3	R	Reaction Time / h
a	Me	25	**f**	4-$ClC_6H_4CH_2$	5
b	Bn	4	**g**	Ph	20
c	4-$MeOC_6H_4CH_2$	3	**h**	4-$MeOC_6H_4$	1
d	4-$MeC_6H_4CH_2$	3	**i**	4-ClC_6H_4	28
e	4-$FC_6H_4CH_2$	3			

Scheme 1

Nucleophilic substitution onto a tropone carrying a mobile substituent is known to take place at C-2 (usual substitution) or at C-7 (unusual substitution) to give 2-substituted tropones.[21] The present reaction of **1a–i** with **2** to give **3a–i** apparently does not involve a straightforward displacement of the halide ion by the enamine-alkylation. Thus, the reaction pathways were proven by labelling the troponoid ring with deuterium. The reaction of **1a** with 2-chloro-3,5,7-trideuteriotropone (**4**) gave a mixture of **7** and **9** in a ratio of 3:1 (Scheme 2). The structural assignment of the mixture was based on HRMS and ^1H NMR spectral data. The HRMS of the mixture showed peaks for

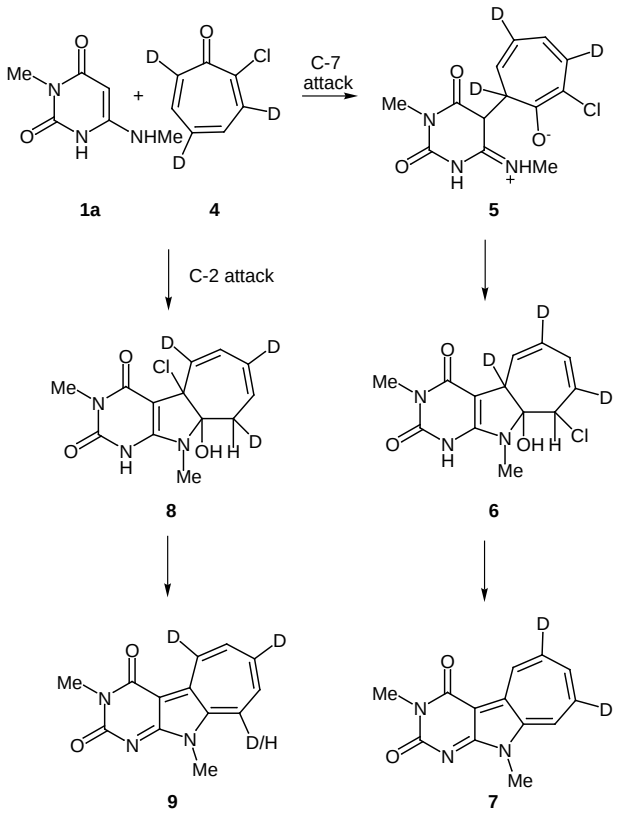
Table 1 6-Amino-3-methyluracils **1c–f** and 6,9-Disubstituted Cyclohepta[*b*]pyrimido[5,4-*d*]pyrrole-8(6*H*),10(9*H*)-diones **3a–i**

