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Studies on Pyrimidine Derivatives. XV.[1] Homolytic Acylation and Amidation of Simply Substituted Pyrimidines

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The reaction of 2,6-disubstituted pyrimidines with acyl radicals generated either from pyruvic acid-$AgNO_3$-$(NH_4)_2S_2O_8$ (method A) or from aldehyde-$FeSO_4$-*t*-BuOOH (method B) in aq. H_2SO_4, gave the corresponding 2,6-disubstituted 4-acylpyrimidines. However, 4,6-disubstituted pyrimidines gave 2-acetyl- and 2,5-diacetyl-4,6-disubstituted pyrimidines under the same conditions (methods A and B).

Similarly, homolytic amidation of pyrimidines in which the 2- or 4-positions are free yielded pyrimidine-2- or -4-carboxamides.

Keywords——homolytic acylation; homolytic amidation; 2-acylpyrimidines; 4-acylpyrimidines; 2,5-diacylpyrimidines; pyrimidine-2-carboxamides; pyrimidine-4-carboxamides

Recently, we have reported[3] that the homolytic hydroxymethylation developed by Minisci *et al.*[4] can be successfully applied for the synthesis of both 2- and 4-pyrimidinemethanols. As regards carbon-carbon bond formation of N-heteroaromatics by means of homolytic reactions, another important improvement was also introduced by Minisci and his co-workers.[5] Namely, acyl radicals generated by the oxidative decarboxylation of α-keto acids (method A), or by the treatment of aldehydes with tert-butyl hydroperoxide and ferrous sulfate (method B), selectively attack the 2- and 4-positions of the quinoline ring to give the corresponding quinolyl ketones.

Although some methods have been reported for the synthesis of pyrimidinyl ketones,[6] the procedures are not without difficulty. Thus our interest was focussed on the application of Minisci's method for a one-step synthesis of pyrimidinyl ketones starting from simply substituted pyrimidines.

First, the reaction of 2,6-disubstituted pyrimidines (Ia—d) with acyl radicals was examined with the aim of substituting the 4-position. When 2-methyl-6-phenylpyrimidine (Ib) was allowed to react with pyruvic acid under the conditions of method A, 4-acetyl-2-methyl-6-phenylpyrimidine (IIb) was isolated in 52% yield. In the nuclear magnetic resonance (NMR) spectrum of IIb, a singlet due to a ring proton was observed at 8.08 ppm together with the signals from two methyl groups. This clearly demonstrated Ib to have been acetylated at the 4-position. The results obtained with 2,6-disubstituted pyrimidines (Ia—d) by method A are summarized in Table I.

Method B was then applied to determine whether it possessed any advantage over method A. As shown in Tables I and II, there were only minor differences in the yields of

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2) Location: *Aobayama, Sendai 980, Japan.*
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Method A
$$Ag^+ + S_2O_8^- \longrightarrow Ag^{2+} + SO_4^{-\cdot} + SO_4^{2-}$$
$$Ag^+ + SO_4^{-\cdot} \longrightarrow Ag^{2+} + SO_4^{2-}$$
$$RCOCOOH + Ag^{2+} \longrightarrow R\dot{C}O + CO_2 + Ag^+ + H^+$$

Method B
$$t\text{-BuOOH} + Fe^{2+} \longrightarrow t\text{-Bu}\dot{O} + Fe(OH)^{2+\cdot}$$
$$t\text{-Bu}\dot{O} + RCHO \longrightarrow R\dot{C}O + t\text{-BuOH}$$

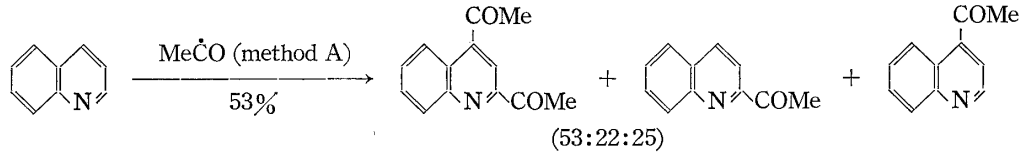

Chart 1

Table I. Homolytic Acetylation of 2,6-Disubstituted Pyrimidines (Ia—d) by Method A

