Synthesis of Imidazoles by the Oxidative Transformation of 5-Aminopyrimidinones[1]

Izumi Matsuura, Taisei Ueda, Nobutoshi Murkami, Shin-ichi Nagai, Akito Nagatsu and Jinsaku Sakakibara*
Faculty of Pharmaceutical Sciences, Nagoya City University, Tanabe-dori, Mizuho-ku, Nagoya 467, Japan

2-Alkoxy-1*H*-imidazoles (**2a–f**, **3a**, **b**, **4a**, **b**) were synthesized from 5-aminopyrimidin-4(3*H*)-ones **1a–d** by treatment with oxidative metal salts (Cu^{II}, Tl^{III}, Fe^{III}, Pb^{IV}) in alkyl alcohols. Oxidative transformation of 5-aminouracils **5a–c** by thallium(III) nitrate trihydrate in methanol gave *gem*-diols **6a–c**, which were rearranged to imidazolones **7a–c**.

Pyrimidines or pyrimidinones are important materials in view of their potential biological activities, and various studies on their syntheses and reactions have been reported.[2] In the course of medicinal and chemical studies of pyrimidinones in our laboratory,[3] we previously found a novel and interesting ring transformation of 5-aminopyrimidinone or 5-acylaminopyrimidinones into imidazoles.[4] Ring transformations of pyrimidines have intrigued many organic chemists. However, the oxidative ring transformations of pyrimidinones are little known.

In this paper we describe the oxidative transformation of 5-aminopyrimidinones into imidazoles.

Results and Discussion

Pyrimidines, heteroaromatic compounds of high π-electron density, are subject to nucleophilic attack. It is apparent that C(2) of 5-aminopyrimidin-4(3*H*)-one is electrophilic. We thought nucleophilic reaction at C(2) might bring about ring opening and transformation and we were interested in the examination of the reaction with metal salts possessing oxidative ability in alkyl alcohols.

The reaction of compound **1a**[5] with $CuCl_2$ (2.0 mol equiv.) in refluxing methanol for 3 h gave the imidazole **2a** in 59% yield. In the ^1H NMR spectrum of compound **2a**, a methyl [δ_H 4.01 (3 H, s)] and two amino group signals [δ_H 8.31 (1 H, br s), 8.82 (1 H, br s)] appeared. The ^{13}C NMR spectrum (DEPT) indicated the presence of a methyl (δ_C 10.8) and a methoxy group (δ_C 56.5). The IR spectrum showed the absorption bands ascribable to the two secondary amide functions (3360, 3340 cm^{-1}) and the amide carbonyl group (1640 cm^{-1}). The absorption bands of the primary amine **1a** disappeared. The EI–MS spectrum of compound **2a** showed molecular ion peak at *m/z* 231 (M^+) and fragment peak at *m/z* 139 (M^+ – NHPh). Its UV spectrum was similar to that of 2,5-dimethyl-4-phenylcarbamoyl-1*H*-imidazole[4] (λ_{max} 269 nm, ε 24 600 dm^3 mol^{-1} cm^{-1}). The structure of compound **2a** was assigned to be 2-methoxy-5-methyl-4-phenylcarbamoyl-1*H*-imidazole. De-*o*-alkylation of compound **2a** to the alcohol **2g** was successfully carried out with 5% HCl in refluxing methanol (Scheme 1).

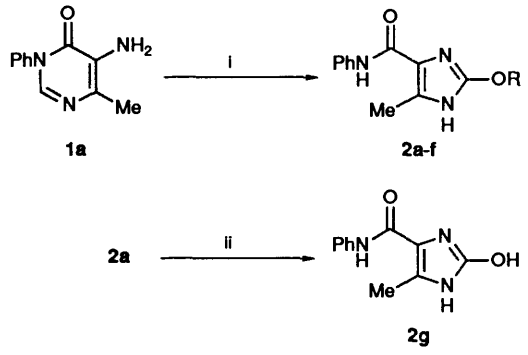
Since the methoxy group of compound **2a** seemed to originate from methanol, the reaction of the amine **1a** with $CuCl_2$ was examined in various other alkyl alcohols: ethyl, propyl, butyl, isopropyl and *sec*-butyl (Table 1). In the case of the primary alcohols the yields were 74–82%, while the yields were reduced when secondary alcohols were used as solvent.