Compound	Yield (%)[a]	Mp (°C)	Molecular Formula[b] (MW)	MS (70 eV) *m/z* (%)	UV (MeCN) λ_{max} (log ε) (nm)
1c	93	273–275	$C_{13}H_{15}N_3O_3$ (261.3)	261 (M^+, 3), 121 (100)	
1d	94	277–279	$C_{13}H_{15}N_3O_2$ (245.3)	245 (M^+,10), 105 (100)	
1e	97	288–290	$C_{12}H_{12}FN_3O_2$ (249.2)	249 (M^+, 63), 109 (100)	
1f	93	288–290	$C_{12}H_{12}ClN_3O_2$ (265.7)	265 (M^+, 6), 125 (100)	
3a	78	298–300	$C_{13}H_{11}N_3O_2$ (241.3)	241 (M^+, 100)	243 (4.19), 298 (4.74), 359 (4.01), 432 (3.46)
3b	85	269–270	$C_{19}H_{15}N_3O_2$ (317.4)	317 (M^+, 24), 91 (100)	251 (4.28), 292 (4.44), 456 (4.33)
3c	89	238–240	$C_{20}H_{17}N_3O_3$ (347.4)	347 (M^+, 40), 121 (100)	229 (4.38), 252 (4.39), 290 (4.53), 456 (4.46)
3d	86	232–234	$C_{20}H_{17}N_3O_2$ (331.4)	331 (M^+, 5), 105 (100)	252 (4.41), 290 (4.55), 457 (4.37)
3e	87	285–286	$C_{19}H_{14}FN_3O_2$(335.3)	335 (M^+, 61), 109 (100)	251 (4.34), 292 (4.49), 455 (4.38)
3f	74	293–295	$C_{19}H_{14}ClN_3O_2$ (351.8)	351 (M^+, 5), 125 (100)	220 (4.36), 252 (4.34), 292 (4.49), 455 (4.37)
3g	87	>320	$C_{18}H_{13}N_3O_2$ (303.3)	303 (M^+, 13), 77 (100)	253 (4.35), 293 (4.46), 456 (4.38)
3h	93	>320	$C_{19}H_{15}N_3O_3$ (333.3)	333 (M^+, 100)	233 (4.41), 252 (4.38), 290 (4.35), 456 (4.34)
3i	49	>320	$C_{18}H_{12}ClN_3O_2$(337.8)	339 (M^+,18), 337 (100)	230 (4.36), 252 (4.33), 294 (4.42), 455 (4.38)

[a] Yield of isolated pure product based on 6-chloro-3-methyluracil for **1c–f** and 6-amino-3-methyluracil for **3a–i**.
[b] Satisfactory microanalysis: C±0.27, H±0.33, N±0.19.

$C_{13}H_9D_2N_3O_2$ and for $C_{13}H_8D_3N_3O_2$. The ^{1}H NMR spectrum showed, besides the methyl group, three other signals at δ = 9.26 (s, 1H, H-1), δ = 7.87 (s, 1H, H-3), and δ = 7.74 (s, 1H, H-5) for **7** and one other signal overlapping at δ = 7.87 (s, 0.7H, H-2 and H-4) for **9**. On the basis of this assignment, the ratio of **7**/**9** was deduced as 3:1, and the mechanistic pathways for the reaction of **1a** with tropone **4** were deduced as shown in Scheme 2. The initial enamine- alkylation takes place at C-7 as well as at C-2, and the following hydrogen migration and condensation lead to the intermediates **6** and **8**. Elimination of DCl and HCl in addition to dehydration easily gives the final products **7** and **9**, respectively. Compounds **1a–i** are expected to react with **2** in a similar way. In conclusion, 6-substituted-amino-3-methyluracils **1a–i** are confirmed to react with 2-chlorotropone (**2**) to provide a convenient route to novel uracil-annulated 1-azaazulene derivatives, which are the isomers of 5-deazaflavins (5-deazaisoalloxazines). Interestingly, it was found that compounds **3a, b, g**, like the 5- deazaflavins, oxidize benzyl alcohol in the presence of potassium carbonate and air to give benzaldehyde in more than 100% yield based on the starting **3a, b, g**. Under these conditions, the 1,7-, 5,7-, or 3,7-dihydrocyclohepta[*b*]pyrimido[5,4-*d*]pyrrole-8(6*H*),10(9*H*)-diones initially formed are reoxidized to the original compounds **3a, b, g** by adventitious oxygen, so that the compounds act as turnover catalysts. The details will be reported in a separate paper in due course.