Compound No.	R_2	R_6	Yield (%)	mp or [bp (mmHg)] (°C)	Formula	Analysis(%) Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
IIa	Me	Me	29	[96—98 (20)]	$C_8H_{10}N_2O$	63.98	6.71	18.65	64.20	6.69	18.59
IIb	Me	Ph	52	94—95	$C_{13}H_{12}N_2O$	73.56	5.70	13.20	73.96	5.53	13.02
IIc	Ph	Me	64	82—83	$C_{13}H_{12}N_2O$	73.56	5.70	13.20	73.47	5.80	13.10
IId	OMe	Me	24	61—62	$C_8H_{10}N_2O_2$	57.82	6.07	16.86	57.89	6.05	16.95

Table II. Homolytic Acylation of 2-Methyl-6-phenylpyrimidine (Ib) by Method B

Compound No.	R	Yield (%)	mp (°C)	Formula	Analysis(%) Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
IIb	Me	75	94—95.5							
IIe	Et	78	95—97	$C_{14}H_{14}N_2O$	74.31	6.24	12.38	74.57	6.17	12.38
IIf	iso-Pr	53	60—62	$C_{15}H_{16}N_2O$	74.97	6.71	11.66	74.77	6.77	11.66
IIg	Ph	12	64—65.5	$C_{18}H_{14}N_2O$	78.81	4.97	10.21	78.99	4.97	10.27

products obtained by the two methods, and since the availability of α-keto acids is more limited than that of aldehydes, method B appears to have wider applicability than method A for the preparation of these ketones.

Next, the acylation of 4,6-disubstituted pyrimidines using methods A and B was investogated. In contrast to the case of Ia, where a single product was formed, acylation of 4,6-dimethylpyrimidine (IIIa) under the conditions of method A provided 2-acetyl-4,6-dimethylpyrimidine (IVa), 38%, and a by-product 2,5-diacetyl-4,6-dimethylpyrimidine (Va), 13%. The structures of these compounds were supported by their spectral data and elemental analyses. Namely, no signal due to pyrimidine ring protons is observed in the NMR spectrum of Va, and the molecular formula, $C_{10}H_{12}N_2O_2$, is consistent with the diacetyl structure. In the NMR spectrum of IVa, the singlet at 7.20 ppm shows the acetyl group to be located at the 2-position of the pyrimidine ring.

When 4-methyl-6-phenylpyrimidine (IIIb) was allowed to react with acetaldehyde according to method B, similar products, 2-acetyl-4-methyl-6-phenyl- (IVb) and 2,5-diacetyl-4-methyl-6-phenylpyrimidine (Vb), were obtained. Separation of the products (IVb, Vb) was so

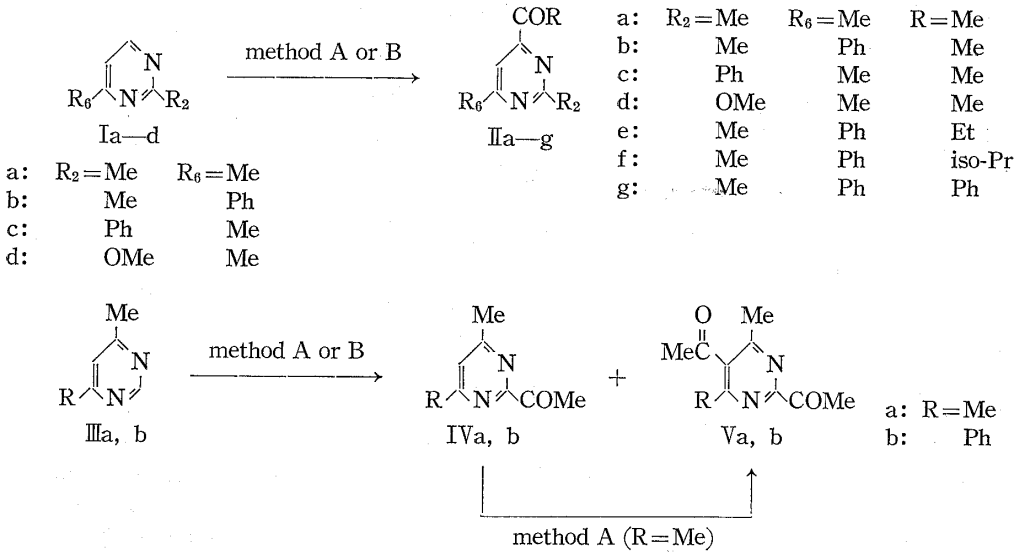

Chart 2

difficult that the yields of IVb and Vb were measured by gas chromatographic analysis of the crude products; the ratio of IVb and Vb was thus found to be 7: 3.