In order to improve the yield of compound **2a**, we examined the reaction of compound **1a** with different amounts of $CuCl_2$, but the amount had little effect on the yield. Next, we examined other metal salts such as $CuBr_2$, $Cu(NO_3)_2$, $CuSO_4$, $Tl(NO_3)_3$, $FeCl_3$ and $Pb(OAc)_4$ (Table 1). Among these metal salts $CuSO_4$ gave the best yield. No reaction was observed when CuCl, CuBr, CuI or $FeCl_2$ was used. Consequently, it appears that the oxidative activity of Cu^{II} is essentially (leastways for the copper-promoted reaction). Other oxidative metal salts such as Tl^{III}, Fe^{III} and Pb^{IV} were also effective. In particular, when Tl^{III} was used, the reaction proceeded under mild conditions and the yield of compound **2a** was moderate.

Table 1 Transformation of amines **1** into amides **2a–f** in the presence of metal salts in alkyl alcohols under reflux unless noted otherwise

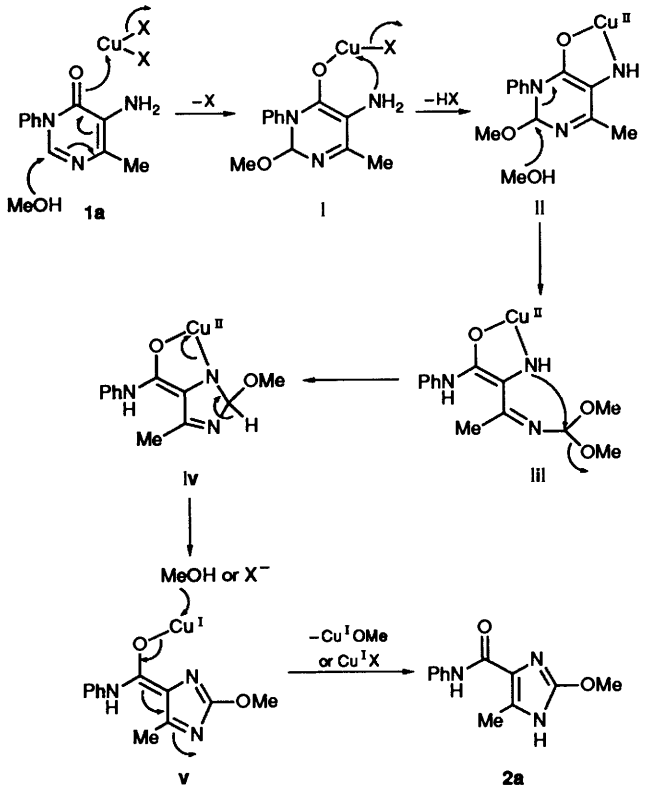
Run	Product	Metal salt (mol equiv.)	Solvent	Reaction time (*t*/h)	Yield (%)
1	**2a**	$CuCl_2$ (2.0)	MeOH	3	59
2	**2b**	$CuCl_2$ (2.0)	EtOH	2.5	74
3	**2c**	$CuCl_2$ (2.0)	PrOH	2	77
4	**2d**	$CuCl_2$ (2.0)	BuOH	2	82
5	**2e**	$CuCl_2$ (2.0)	Pr^iOH	4	48
6	**2f**	$CuCl_2$ (2.0)	Bu^sOH	4	22
7	**2a**	$CuCl_2$ (1.0)	MeOH	4	54
8	**2a**	$CuCl_2$ (3.0)	MeOH	1.5	62
9	**2a**	$CuBr_2$ (2.0)	MeOH	1	54
10	**2a**	$Cu(NO_3)_2$ (2.0)	MeOH	15	51
11	**2a**	$CuSO_4$ (2.0)	MeOH	24	71
12	**2a**[a]	$Tl(NO_3)_3$ (1.0)	MeOH	3	51
13	**2a**	$FeCl_3$ (1.0)	MeOH	10	47
14	**2a**[a]	$Pb(OAc)_4$ (1.0)	MeOH	1.5	31

[a] At room temperature.



Scheme 1 *Reagents:* i, oxidative metal salt (Cu^{II}, Tl^{III}, Fe^{III}, Pb^{IV}), ROH (R = Me, Et, Pr, Bu, Pr^i, Bu^s); ii, 5% aq. HCl, MeOH

It therefore seems that the reaction of pyrimidinones **1** with metal salts involves an oxidative process. A possible mechanism is shown in Scheme 2. We have previously found that the reaction of compound **1a** with Lewis acids and oxidizing agents in methanol also gave the imidazole **2a**.[6] Therefore, this is further evidence that metal salts must have both Lewis acidity



