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An Efficacious Protocol for the Oxidation of 3,4-Dihydropyrimidin-2(1*H*)-ones using Pyridinium Chlorochromate as Catalyst

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4-Unsubstituted as well as 4,6-aryl/alkyl-3,4-dihydropyrimidin-2(1*H*)-ones were oxidized under neutral conditions using pyridinium chlorochromate to obtain the corresponding pyrimidin-2(1*H*)-ones in a synthetically useful manner.

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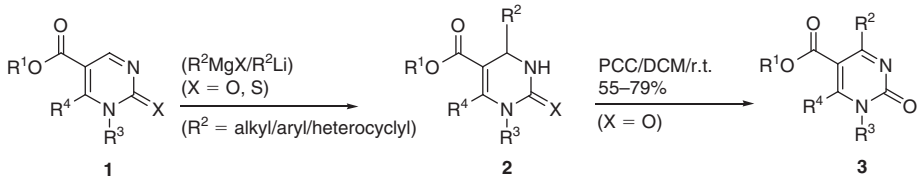
Introduction

Structurally diverse 4-substituted 3,4-dihydropyrimidin-2(1*H*)-ones (DHPMs), such as Hantzsch 1,4-dihydropyridines (DHPs), have emerged as effective calcium antagonists.[1] These compounds inhibit the movement of calcium through certain membrane channels.[2] Unlike DHPs, which depict a facile in-vivo and in-vitro oxidation,[3] a key step in the initial metabolism of DHP-based drugs, structurally related DHPMs are resistant. Many attempts to oxidize (i.e., dehydrogenate) DHPMs using several different oxidizing agents failed. For example, oxidants such as ceric ammonium nitrate,[4] $NaNO_2$ in acetic acid,[5] $KMnO_4$,[6] MnO_2,[7] 2,3-dichloro-5,6-dicyanobenzoquinone, and chloranil[8] are inefficient for the conversion of DHPMs into corresponding pyrimidines. Use of Eynde's procedure[9] to obtain pyrimidines is not only multistep, but also furnishes moderate yields of the desired products. $CuCl_2$/tert-butylhydroperoxide (TBHP)/K_2CO_3,[10] Jones reagent,[11] and potassium peroxydisulfate[12] have also been employed for the oxidation of DHPMs. In these protocols, the desired dehydrogenation is attended by C4 dealkylation in the case of a secondary alkyl or benzyl group.[13] In a recently disclosed method that employs hydrated $Co(NO_3)_2/K_2S_2O_8$ in aqueous acetonitrile,[14] the formation of rather unusual products resulting from C6 dealkylation along with dehydrogenation has been reported. Thus, an efficient and direct route that leads to the exclusive formation of pyrimidin-2(1*H*)-ones through oxidation of DHPMs is still not available. In this manuscript, we describe our findings on the selective and mild oxidation of DHPMs into pyrimidin-2(1*H*)-ones using pyridinium chlorochromate (PCC) as catalyst under neutral reaction conditions.

Results and Discussion

We have recently reported a highly regio- as well as chemo-selective scaffold decoration of 4-substituted-3,4-dihydropyrimidin-2(1*H*)-ones (DHPMs)/thiones using a flexible C6 lithiation–substitution protocol.[15] An extension of this site-selective lithiation–substitution sequence culminated in the regioselective N3-acylation approach,[16] the synthetic utility of which was demonstrated by choosing several acylating agents. In continuation of our interest in obtaining DHPMs as potential candidates for calcium antagonistic evaluation as well as for structure activity relationship studies, pyrimidine-2(1*H*)-one precursors were required.

Pyrimidine-2(1*H*)-ones **1** undergo regioselective nucleophilic addition reactions[17] at C4 (Scheme 1) and furnish DHPMs bearing tailor-made (4-aryl/heterocyclyl/alkyl) fragments, not available through the traditional three-component Biginelli condensation.[18] We obtained **1** through oxidation of DHPMs **2** ($R^4 = H$) using nitric acid[19] which is tedious, both from the point of view of running the reaction as well as the isolation of products from the highly acidic solution. To further widen the scope of C4 elaboration, **1** was required in multigram quantities. In the absence of a general selective protocol, we found that pyrimidine-2(1*H*)-ones could be obtained through the N3–C4 oxidation of DHPMs **2** with PCC[20] under neutral reaction conditions and in a synthetically useful manner. The



1 2 3

Scheme 1. C4 elaboration and PCC-catalyzed oxidation of structurally diverse 3,4-dihydropyrimidin-2(1*H*)-ones **2**.