Since the monoacetyl compound (IVa) was converted into the diacetyl compound (Va) under identical conditions, the formation of the by-product V *via* IV seems likely. The electron-withdrawing effect of the 2-acetyl group introduced in the first step may accelerate the second acetylation at the 5-position.

Accordingly, it is clear that the homolytic acylation of pyrimidine derivatives whose 2- and 5-positions are both free results in contamination of the desired monoacyl pyrimidines with considerable amounts of the 2,5-diacylpyrimidines.

In the homolytic acylation by method B, formamide or N,N-dimethylformamide (DMF) can be employed instead of aldehyde.[7] Thus, 2,6-disubstituted pyrimidines (Ib, c) were treated with the above amides under conditions corresponding to method B, and the pyrimidine-4-carboxamides (VIa—d) were obtained as expected. The spectral data and the results of elemental analysis of these products are in good agreement with the structures shown.

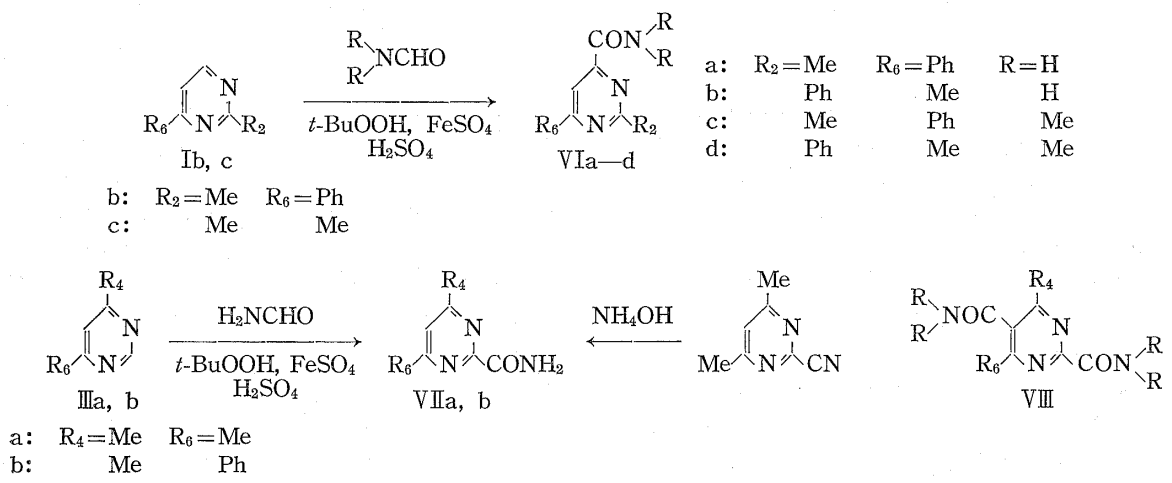

Chart 3

7) A. Arnone, M. Cecere, R. Galli, F. Minisci, M. Perchinunno, O. Porta, and G. Gardini, *Gazz. Chim. Ital.*, **103**, 13 (1973).

Unlike the homolytic acylation described above, the reaction of formamide with 4,6-disubstituted pyrimidines (III) did not afford any of the diamides (VIII), although the reason for this is not clear at present. The sole product of the reaction of IIIa, 4,6-dimethylpyrimidine-2-carboxamide (VIIa), was identical with an authentic specimen prepared from the corresponding pyrimidine-2-carbonitrile.[6b]

Table III. Homolytic Amidation of 2,6-Disubstituted (Ib, c) and 4,6-Disubstituted Pyrimidines (IIIa, b)

No.	Compound R_2	Compound R_4	R_6	Yield (%)	mp (°C)	Formula	Analysis (%) Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
VIa	Me	$CONH_2$	Ph	93	149—152	$C_{12}H_{11}N_3O$	67.59	5.20	19.71	67.84	5.08	19.70
VIb	Ph	$CONH_2$	Me	75	149—150	$C_{12}H_{11}N_3O$	67.59	5.20	19.71	67.79	5.17	19.81
VIc	Me	$CONMe_2$	Ph	36	81—83	$C_{14}H_{15}N_3O$	69.69	6.27	17.42	69.67	6.21	17.78
VId	Ph	$CONMe_2$	Me	20	90—92	$C_{14}H_{15}N_3O$	69.69	6.27	17.42	69.87	6.30	17.45
VIIa	$CONH_2$	Me	Me	43	183—184[6b]							
VIIb	$CONH_2$	Me	Ph	39	165—167	$C_{12}H_{11}N_3O$	67.59	5.20	19.71	67.70	5.15	20.13