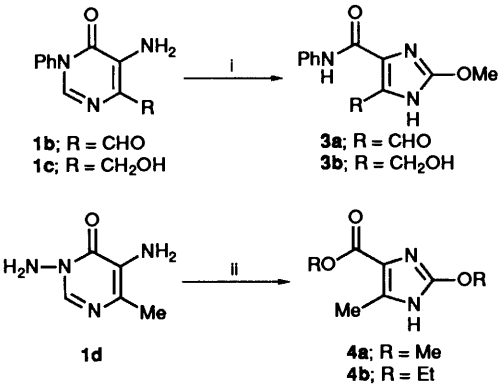
Scheme 2

and oxidative activity for the transformation to occur, and the reaction might then proceed by a similar reaction mechanism in the case of separate Lewis acids and oxidizing agents. Initial nucleophilic attack by the alcohol on C(2) aided by chelation of copper(II) to the C(4) carbonyl group would form intermediate **i**. Ring opening (**ii**) and rotation (**iii**) followed by recyclization would give the imidazoline species **iv**, which would, *via* intermediate **v**, form products **2** because of the oxidative activity of Cu^{II}. There are some reports on oxidative reactions with copper(II) halides.[7]

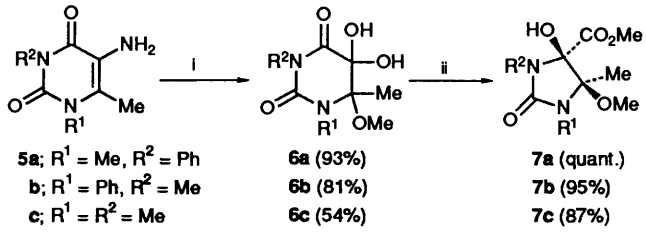
The reaction of compounds **1b**[8] and **1c*** with $CuCl_2$ in refluxing methanol did not give 2-methoxy-1*H*-imidazole. This seems to be due to the formation of a copper(II) complex between the amino group and the aldehyde or hydroxymethyl group. However, use of thallium(III) nitrate as oxidizing metal salt afforded imidazoles **3a** and **3b** in each of 26 and 38% yield (Scheme 3). We also examined the reaction of compound **1d**[5] with $CuCl_2$ in refluxing methanol or ethanol. The hydrazine moiety was cleaved by alcoholysis to give methyl 2-methoxy-5-methyl-1*H*-imidazole-4-carboxylate **4a** in 51% yield and ethyl 2-methoxy-5-methyl-1*H*-imidazole-4-carboxylate **4b** in 54% yield.

5-Aminouracil derivatives are important precursors of xanthines or purines, and it will be of interest to examine their reactivities. Since 5-aminouracils have a similar pyrmidinone skeleton to the compounds studied here, we are interested in examining their oxidative transformation.

5-Amino-1,6-dimethyluracil **5a**[9] was allowed to react with thallium(III) nitrate trihydrate for 1.5 h at room temperature in methanol. The reaction mixture was worked up to give compound **6a** in 93% yield (Scheme 4). Elemental analysis and EI–MS of compound **6a** gave results consistent with the formula $C_{13}H_{16}N_2O_5$. Its ^1H and ^{13}C NMR spectra indicated the



Scheme 3 *Reagents:* i, $Tl(NO_3)_3 \cdot 3H_2O$, MeOH; ii, $CuCl_2$, ROH



Scheme 4 *Reagents:* i, $Tl(NO_3)_3 \cdot 3H_2O$, MeOH; ii, MeOH

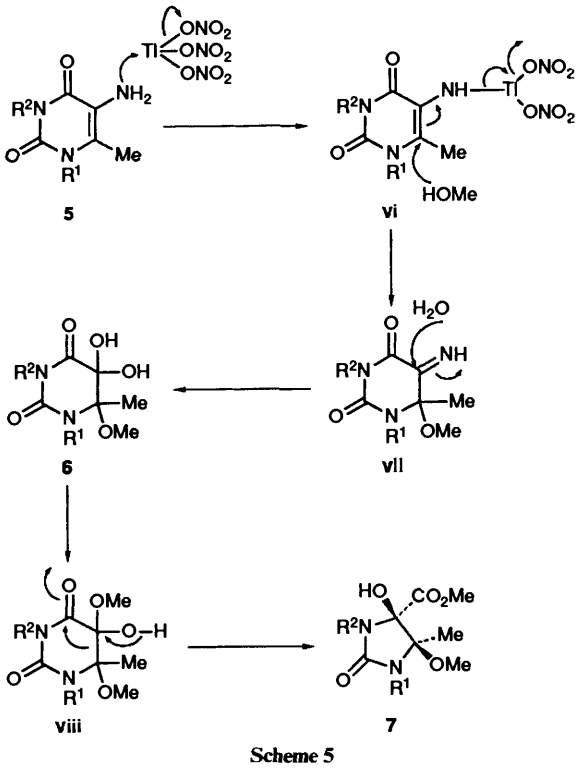
structure of compound **6a**. However, final structural conformation was carried out by X-ray crystallographic analysis.[1] Thus, the structure of compound **6a** was established to be 5,5-dihydroxy-6-methoxy-1,6-dimethyl-3-phenyl-5,6-dihydropyrimidine-2,4(1*H*,3*H*)-dione, as depicted in Scheme 4.