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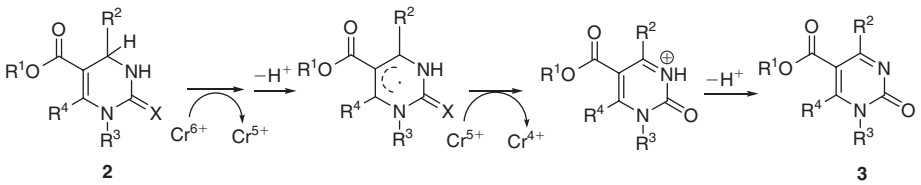
Table 1. Synthesis of pyrimidin-2(1*H*)-ones 3 through PCC oxidation of 2

Entry	Pyrimidin-2(1*H*)-ones **3**				Reaction time [h]	Isolated yields[A,B] [%]
	R^1	R^2	R^3	R^4		
a	Et	H	H	Me	20	79
b	Et	H	Me	Me	18	63
c	Et	Ph	H	Me	26	63
d	Et	Ph	Me	Me	16	60[C]
e	Me	Ph	H	Me	18	71
f	Et	4-$MeOC_6H_4$	H	Me	25	60
g	Et	4-$NO_2C_6H_4$	Me	Me	25	60[C]
h	Et	3,4,5-$(MeO)_3C_6H_2$	H	Me	23	60[C]
i	$(Me)_2CH$	3-$NO_2C_6H_4$	H	Me	21	55[C]
j	Et	Me	H	Me	20	69
k	Me	Me	H	Me	20	65
l	Et	Ph	H	C_3H_7	23	70
m	Et	Me	H	Ph	19	71
n	Et	C_5H_{11}	H	Me	20	62

[A]Yields based on isolated purified products.
[B]3.0 equivalents of PCC were used.
[C]4.0 equivalents of PCC were required for complete conversion.



Scheme 2. Proposed mechanism for the formation of **3**.

reaction requires 3.0 equivalents of PCC to drive the oxidation to completion; however, if 1.0 equivalent of the reagent is used, prolonged stirring is required. However, the modest excess of PCC is largely offset by the simplicity of the operation and reasonably good yields (Table 1) of the purified products. Furthermore, in comparison with literature protocols, no side product arising from C4/C6 dealkylation[14] was formed.

The completion of the reaction and formation of the products could be monitored by using ^{1}H NMR ($CDCl_3$) spectroscopy by the shift in the C6 methyl resonance in the products. The intense singlet of the protons of the C6 methyl group resonates around δ 2.46–2.71, whereas the corresponding protons in the precursor DHPMs **2** resonate upfield (δ 2.22–2.37, Δ_δ 0.20–0.45). Likewise, the disappearance of splitting of the C4-alkyl substituents in **3**, and the disappearance of the doublet of H4 in the case of C4 aryl substituted DHPMs, offered an unambiguous monitoring of the reaction progress for the optimization of the reaction times.

The mechanism of dehydrogenation mediated by PCC is not certain, as the precise nature of the reduced chromium product has not been investigated,[21] presumably it is chromium dioxide (Cr^{4+}) or some other intermediate formed from chromium dioxide and pyridinium chloride. It might involve a two-electron transfer process as proposed in Scheme 2.

PCC adsorbed on a solid support (alumina, silica gel, or montmorillonite K-10 clay) is remarkably efficient in oxidizing 1,4-DHPs to the corresponding pyridines.[13] During optimization of the reaction conditions for the oxidation of **2**, when PCC was supported on these solid supports, and used in dehydrogenation experiments, the reactions neither proceeded to completion nor did the process offer any operational advantage, thus PCC was used as such. However, in using PCC, reactions did not proceed to completion when an equimolar quantity of PCC was employed. As the literature reports suggest,[22,23] in similar oxidations, even a 5.0 molar excess of oxidant has been employed to drive the reaction to completion. Thus the excess amount of PCC (3.0 equivalents) used in the current protocol is offset by the reasonably high yields obtained at the end of the process. The synthetic scope of this transformation is depicted in Table 1, and it is evident that the reaction tolerates functional variations around the DHPM core (C4, C5, C6), which is an additional advantage.

Conclusions

We have shown that DHPMs can be efficaciously dehydrogenated using PCC at the key diversity oriented C4–N3 position to obtain pyrimidine-2(1*H*)-ones in a synthetically useful manner. This method has operational advantages such as clean reaction profiles and simple experimental/product isolation procedures, which make it a useful and attractive strategy for the dehydrogenation of DHPMs to obtain pyrimidine-2(1*H*)-ones of synthetic importance.