Experimental

All melting points and boiling points are uncorrected. IR spectra were measured with a JASCO IRA-1 spectrometer. NMR spectra were obtained at 60 MHz with a Hitachi-Perkin Elmer R-20 spectrometer. Chemical shifts are expressed in ppm downfield from TMS as an internal standard. The following abbreviations are used: s=singlet, d=doublet, t=triplet, and m=multiplet.

General Procedure for Acetylation with Pyruvic Acid (Method A)——An aq. solution of $(NH_4)_2S_2O_8$ (0.02 mol in 40 ml H_2O) was added to a solution of the pyrimidine (0.01 mol), $AgNO_3$ (0.001 mol), pyruvic acid (0.02 mol), and conc. H_2SO_4 (3 ml) in H_2O (30 ml) at 50° with stirring. After stirring the reaction mixture at 50° for 1.5 hr, it was made alkaline by the addition of K_2CO_3 and then extracted with ether. The crude product was purified by vacuum distillation, recrystallization, or column chromatography.

4-Acetyl-2,6-dimethylpyrimidine (IIa)——Compound IIa was obtained from 2,6-dimethylpyrimidine (2.16 g, 0.02 mol) according to method A. Vacuum distillation gave a colorless liquid. Yield 0.88 g. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1710. NMR ($CDCl_3$) ppm: 2.58 (3H, s), 2.68 (3H, s), 2.76 (3H, s), 7.52 (1H, s).

4-Acetyl-2-methyl-6-phenylpyrimidine (IIb)——Compound IIb was obtained from 2-methyl-6-phenyl pyrimidine (7.0 g, 0.041 mol) according to method A. The crude product was purified by Al_2O_3 column chromatography, eluting with ether. Recrystallization from petr. benzin gave colorless needles. Yield 4.7 g. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1708. NMR ($CDCl_3$) ppm: 2.74 (3H, s), 2.88 (3H, s), 7.50—7.70 (3H, m), 8.10—8.35 (2H, m), 8.18 (1H, s).

4-Acetyl-6-methyl-2-phenylpyrimidine (IIc)——Compound IIc was obtained from 6-methyl-2-phenylpyrimidine (1.0 g, 0.006 mol) according to method A. The crude product was recrystallized from petr. benzin to give colorless scales. Yield 0.8 g. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1710. NMR ($CDCl_3$) ppm : 2.64 (3H, s), 2.78 (3H, s), 7.40—7.60 (4H, m), 8.40—8.60 (2H, m).

4-Acetyl-2-methoxy-6-methylpyrimidine (IId)——Compound IId was obtained from 2-methoxy-6-methylpyrimidine (2.48 g, 0.02 mol) according to method A. The crude product was purified by SiO_2 column chromatography, eluting with $CHCl_3$. Recrystallization from petr. ether gave colorless needles. Yield 0.8 g. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1715. NMR ($CDCl_3$) ppm: 2.54 (3H, s), 2.66 (3H, s), 4.04 (3H, s), 7.32 (1H, s).

General Procedure for Acylation with Aldehydes (Method B)——A solution of $FeSO_4 \cdot 7H_2O$ (0.06 mol) in H_2O (40 ml) and 70% *t*-butyl hydroperoxide (0.06 mol) were separately but simultaneously added to a stirred and cooled (10—20°) mixture of the pyrimidine (0.01 mol), 4 M H_2SO_4 (5 ml), and the aldehyde (0.06 mol). After stirring the reaction mixture at 10—20° for 15 min, it was extracted with ether. The extract was washed with 2 N H_2SO_4 and dried over Na_2SO_4. The crude product was purified by recrystallization, disyillation, or column chromatography.

4-Acetyl-2-methyl-6-phenylpyrimidine (IIb)——Compound IIb was obtained from 2-methyl-6-phenylpyrimidine (1.70 g, 0.01 mol) and 90% acetaldehyde (2.93 g, 0.06 mol) according to method B. The crude product was recrystallized from petr. benzin to give colorless needles. Yield 1.6 g.