When compound **6a** was stirred for 10 min at room temperature in methanol, an interesting ring contraction occurred to give the imidazolidinone **7a** quantitatively. From elemental analysis and EI–MS, its formula was determined to be $C_{14}H_{18}N_2O_5$. Since an unambiguous structure was not delineated from the ^1H and ^{13}C spectra, an X-ray crystallographic analysis was carried out.[1] Thus, the structure of compound **7a** was established to be methyl 4-hydroxy-5-methoxy-1,5-dimethyl-2-oxo-3-phenylimidazoline-4-carboxylate. Since prolonged reaction of compound **5a** with thallium(III) nitrate in methanol did not give compound **7a**, it seems to be necessary to isolate the intermediate **6a** which would be formed by the reaction with water during the work-up. Next we examined the similar reaction of 5-aminouracils **5b** and **5c** with thallium(III) nitrate in methanol in order to explore the effect of *N*-substituted groups. The reaction of substrates **5b**, **c** gave products **6b**, **c**, which readily produced esters **7b**, **c** in 95% and 87% yield respectively. In the transformation of amines **5** into diols **6**, the substrate *N*-phenyl group was preferable for a good yield of *gem*-diol to be attained.

A possible reaction mechanism for the formation of compounds **6** and **7** from amines **5** is shown in Scheme 5. Initially the 5-amino group of substrate **5** would be oxidized by thallium(III) nitrate accompanied by nucleophilic attack of methanol on C(6) to give intermediate **vii** *via* **vi**. The water produced during the work-up, or the water of crystallization of thallium(III) nitrate trihydrate, may participate[10] in the hydrolysis of the imino group and deamination. The transformation of diols **6** into esters **7** would be explained by the nucleophilic attack of methanol on C(5) of diols **6** followed by dehydration and rearrangement of the C(5)–C(6) bond to the C(4) carbonyl carbon **viii**.

It is noteworthy that the structurally uncommon *gem*-diols **6** were isolated as stable products and in good yield, by the oxidation of 5-aminouracils **5** by thallium(III) nitrate, and that diols **6** were easily ring-contracted to give imidazolones **7**.

* Compound **1c** was obtained by the reduction of aldehyde **1b** with sodium borohydride in methanol.



Scheme 5

Experimental

M.p.s were determined with a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were measured with an IR-810 machine from Nihon Bunko Spectroscopic Co. Ltd. Mass spectra were measured with a JOEL JMS-DX 300 mass spectrometer. ^1H and ^{13}C NMR spectra were recorded with a JEOL JNM-FX-100, JNM-EX-270 or JNM-GSX-400 spectrometer using tetramethylsilane as internal standard. *J*-Values are given in Hz. UV spectra were recorded on a Hitachi 228 spectrophotometer.

General Procedure for the Synthesis of Compounds **2a–f** *by the Oxidative Transformation of* 5-*Amino*-6-*methyl*-3-*phenylpyrimidin*-4(3H)-*one* **1a**.—Copper(II) chloride (134 mg, 2 mol equiv.) was added to a solution of 5-amino-6-methyl-3-phenylpyrimidin-4(3*H*)-one **1a** (100 mg, 0.497 mmol) in dry alcohol (10 cm^3) under nitrogen, and the mixture was refluxed. After cooling, the reaction mixture was poured into water and extracted with dichloromethane. The extract was dried over anhydrous magnesium sulfate. Solvent was distilled off and the residue was purified by column chromatography on silica gel, with hexane–ethyl acetate (3:2) as solvent. The yield, reaction time, and metal salt are given in Table 1.