Experimental

General

All compounds were characterized by ^{1}H NMR, ^{13}C NMR, mass spectrometry (MS), and elemental analysis. NMR spectra were recorded on a JEOL FT-NMR AL-300 MHz using $CDCl_3$ and/or (D_6)DMSO as solvents and tetramethylsilane as an internal standard, chemical shifts are given in δ. MS were recorded on a Bruker Esquire 3000 instrument. Elemental analyses (C, H, N)

were performed on a Thermo Flash EA112. Melting points were recorded in open capillaries and are uncorrected.

General Procedure for the Oxidation of 3,4-Dihydropyrimidin-2(1H)-ones ***2***

A solution of DHPM **2** (0.5 g, 1.97 mmol) (Scheme 1) in CH_2Cl_2 was stirred with PCC (1.3 g, 5.90 mmol, Aldrich) until the reaction was complete (16–25 h, TLC). The reaction mixture was filtered over Celite to remove any suspension, and the residue obtained after removal of the solvent was flash-chromatographed to obtain the corresponding pyrimidinone **3**.

6-Methyl-2-oxo-1,2-dihydropyrimidine-5-carboxylic Acid Ethyl Ester ***3a***

Yield (390 mg, 79%). R_F (ethyl acetate) 0.2, mp 210–215°C. (Found: C 52.4, H 5.2, N 15.8. $C_8H_{10}N_2O_3$ requires C 52.8, H 5.5, N 15.4%). δ_H ((D$_6$)DMSO) 8.69 (1H, s, CH), 5.69 (1H, s, NH, exch. with D_2O), 4.17 (2H, q, CH_2CH_3), 2.46 (3H, s, CH_3), 1.23 (3H, t, *J* 7.2, CH_2CH_3). δ_C ((D$_6$)DMSO) 182.64, 163.62, 106.44, 60.63, 14.19. *m*/*z* 205 [M^+].

1,6-Dimethyl-2-oxo-1,2-dihydropyrimidine-5-carboxylic Acid Ethyl Ester ***3b***

Yield (310 mg, 63%). R_F (ethyl acetate) 0.3, mp 130–132°C. (Found: C 54.4, H 6.2, N 14.4. $C_9H_{12}N_2O_3$ requires C 55.1, H 6.1, N 14.3%). δ_H ($CDCl_3$) 8.35 (1H, s, CH), 4.25 (2H, q, CH_2CH_3), 3.55 (3H, s, NCH_3), 2.63 (3H, s, CH_3), 1.30 (3H, t, *J* 7.2, CH_2CH_3). δ_C ($CDCl_3$) 176.59, 163.15, 154.99, 152.69, 108.12, 61.17, 48.46, 39.07, 30.85, 26.04, 23.0, 14.19. *m*/*z* 219 [M^+].

6-Methyl-2-oxo-4-phenyl-1,2-dihydropyrimidine-5-carboxylic Acid Ethyl Ester ***3c***

Yield (310 mg, 63%). R_F (ethyl acetate) 0.4, mp 175–178°C. (Found: C 65.4, H 5.6, N 11.0. $C_{14}H_{14}N_2O_3$ requires C 65.1, H 5.4, N 10.9%). δ_H ($CDCl_3$) 7.40–7.61 (5H, m, ArH), 4.05 (2H, q, CH_2CH_3), 2.61 (3H, s, CH_3), 1.25 (1H, s, OH, exch. with D_2O), 0.938 (3H, t, *J* 6.9, CH_2CH_3). δ_C ($CDCl_3$) 166.09, 158.31, 130.80, 128.36, 127.99, 111.49, 61.60, 45.52, 13.42, 6.28. *m*/*z* 281 [M^+].

1,6-Dimethyl-2-oxo-4-phenyl-1,2-dihydropyrimidine-5-carboxylic Acid Ethyl Ester ***3d***

Yield (300 mg, 60%). R_F (ethyl acetate) 0.5, mp 116–118°C. (Found: C 66.9, H 5.6, N 10.5. $C_{15}H_{16}N_2O_3$ requires C 66.2, H 5.9, N 10.3%). δ_H ($CDCl_3$) 7.37–7.60 (5H, m, ArH), 4.00 (2H, q, CH_2CH_3), 3.65 (3H, s, NCH_3), 2.55 (3H, s, CH_3), 0.87 (3H, t, *J* 6.9, CH_2CH_3). δ_C ($CDCl_3$) 166.90, 158.59, 148.27, 138.24, 130.35, 127.95, 111.56, 61.70, 33.04, 17.99, 13.27. *m*/*z* 295 [M^+].