2-Methyl-6-phenyl-4-propionylpyrimidine (IIe)——Compound IIe was obtained from 2-methyl-6-phenylpyrimidine (1.70 g, 0.01 mol) and propionaldehyde (3.5 g, 0.06 mol) according to method B. The crude product was recrystallized from hexane to give colorless needles. Yield 1.76 g. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1707.

NMR (CCl_4) ppm: 1.20 (3H, t, J=7.0 Hz), 2.82 (3H, s), 3.21 (2H, q, J=7.0 Hz), 7.44—7.70 (3H, m), 8.13 (1H, s), 8.10—8.48 (2H, m).

4-Isobutyroyl-2-methyl-6-phenylpyrimidine (IIf)——Compound IIf was obtained from 2-methyl-6-phenylpyrimidine (1.70 g, 0.01 mol) and isobutyldehyde (4.33 g, 0.06 mol) according to method B. The crude product was purified by Al_2O_3 column chromatography, eluting with C_6H_6. Recrystallization from hexane gave colorless needles. Yield 1.20 g. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1703. NMR (CCl_4) ppm: 1.20 (6H, d, J= 7.0 Hz), 2.28 (3H, s), 3.21 (1H, septet, J=7.0 Hz), 7.44 (3H, m), 8.13 (1H, s), 8.10—8.48 (2H, m).

4-Benzoyl-2-methyl-6-phenylpyrimidine (IIg)——The crude extract was obtained from 2-methyl-6-phenylpyrimidine (1.70 g, 0.01 mol) and benzaldehyde (6.4 g, 0.06 mol) according to method B, although in this case acetic acid (15 ml) was added to obtain a homogeneous solution. After removal of benzaldehyde by steam distillation, the crude product was extracted with ether and purified by column chromatography, eluting with C_6H_6. Yield 0.33 g. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1672. NMR ($CDCl_3$) ppm: 2.92 (3H, s), 7.56—7.85 (6H, m), 8.18 (1H, s), 8.14—8.45 (4H, m).

Acetylation of 4,6-Dimethylpyrimidine with Pyruvic Acid——The crude product was obtained from 4,6-dimethylpyrimidine (2.16 g, 0.02 mol) according to method A. Vacuum distillation gave two fractions, bp 70—72° (3 mmHg) (IVa) and bp 110—112° (3 mmHg) (Va). 2-Acetyl-4,6-dimethylpyrimidine (IVa): Yield 1.14 g (38%). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1720. NMR ($CDCl_3$) ppm: 2.60 (6H, s), 2.77 (3H, s), 7.20 (1H, s). *Anal.* Calcd for $C_8H_{10}N_2O$: C, 63.98; H, 6.71; N, 18.65. Found: C, 63.97; H, 6.82; N, 18.55. Tosylhydrazone, mp 158—159° (EtOH). 2,5-Diacetyl-4,6-dimethylpyrimidine (Va): Yield 0.5 g (13%). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1720. NMR ($CDCl_3$) ppm: 2.54 (6H, s), 2.57 (3H, s), 2.74 (3H, s). *Anal.* Calcd for $C_{10}H_{12}N_2O_2$: C, 62.48; H, 6.29; N, 14.58. Found: C, 62.66; H, 6.29; N, 14.30.

Acetylation of 4-Methyl-6-phenylpyrimidine with Acetaldehyde——The crude extract was obtained from 4-methyl-6-phenylpyrimidine (1.70 g, 0.01 mol) and acetaldehyde (2.9 g 0.06 mol) according to method B. The crude product was purified by SiO_2 column chromatography, eluting with C_6H_6: AcOEt (20: 1). The first fraction gave colorless needles (Vb) which were recrystallized from hexane, mp 123—125°. Yield 75 mg (0.3%). IR ν_{max}^{KBr} cm^{-1}: 1718, 1703. NMR ($CDCl_3$) ppm: 2.15 (3H, s), 2.68 (3H, s), 2.86 (3H, s), 7.55—8.00 (5H, m). *Anal.* Calcd. for $C_{15}H_{14}N_2O_2$: C, 70.85; H, 5.55; N, 11.02. Found: C, 70.91; H, 5.46; N, 11.09. The second fraction gave a liquid (IVb), which was converted to the tosylhydrazone, mp 151—152° (EtOH). Yield 0.26 g (7%). NMR ($CDCl_3$) ppm: 2.39 (3H, s), 2.42 (3H, s), 2.62 (3H, s), 7.20—8.30 (10H, m), 15.00—15.40 (1H, broad). *Anal.* Calcd. for $C_{20}H_{20}N_4O_2S$: C, 63.13; H, 5.30; N, 14.73; S, 8.43. Found: C, 63.42; H, 5.46; N, 15.00; S, 8.41. The crude product was analyzed by gas chromatography (FID). Column, 10% SE 30, 1 m; carrier gas (N_2), 60 ml/min; column temperature, 200°.