2-*Methoxy*-5-*methyl*-N-*phenyl*-1H-*imidazole*-4-*carboxamide* **2a**. M.p. 193–194 °C (Found: C, 62.3; H, 5.6; N, 18.1. $C_{12}H_{13}N_3O_2$ requires C, 62.3; H, 5.7; N, 18.2%); ν_{max}(KBr)/cm^{-1} 3360, 3340, 1640 and 1520; λ_{max}(EtOH)/nm 277 (ε 23 900 dm^3 mol^{-1} cm^{-1}); δ_H(100 MHz; $CDCl_3$) 2.54 (3 H, s, 5-Me), 4.01 (3 H, s, OMe), 7.06–7.68 (5 H, m, Ph), 8.31 (1 H, br s, NH) and 8.82 (1 H, br s, NH); δ_C(67.5 MHz; $CDCl_3$) 10.8 (5-Me), 56.5 (OMe), 119.9 (C-2′, -6′), 123.8 (C-4′), 125.1 (C-5), 128.9 (C-3′, -5′), 129.3 (C-4), 138.1 (C-1′), 151.4 (C-2) and 162.6 (C=O); *m*/*z* 231 (M^+) and 139 (M^+ − NHPh).

2-*Ethoxy*-5-*methyl*-N-*phenyl*-1H-*imidazole*-4-*carboxamide* **2b**. M.p. 162–163 °C (Found: C, 63.5; H, 6.1; N, 17.3. $C_{13}H_{15}N_3O_2$ requires C, 63.4; H, 6.2; N, 17.1%); ν_{max}(KBr)/cm^{-1} 3380, 1650 and 1510; δ_H(100 MHz; $CDCl_3$) 1.39 (3 H, t, *J* 7, CH_2Me), 2.51 (3 H, s, 5-Me), 4.40 (2 H, q, *J* 7, CH_2), 6.90–7.70 (5 H, m, Ph), 8.54 (1 H, br s, NH) and 8.82 (1 H, br s, NH); *m*/*z* 245 (M^+).

5-*Methyl*-N-*phenyl*-2-*propoxy*-1H-*imidazole*-4-*carboxamide* **2c**. M.p. 189–190 °C (Found: C, 64.7; H, 6.6; N, 16.1. $C_{14}H_{17}N_3O_2$ requires C, 64.85; H, 6.6; N, 16.2%); ν_{max}(KBr)/cm^{-1} 3380, 1650 and 1510; δ_H(100 MHz; $CDCl_3$) 1.01 (3 H, t, *J* 7.3, CH_2Me), 1.76 (2 H, m, CH_2Me), 2.53 (3 H, s, 5-Me), 4.30 (2 H, t, *J* 6.5, OCH_2), 7.06–7.70 (5 H, m, Ph), 8.37 (1 H, br s, NH) and 8.83 (1 H, br s, NH); *m*/*z* 259 (M^+) and 167 (M^+ − NHPh).

2-*Butoxy*-5-*methyl*-N-*phenyl*-1H-*imidazole*-4-*carboxamide* **2d**. M.p. 112–113 °C (Found: C, 65.7; H, 7.0; N, 15.2. $C_{15}H_{19}N_3O_2$ requires C, 65.9; H, 7.0; N, 15.4%); ν_{max}(KBr)/cm^{-1} 3250, 1630 and 1535; δ_H(100 MHz; $CDCl_3$) 1.02 (3 H, t, *J* 6.5, CH_2Me), 1.60 (2 H × 2, m, CH_2CH_2Me), 2.56 (3 H, s, 5-Me), 4.38 (2 H, t, *J* 6.5, OCH_2), 7.10–7.76 (5 H, m, Ph), 8.46 (1 H, br s, NH) and 8.85 (1 H, br s, NH); *m*/*z* 273 (M^+) and 181 (M^+ − NHPh).

2-*Isopropoxy*-5-*methyl*-N-*phenyl*-1H-*imidazole*-4-*carboxamide* **2e**. M.p. 170–172 °C (Found: C, 64.7; H, 6.6; N, 16.1. $C_{14}H_{17}N_3O_2$ requires C, 64.85; H, 6.6; N, 16.2%); ν_{max}(KBr)/cm^{-1} 3370 and 1630; δ_H(100 MHz; $CDCl_3$) 1.33 (3 H, s, $CHMe$), 1.39 (3 H, s, $CHMe$), 2.51 (3 H, s, 5-Me), 5.10 (1 H, m, OCH), 6.69–7.71 (5 H, m, Ph), 8.54 (1 H, br s, NH) and 8.82 (1 H, br s, NH); *m*/*z* 259 (M^+) and 167 (M^+ − NHPh).