6-Methyl-2-oxo-4-phenyl-1,2-dihydropyrimidine-5-carboxylic Acid Methyl Ester ***3e***

Yield (350 mg, 71%). R_F (ethyl acetate) 0.2, mp 195–197°C. (Found: C 63.1, H 5.2, N 10.7. $C_{13}H_{12}N_2O_3$ requires C 63.9, H 4.9, N 11.5%). δ_H ($CDCl_3$) 13.5 (1H, br, OH, exch. with D_2O), 7.41–7.61 (5H, m, ArH), 3.58 (3H, s, OCH_3), 2.61 (3H, s, CH_3). δ_C ($CDCl_3$) 196.59, 130.98, 128.42, 127.97, 96.43, 52.28. *m*/*z* 267 [M^+].

4-(4-Methoxyphenyl)-6-methyl-2-oxo-1,2-dihydropyrimidine-5-carboxylic Acid Ethyl Ester ***3f***

Yield (300 mg, 60%). R_F (ethyl acetate) 0.3, mp 153–155°C. (Found: C 61.7, H 5.7, N 9.5. $C_{15}H_{16}N_2O_4$ requires C 62.5, H 5.6, N 9.7%). δ_H ($CDCl_3$) 7.60 (2H, d, *J* 8.1, ArH), 6.94 (2H, d, *J* 8.4, ArH), 5.36 (1H, br, NH, exch. with D_2O), 4.12 (2H, q, CH_2CH_3), 3.85 (s, 3H, OCH_3), 2.56 (3H, s, CH_3), 1.05 (3H, t, *J* 6.9, CH_2CH_3). δ_C ($CDCl_3$) 166.57, 162.05, 130.08, 127.82, 113.80, 61.61, 55.37, 13.65. *m*/*z* 311 [M^+].

1,6-Dimethyl-4-(4-nitrophenyl)-2-oxo-1,2-dihydropyrimidine-5-carboxylic Acid Ethyl Ester ***3g***

Yield (300 mg, 60%). R_F (ethyl acetate) 0.5, mp 128–130°C. (Found: C 56.1, H 4.6, N 13.3. $C_{15}H_{15}N_3O_5$ requires C 56. 8, H 4.7, N 13.3%). δ_H ($CDCl_3$) 8.27 (2H, d, *J* 8.7, ArH), 7.75 (2H, d, *J* 8.7, ArH), 4.03 (2H, q, CH_2CH_3), 3.69 (3H, s, NCH_3), 2.61 (3H, s, CH_3), 0.93 (3H, t, *J* 7.2, CH_2CH_3). δ_C ($CDCl_3$) 169.05, 166.01, 160.10, 155.25, 148.72, 144.31, 128.81, 123.40, 111.14, 61.95, 33.36, 18.24, 13.44. *m*/*z* 340 [M^+].

6-Methyl-2-oxo-4-(3,4,5-trimethoxyphenyl)-1,2-dihydropyrimidine-5-carboxylic Acid Ethyl Ester ***3h***

Yield (300 mg, 60%). R_F (ethyl acetate) 0.2. (Found: C 57.9, H 5.0, N 9.1. $C_{17}H_{20}N_2O_6$ requires C 57.6, H 5.7, N 8.0%). δ_H ($CDCl_3$) 6.80 (2H, s, ArH) 5.23 (1H, s, NH, exch. with D_2O), 4.03 (2H, q, CH_2CH_3), 3.82 (9H, s, OCH_3), 2.52 (3H, s, CH_3), 0.96 (3H, t, *J* 7.2, CH_2CH_3). δ_C ($CDCl_3$) 166.40, 158.59, 153.14, 140.44, 111.65, 105.43, 61.79, 60.94, 56.23, 8.20. *m*/*z* 371 [M^+].

6-Methyl-4-(3-nitro-phenyl)-2-oxo-1,2-dihydropyrimidine-5-carboxylic Acid Isopropyl Ester ***3i***

Yield (270 mg, 55%). R_F (ethyl acetate) 0.4, mp 203–205°C. (Found: C 56.1, H 5.1, N 13.2. $C_{15}H_{15}N_3O_5$ requires C 56.8, H 4.7, N 13.3%). δ_H ($CDCl_3$) 13.75 (1H, br, OH, exch. with D_2O), 8.47 (1H, s, ArH), 8.35 (1H, d, *J* 7.8, ArH), 7.79 (1H, d, *J* 8.7, ArH), 7.64 (1H, t, *J* 7.8, ArH), 5.03 (IH, m, $CH(CH_3)_2$), 2.67 (3H, s, CH_3), 1.08 (6H, d, *J* 6.3, $CH(CH_3)_2$). δ_C ($CDCl_3$) 164.60, 158.06, 147.92, 134.03, 129.47, 125.13, 123.21, 111.67, 70.20, 21.29, 18.35. *m*/*z* 356 [M^+].