Mps are uncorrected. IR and UV spectra were recorded on Horiba FT-710 and Shimadzu UV-3101PC spectrophotometers. The ^{1}H NMR spectra were recorded on a JEOL JNM-300 spectrometer; the



Scheme 2

Table 2 Spectral Data of 6-Amino-3-methyluracils **1c–f** and 6,9-Disubstituted Cyclohepta[*b*]pyrimido[5,4-*d*]pyrrole-8(6*H*),10(9*H*)-diones **3a–i**

Compound	IR ν (cm^{-1})[a]	^1H NMR (300 MHz) (solvent/TMS)[b] δ, *J* (Hz)	^{13}C NMR (126 MHz) (solvent/TMS)[b] δ
1c	1717, 1600	3.01 (s, 3 H, MeN), 3.73 (s, 3 H, MeO), 4.19 (d, 2 H, *J* = 5.7, CH_2), 4.55 (s, 1 H, H-5), 6.53 (br t, 1 H, NH-6), 6.91 (d, 2 H, *J* = 8.8, H-3', H-5'), 7.24 (d, 2 H, *J* = 8.8, H-2', H-6')	25.74, 44.28, 54.97, 73.20, 113.83, 128.39, 129.53, 150.78, 152.17, 158.43, 162.95
1d	1718, 1604	2.28 (s, 3 H, MePh), 3.01 (s, 3 H, MeN), 4.22 (d, 2 H, *J* = 5.7, CH_2), 4.53 (s, 1 H, H-5), 6.48 (br t, 1 H, NH-6), 7.16 (d, 2 H, *J* = 8.0, H-3', H-5'), 7.20 (d, 2 H, *J* = 8.0, H-2', H-6'), 10.23 (br s, 1 H, NH-1)	20.56, 25.80, 44.51, 73.27, 126.99, 128.95, 134.77, 136.22, 150.84, 150.22, 162.96
1e	1717, 1600	3.01 (s, 3 H, Me), 4.26 (d, 2 H, *J* = 6.0, CH_2), 4.55 (s, 1 H, H-5), 6.55 (br t, 1 H, NH-6), 7.17 (t, 2 H, *J* = 8.8, H-2', H-6'), 7.35 (dd, 2 H, *J* = 5.7, 8.8, H-3', H-5'), 10.29 (s, 1 H, H-1)	5.81, 43.94, 73.33, 115.13 (d, *J* = 22), 129.02 (d, *J* = 9), 134.11 (d, *J* = 2), 150.86, 152.20, 161.53 (d, *J* = 242), 162.97
1f	1729, 1691, 1574	3.01 (s, 3 H, MeN), 4.28 (d, 2 H, *J* = 6.1, CH_2), 4.52 (s, 1 H, H-5), 6.58 (br t, 1 H, NH-6), 7.33 (d, 2 H, *J* = 8.4, H-2', H-6'), 7.40 (d, 2 H, *J* = 8.4, H-3', H-5'), 10.33 (br s, 1 H, H-1)	25.80, 43.94, 73.40, 128.32, 128.79, 131.57,137.07, 150.86, 152.21, 162.95
3a	1684, 1636, 1600	3.47 (s, 3 H, Me-9), 3.96 (s, 3 H, Me-6), 7.69–7.78 (m, 1 H, H-5), 7.85–7.96 (m, 3 H, H-2, H-3, H-4), 9.26 (d,1 H, *J* = 10.5, H-1)	27.50, 28.42, 99.32, 121.60, 132.22, 135.52, 135.85, 138.34, 143.14, 148.47, 159.60, 161.45, 164.23
3b	1684, 1637, 1587	3.52 (s, 3 H, Me-9), 5.69 (s, 2 H, CH_2), 7.26–7.33 (m, 5 H, Ph), 7.66–7.90 (m, 4 H, H-2, H-3, H-4, H-5), 9.29 (d, 1 H, *J* = 10.6, H-1)	27.58, 44.65, 99.36, 122.24, 128.67, 129.38, 132.49,133.10, 134.39, 135.80, 135.98, 138.68, 143.78, 148.10, 159.71, 161.57, 164.24