2-(sec-*Butoxy*)-5-*methyl*-N-*phenyl*-1H-*imidazole*-4-*carboxamide* **2f**. M.p. 138–139 °C (Found: C, 65.7; H, 7.1; N, 15.15. $C_{15}H_{19}N_3O_2$ requires C, 65.9; H, 7.0; N, 15.4%); ν_{max}(KBr)/cm^{-1} 3230, 1650 and 1520; δ_H(100 MHz; $CDCl_3$) 0.97 (3 H, t, *J* 7.3, CH_2Me), 1.35 (3 H, d, *J* 6, $CHMe$), 1.71 (2 H, m, CH_2), 2.52 (3 H, s, 5-Me), 4.92 (1 H, m, OCH), 7.06–7.72 (5 H, m, Ph), 8.31 (1 H, br s, NH) and 8.82 (1 H, br s, NH); *m*/*z* 273 (M^+).

2-*Hydroxy*-5-*methyl*-N-*phenyl*-1H-*imidazole*-4-*carboxamide* **2g**. A mixture of compound **2a** (50 mg, 0.216 mmol), 5% aq. hydrochloric acid (2.5 cm^3) and methanol (2.5 cm^3) was refluxed for 7 h. After cooling, the reaction mixture was neutralized with saturated aq. sodium hydrogen carbonate and extracted with dichloromethane. The extract was evaporated to dryness. The residue was purified by silica gel column chromatography to give *title compound* **2g** (77%), m.p. 257 °C (decomp.) (Found: M^+, 217.0846. $C_{11}H_{11}N_3O_2$ requires *M*, 217.0851); ν_{max}(KBr)/cm^{-1} 3300, 3020, 1740, 1700, 1625 and 1530; δ_H(100 MHz; $CDCl_3$–CD_3OD) 2.43 (3 H, s, 5-Me) and 7.11–7.65 (5 H, m, Ph); *m*/*z* 217 (M^+) and 125 (M^+ − NHPh).

General Procedure for the Synthesis of Compounds **3a, b** *from Amines* **1b, c**.—A solution of compound **1b** or **1c** (100 mg) and thallium(III) nitrate (1.2 mol equiv.) in methanol (10 cm^3) was stirred at room temperature. The reaction mixture was treated by the same procedure as described above to give the imidazole **3a** or **3b**.

5-*Formyl*-2-*methoxy*-N-*phenyl*-1H-*imidazole*-4-*carboxamide* **3a**. (26%), m.p. 211–212 °C (Found: M^+, 245.0784. $C_{12}H_{11}N_3O_3$ requires *M*, 245.0800); ν_{max}(KBr)/cm^{-1} 3450 and 1660; δ_H(100 MHz; $CDCl_3$–CD_3OD) 4.14 (3 H, s, OMe), 7.16–7.46 (5 H, m, Ph), 9.10 (1 H, s, NH) and 10.34 (1 H, s, CHO); δ_C(100 MHz; $CDCl_3$–CD_3OD) 57.6 (OMe), 120.6 (C-2′, -6′), 125.1 (C-4′), 129.4 (C-3′, -5′), 130.1 (C-4), 137.6 (C-1′), 139.5 (C-5), 156.2 (C-2), 160.3 (C=O) and 182.1 (CHO); *m*/*z* 245 (M^+), 216 (M^+ − CHO) and 153 (M^+ − NH_2Ph).

5-*Hydroxymethyl*-2-*methoxy*-N-*phenyl*-1H-*imidazole*-4-*carboxamide* **3b**. (38%), m.p. 162–163 °C (Found: M^+, 247.0926. $C_{12}H_{13}N_3O_3$ requires *M*, 247.0956); ν_{max}(KBr)/cm^{-1} 3400, 3190, 1650 and 1580; δ_H(270 MHz; $CDCl_3$) 4.04 (3 H, s, OMe), 4.77 (2 H, d, *J* 5.5, CH_2), 5.01 (1 H, t, *J* 5.5, OH), 7.13–7.68 (5 H, m, Ph), 8.64 (1 H, br s, NH) and 8.82 (1 H, s, NH); δ_C(100 MHz; $CDCl_3$–CD_3OD) 55.2 (CH_2), 56.7 (OMe), 120.1 (C-2′, -6′), 124.3 (C-4′), 126.1 (C-5), 129.1 (C-3′, -5′), 133.3

(C-4), 137.9 (C-1'), 152.4 (C-2) and 162.8 (C=O); *m/z* 247 (M^+) and 154 ($M^+ - NH_2Ph$).

General Procedure for the Synthesis of Esters **4a**, **b** *from Diamine* **1d**.—Compound **1d** (100 mg, 0.714 mmol) and copper(II) chloride (192 mg, 2.0 mol equiv.) were stirred in methanol or ethanol (10 cm^3) at reflux (**4a**, 7 h; **4b**: 8 h). The reaction mixture was treated by the same procedure as described above to give title compounds **4a** and **4b**.