4,6-Dimethyl-2-oxo-1,2-dihydropyrimidine-5-carboxylic Acid Ethyl Ester ***3j***

Yield (340 mg, 69%). R_F (ethyl acetate) 0.2, mp 134–136°C. (Found: C 54.5, H 6.6, N 15.0. $C_9H_{12}N_2O_3$ requires C 55.1, H 6.2, N 14.3%). δ_H ($CDCl_3$) 5.43 (1H, br, NH, exch. with D_2O), 4.36 (2H, q, CH_2CH_3), 2.56 (6H, s, $2CH_3$), 1.38 (3H, t, *J* 7.2, CH_2CH_3). δ_C ($CDCl_3$) 165.26, 158.01, 111.19, 61.52, 14.12. *m*/*z* 219 [M^+].

4,6-Dimethyl-2-oxo-1,2-dihydropyrimidine-5-carboxylic Acid Methyl Ester ***3k***

Yield (320 mg, 65%). R_F (ethyl acetate) 0.2, mp 160–162°C. (Found: C 52.1, H 5.4, N 15.9. $C_8H_{10}N_2O_3$ requires C 52.7, H 5.5, N 15.4%). δ_H ($CDCl_3$) 13.53 (1H, br, OH, exch. with D_2O), 3.89 (3H, s, OCH_3), 2.56 (6H, s, $2CH_3$). δ_C ($CDCl_3$) 165.72, 158.10, 110.96, 52.24, 20.77. *m*/*z* 205 [M^+].

2-Oxo-4-phenyl-6-propyl-1,2-dihydropyrimidine-5-carboxylic Acid Ethyl Ester ***3l***

Yield (350 mg, 70%). R_F (ethyl acetate) 0.6, mp 143–145°C. (Found: C 66.9, H 6.9, N 10.2. $C_{16}H_{18}N_2O_3$ requires C 67.1, H 6.3, N 9.8%). δ_H ($CDCl_3$) 8.12 (1H, s, NH, exch. with D_2O), 7.40–7.61 (5H, m, ArH), 4.03 (2H, q, CH_2CH_3), 2.85 (2H, t, *J* 7.2, CH_2CH_2), 1.82 (2H, m, $CH_3CH_2CH_2$), 1.03 (3H, t, *J* 7.2, CH_3CH_2), 0.93 (t, 3H, *J* 7.2, CH_3CH_2). δ_C ($CDCl_3$) 179.65, 166.21, 158.25, 130.68, 128.55, 126.58, 111.30, 101.03, 61.56, 29.62, 22.43, 13.66. *m*/*z* 309 [M^+].

4-Methyl-2-oxo-6-phenyl-1,2-dihydropyrimidine-5-carboxylic Acid Ethyl Ester ***3m***

Yield (355 mg, 71%). R_F (ethyl acetate) 0.5, mp 183–185°C. (Found: C 65.1, H 5.9, N 11.0. $C_{14}H_{14}N_2O_3$ requires C 65.1, H 5.4, N 10.9%). δ_H ($CDCl_3$) 13.63 (1H, br, OH, exch. with D_2O), 7.40–7.61 (5H, m, ArH), 4.05 (2H, q, CH_3CH_2), 2.62 (3H, s, CH_3), 0.937 (3H, t, *J* 7.2, CH_3CH_2). δ_C ($CDCl_3$) 166.05, 158.30, 130.76, 128.14, 111.45, 61.57, 13.39. *m*/*z* 281 [M^+].

6-Methyl-2-oxo-4-pentyl-1,2-dihydropyrimidine-5-carboxylic Acid Ethyl Ester ***3n***

Yield (320 mg, 62%). R_F (ethyl acetate) 0.4. (Found: C 60.2, H 7.1, N 10.8. $C_{13}H_{20}N_2O_3$ requires C 61.9, H 7.9, N 11.1%). δ_H ($CDCl_3$) 4.29 (2H, q, CH_2CH_3), 2.73 (2H, t, *J* 7.5, $CH_2(CH_2)_3CH_3$), 2.45 (3H, s, CH_3), 2.10 (1H, s, OH, exch. with D_2O), 1.29 (9H, m, $CH_2(CH_2)_3CH_3$), 0.82 (3H, t, *J* 6.9, CH_2CH_3). δ_C ($CDCl_3$) 61.67, 31.55, 22.34, 14.12, 13.86, 0.98. *m*/*z* 275 [M^+].

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