3c	1684, 1636, 1588	3.52 (s, 3 H, Me-9), 3.76 (s, 3 H, MeO), 5.62 (s, 2 H, CH_2), 6.83 (d, 2 H, *J* = 8.6, H-3', H-5'), 7.24 (d, 2 H, *J* = 8.6, H-2', H-6'), 7.63–7.78 (m, 2 H, H-3, H-5), 7.82–7.93 (m, 2 H, H-2, H-4), 9.28 (d, 1 H, *J* = 10.5, H-1)	27.55, 44.87, 55.30, 99.26, 114.50, 122.53, 126.69, 128.79, 132.35, 135.60, 135.96, 138.44, 143.66, 148.28, 159.56, 159.84, 161.68, 164.28
3d	1684, 1635, 1598, 1588	2.30 (s, 3 H, MePh), 3.51 (s, 3 H, Me-9), 5.64 (s, 2 H, CH_2), 7.11 (d, 2 H, *J* = 8.1, H-3', H-5'), 7.16 (d, 2 H, *J* = 8.1, H-2', H-6'), 7.63–7.93 (m, 4 H, H-2, H-3, H-4, H-5), 9.28 (d, 1 H, *J* = 10.5, H-1)	21.10, 27.54, 45.15, 99.24, 122.63, 127.26, 129.78, 131.60, 132.36, 135.63, 136.01, 138.19, 138.46, 143.65, 148.31, 159.86, 161.67, 164.28
3e[c]	1684, 1635, 1588	3.51 (s, 3 H, Me-9), 5.65 (s, 2 H, CH_2), 7.01 (t, 2 H, *J* = 8.6, H-2', H-6'), 7.27 (t, 2 H, *J* = 8.6, H-3', H-5'), 7.68–7.80 (m, 3 H, H-3, H-4, H-5), 7.91 (t, 1 H, *J* = 10.5, H-2), 9.29 (d, 1 H, *J* = 10.5, H-1)	27.57, 44.62, 99.32, 116.17 (d, *J* = 22), 122.27, 129.15 (d, *J* = 8), 130.42 (d, *J* = 2), 132.48, 135.77, 135.97, 138.63, 143.74, 148.15, 159.75, 162.58 (d, *J* = 246), 164.24
3f	1685, 1635, 1597, 1588	3.51 (s, 3 H, Me-9), 5.65 (s, 2 H, CH_2), 7.22 (d, 2 H, *J* = 8.4, H-2', H-6'), 7.30 (d, 2 H, *J* = 8.4, H-3', H-5'), 7.67–7.76 (m, 3 H, H-2, H-3, H-5), 7.91 (t, 1 H, *J* = 9.5, H-4), 9.29 (d, 1 H, *J* = 10.6, H-1)	27.57, 45.32, 99.31, 122.52, 127.21, 128.35, 129.15, 132.41, 134.61, 135.66, 136.01, 138.53, 143.70, 148.33, 159.81, 161.69, 164.33
3g	1685, 1635, 1602, 1583	3.49 (s, 3 H, Me-9), 7.44 (d, 2 H, *J* = 7.7, H-2', H-6'), 7.56–7.75 (m, 6 H, H-2, H-4, H-5, H-3', H-4', H-5'), 7.90–7.98 (m, 1 H, H-3), 9.37 (d, 1 H, *J* = 10.5, H-1)	27.54, 99.23, 123.27, 128.42, 130.18, 130.31, 132.63, 132.81, 136.04, 136.21, 138.59, 143.32, 149.81, 159.64, 161.75, 165.06
3h	1684, 1635, 1595, 1584	3.49 (s, 3 H, Me-9), 3.90 (s, 3 H, MeO), 7.11 (d, 2 H, *J* = 9.2, H-3', H-5'), 7.34 (d, 2 H, *J* = 9.2, H-2', H-6'), 7.68–7.71 (m, 3 H, H-2, H-4, H-5), 7.88–7.98 (m, 1 H, H-3), 9.35 (d, 1 H, *J* = 10.8, H-1)	27.52, 55.75, 99.12, 115.54, 123.27, 125.12, 129.50, 132.49, 135.88, 136.14, 138.45, 143.14, 150.13, 159.67, 160.75, 161.82, 165.15
3i	1683, 1635, 1603, 1588	3.49 (s, 3 H, Me-9), 7.40 (d, 2 H, *J* = 8.6, H-2', H-6'), 7.61 (d, 2 H, *J* = 8.6, H-3', H-5'), 7.66–7.72 (m, 3 H, H-2, H-4, H-5), 7.73–7.98 (m, 1 H, H-3), 9.36 (d, 1 H, *J* = 10.8, H-1)	27.54, 99.17, 122.99, 129.74, 130.59, 131.15, 132.70, 136.23,136.39, 138.81, 143.44,145.90, 149.49, 159.49, 161.62, 164.89