Methyl 2-methoxy-5-methyl-1H-imidazole-4-carboxylate **4a**. (51%), m.p. 146–147 °C (Found: C, 49.2; H, 5.9; N, 16.4. $C_7H_{10}N_2O_3$ requires C, 49.1; H, 5.9; N, 16.5%); ν_{max}(KBr)/cm^{-1} 3450, 1700 and 1570; δ_H(100 MHz; $CDCl_3$) 2.43 (3 H, s, 5-Me), 3.84 (3 H, s, OMe), 4.02 (3 H, s, OMe) and 9.11 (1 H, br s, NH); δ_C(67.5 MHz; $CDCl_3$) 14.6 (5-Me), 51.4 (OMe), 56.8 (2-OMe), 114.0 (C-5), 144.1 (C-4), 153.3 (C-2) and 160.1 (C=O); *m/z* 170 (M^+) and 138 (M^+ – MeOH).

Ethyl 2-ethoxy-5-methyl-1H-imidazole-4-carboxylate **4b**. (54%), m.p. 102–103 °C (Found: M^+, 198.1009. $C_9H_{14}N_2O_3$ requires *M*, 198.1004); ν_{max}(KBr)/cm^{-1} 3450, 1700 and 1570; δ_H(100 MHz; $CDCl_3$) 1.35 (3 H, t, *J* 7, CH_2Me), 1.38 (3 H, t, *J* 7, CH_2Me), 2.42 (3 H, s, 5-Me), 4.30 (2 H, q, *J* 7, CH_2), 4.42 (2 H, q, *J* 7, CH_2) and 8.76 (1 H, br s, NH); δ_C(67.5 Hz; $CDCl_3$) 14.4 (Me), 14.6 (Me × 2), 60.2 (CH_2), 65.8 (CH_2), 113.8 (C-5), 144.0 (C-4), 153.2 (C-2) and 161.0 (C=O); *m/z* 198 (M^+).

General Procedure for the Synthesis of Diols **6a–c** *from Amines* **5a–c**.—To a solution of a compound **5a–c** (100 mg) in methanol (10 cm^3) was added thallium(III) nitrate trihydrate (1.2 mol equiv.). The mixture was stirred at room temperature (**6a**: 1.5 h; **6c**: 2 h). The reaction mixture was treated by the same procedure as described above to give the corresponding product **6a–c**.

5,5-Dihydroxy-6-methoxy-1,6-dimethyl-3-phenyl-5,6-dihydropyrimidine-2,4(1H,3H)-dione **6a**. (93%), m.p. 107–108 °C (Found: C, 55.95; H, 5.8; 10.0. $C_{13}H_{16}N_2O_5$ requires C, 55.7; H, 5.75; N, 10.0%); ν_{max}(KBr)/cm^{-1} 3350, 3250, 1720, 1675 and 1665; δ_H(270 MHz; $CDCl_3$) 1.71 (3 H, s, 6-Me), 3.19 (3 H, s, OMe), 3.40 (3 H, s, NMe), 3.43 and 4.84 (each 1 H, each s, erased on D_2O addition, OH × 2) and 7.17–7.49 (5 H, m, Ph); δ_C(67.5 MHz; $CDCl_3$) 13.3 (6-Me), 29.8 (NMe), 52.1 (OMe), 89.1 (C-6), 90.2 (C-5), 128.2 (C-2', -6'), 128.8 (C-4'), 129.2 (C-3', -5'), 134.9 (C-1'), 152.0 (C=O) and 169.0 (C=O); *m/z* 280 (M^+), 262 ($M^+ - H_2O$), 234 [$M^+ - C(OH)_2$] and 206 [$M^+ - COC(OH)_2$].

5,5-Dihydroxy-6-methoxy-3,6-dimethyl-1-phenyl-5,6-dihydropyrimidine-2,4(1H,3H)-dione **6b**. (81%), m.p. 122–123 °C (Found: C, 55.6; H, 5.7; N, 9.6); ν_{max}(KBr)/cm^{-1} 3450, 3300, 1720, 1650 and 1645; δ_H(270 MHz; $CDCl_3$) 1.28 (3 H, s), 3.28 (3 H, s), 3.43 (3 H, s), 3.51 (1 H, s), 4.93 (1 H, s) and 7.29–7.46 (5 H, m); δ_C(67.5, MHz; $CDCl_3$) 14.4, 28.5, 51.5, 88.9, 90.9, 129.0, 129.3, 129.5, 138.3, 152.4 and 170.6; *m/z* 279 ($M^+ - 1$), 262 ($M^+ - H_2O$) and 234 [$M^+ - C(OH)_2$].