[a] Recorded in KBr disk for **1c–f** and in $CHCl_3$ for **3a–i**.
[b] Recorded in DMSO-d_6 for **1c–f** and in $CDCl_3$ for **3a–i**.
[c] One carbon signal was not recorded probably because of overlapping.

^{13}C NMR spectra were obtained at 126 MHz on a JNM Lambda 500 spectrometer in $CDCl_3$; chemical shifts were related to TMS. Mass spectra were recorded on a JMS-Automass 150 instrument.

6-Substituted-amino-3-methyluracils **1a, b**[17] and **1g−i**[18,19] were prepared by the reaction of 6-chloro-3-methyluracil with appropriate substituted amines according to the original procedure. All the compounds gave correct spectral data.

6-Amino-3-methyluracils (1c−f); General Procedure

A solution of 6-chloro-3-methyluracil (1.6 g, 10 mmol) and the appropriate 4-substituted benzylamine (30 mmol) in *n*-BuOH (50 mL) was heated under reflux for 3 h. The reaction mixture was cooled to r.t., and the crystals were collected by filtration. The crystals were washed with H_2O, EtOH, and then Et_2O, and were recrystallized from *n*-BuOH to give **1c−f** as colorless needles (Tables 1 and 2).

6,9-Disubstituted Cyclohepta[*b*]pyrimido[5,4-*d*]-pyrrole-8(6*H*),10(9*H*)-diones (3a−i) and a mixture of 7 and 9; General Procedure

To a solution of the appropriate 6-amino-3-methyluracil **1** (1.0 mmol) and 2-chlorotropone **2** or **4** (1.5 mmol) in dioxane (80 mL) was added K_2CO_3 (414 mg, 3.0 mmol) and Et_3N (20 mL). The resultant mixture was stirred at 90 °C for the period recorded in Scheme 1. The mixture was then filtered, washed with CH_2Cl_2, and the filtrate concentrated under reduced pressure. The resultant residue was chromatographed on Al_2O_3. The fractions eluted with CH_2Cl_2/acetone (1:1) were concentrated and the residual solid was recrystallized from EtOH to give **3** as light orange needles (Tables 1, 2).

For a mixture of 2,4-dideuterio- and 1,3,5-trideuterio-6,9-dimethylcyclohepta[*b*]pyrimido[5,4-*d*]pyrrole-8(6*H*),10(9*H*)-diones **7** and **9** in a ratio of 3:1.

Compound 7

^1H NMR (300 MHz, $CDCl_3$) δ = 3.48 (s, 3H, Me-9), 3.95 (s, 3H, Me-6), 7.74 (s, 1H, H-5), 7.87 (s, 1H, H-3), 9.26 (s, 1H, H-1).

HRMS: *m/z* calc for $C_{13}H_9D_2N_3O_2$ (M^+) 243.0978. Found: 243.0971.

Compound 9

^1H NMR (300 MHz, $CDCl_3$) δ = 3.48 (s, 3H, Me-9), 3.95 (s, 3H, Me-6), 7.87 (s, 2H, H-2 and H-4).

HRMS: *m/z* calc for $C_{13}H_8D_3N_3O_2$ (M^+) 244.1039. Found: 244.1043.

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