5,5-Dihydroxy-6-methoxy-1,3,6-trimethyl-5,6-dihydropyrimidine-2,4(1H,3H)-dione **6c**. (54%), m.p. 120–121 °C (Found: C, 43.9; H, 6.3; N, 12.9. $C_8H_{14}N_2O_5$ requires C, 44.0; H, 6.5; N, 12.8%); ν_{max}(KBr)/cm^{-1} 3445, 3260, 1720, 1665 and 1640; δ_H(270 MHz; $CDCl_3$) 1.61 (3 H, s), 3.14 (3 H, s), 3.30 (3 H, s), 3.57 (3 H, s) and 4.81 (1 H, s); δ_C(67.5 MHz; $CDCl_3$) 12.4, 28.5, 29.3, 52.0, 89.2, 89.8, 151.6 and 170.0; *m/z* 201 (M^+ – OH) and 184 (M^+ – OH × 2).

General Procedure for the Synthesis of Esters **7a–c** *from Diols* **6a–c**.—A compound **6a–c** was stirred in methanol (**7a**: room temp., 10 min; **7b**: reflux, 30 min; **7c**: reflux, 2 h). The reaction mixture was treated by the same procedure as described above to give the corresponding esters **7a–c**.

Methyl 4-hydroxy-5-methoxy-1,5-dimethyl-2-oxo-3-phenyl-2,3,4,5-tetrahydro-1H-imidazole-4-carboxylate **7a**. Quantitative yield, m.p. 125–126 °C (Found: C, 56.8; H, 6.1; N, 9.2. $C_{14}H_{18}N_2O_5$ requires C, 57.1; H, 6.2; N, 9.5%); ν_{max}(KBr)/cm^{-1} 3400, 1740 and 1720; δ_H(270 MHz; $CDCl_3$) 1.41 (3 H, s, 5-Me), 2.92 (3 H, s, NMe), 3.40 (3 H, s, OMe), 3.75 (3 H, s, OMe), 4.50 (1 H, s, erased on D_2O addition, OH) and 7.20–7.42 (5 H, m, Ph); δ_C(67.5 MHz; CD_3OD) 20.1 (5-Me), 25.5 (NMe), 52.4 (OMe), 53.5 (OMe), 90.9 (C-5), 92.7 (C-4), 127.1 (C-2', -6'), 127.4 (C-4'), 129.7 (C-3', -5'), 137.2 (C-1'), 159.1 (C=O) and 174.1 (C=O); *m/z* 294 (M^+) and 262 (M^+ – MeOH).

Methyl 4-hydroxy-5-methoxy-3,5-dimethyl-2-oxo-1-phenyl-2,3,4,5-tetrahydro-1H-imidazole-4-carboxylate **7b**. (95%), m.p. 141–142 °C (Found: M^+, 294.1226. $C_{14}H_{18}N_2O_5$ requires *M*, 294.1216); ν_{max}(KBr)/cm^{-1} 3370 and 1735; δ_H(270 MHz; $CDCl_3$) 1.28 (3 H, s), 2.79 (3 H, s), 3.49 (3 H, s), 3.87 (3 H, s), 4.29 (1 H, s) and 7.20–7.49 (5 H, m); δ_C(67.5 MHz; CD_3OD) 20.6, 25.9, 52.6, 53.7, 92.0, 92.3, 127.2, 127.6, 130.0, 137.1, 159.1 and 171.2; *m/z* 294 (M^+) and 262 (M^+ – MeOH).

Methyl 4-hydroxy-5-methoxy-1,3,5-trimethyl-2-oxo-2,3,4,5-tetrahydro-1H-imidazole-4-carboxylate **7c**. (87%), m.p. 113–114 °C (Found: M^+, 232.1053. $C_9H_{16}N_2O_5$ requires *M*, 232.1059); ν_{max}(KBr)/ cm^{-1} 3370, 1740 and 1720; δ_H(270 MHz; $CDCl_3$) 1.33 (3 H, s), 2.70 (3 H, s), 2.81 (3 H, s), 3.27 (3 H, s), 3.84 (3 H, s) and 4.18 (1 H, s); δ_C(67.5 MHz; CD_3OD) 20.2, 25.3, 25.8, 52.3, 91.1, 92.2, 160.5 and 171.2; *m/z* 232 (M^+) and 200 (M^+ – MeOH).

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