2,5-Diacetyl-4,6-dimethylpyrimidine (Va)——The crude product was obtained from 2-acetyl-4,6-dimethylpyrimidine (IVa) (0.73 g, 4.86 mmol) according to method A. Vacuum distillation gave the starting material (IVa), bp 80—110° (1 mmHg) (0.22 g, 30%) and Va, bp 118—130° (1 mmHg) (0.27 g, 29%).

General Procedure for Amidation with Formamide or N,N-Dimethylformamide——A solution of $FeSO_4 \cdot 7H_2O$ (0.06 mol) in H_2O (40 ml) and 70% *t*-butyl hydroperoxide (0.06 mol) were separately but simultaneously added to a stirred and cooled (10—20°) mixture of the pyrimidine (0.01 mol), 4 M H_2SO_4 (10 ml, 0.04 mol), and formamide or DMF (15 ml). The reaction mixture was stirred at 10—20° for 1 hr.

2-Methyl-6-phenylpyrimidine-4-carboxamide (VIa)——2-Methyl-6-phenylpyrimidine (1.70 g, 0.01 mol) was allowed to react with formamide according to the general procedure. The reaction mixture was diluted with H_2O and extracted with AcOEt. The crude product was recrystallized from C_6H_6 to give colorless needles. Yield 2.0 g. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3540, 3400, 1704. NMR ($CDCl_3$) ppm: 2.86 (3H, s), 6.20—6.60 (1H, broad), 7.40—7.65 (3H, m), 7.80—8.06 (1H, broad), 8.06—8.30 (2H, m), 8.34 (1H, s).

6-Methyl-2-phenylpyrimidine-4-carboxamide (VIb)——6-Methyl-2-phenylpyrimidine (1.70 g, 0.01 mol) was allowed to react with formamide according to the general procedure. The reaction mixture was diluted with H_2O and extracted with $CHCl_3$. The crude product was recrystallized from C_6H_6 to give colorless needles. Yield 1.71 g. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3540, 3400, 1705. NMR ($CDCl_3$) ppm: 2.67 (3H, s), 6.52 (1H, broad), 7.23—7.63 (3H, m), 7.85 (1H, s), 7.97 (1H, broad), 8.37—8.63 (2H, m).

2-Methyl-6-phenylpyrimidine-4-(N,N-dimethyl)carboxamide (VIc)——2-Methyl-6-phenylpyrimidine (1.70 g, 0.01 mol) was allowed to react with DMF according to the general procedure. The reaction mixture was diluted with H_2O and extracted with C_6H_6. The crude product was purified by Al_2O_3 column chromatography, eluting with C_6H_6–AcOEt (19: 1). Yield 0.86 g. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1642. NMR ($CDCl_3$) ppm: 2.78 (3H, s), 3.04 (3H, s), 3.10 (3H, s), 7.37—7.60 (3H, m), 7.73 (1H, s), 7.93—8.23 (2H, m).

6-Methyl-2-phenylpyrimidine-4-(N,N-dimethyl)carboxamide (VId)——4-Methyl-2-phenylpyrimidine (1.70 g, 0.01 mol) was allowed to react with DMF. The reaction mixture was diluted with H_2O and extracted with C_6H_6. The crude product was purified by Al_2O_3 column chromatography, eluting with C_6H_6 and C_6H_6–MeOH (9: 1). Starting pyrimidine, 1.2 g (71%), was recovered from the C_6H_6 eluate. Compound VId was eluted with C_6H_6–MeOH (9: 1). Recrystallization from hexane gave colorless needles. Yield 0.49 g. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1641. NMR ($CDCl_3$) ppm: 2.60 (3H, s), 3.15 (6H, s), 7.33 (1H, s), 7.40—7.60 (3H, m), 8.35—8.60 (2H, m).

4,6-Dimethylpyrimidine-2-carboxamide (VIIa)——4,6-Dimethylpyrimidine (2.16 g, 0.02 mol) was allowed to react with formamide according to the general procedure. The reaction mixture was made alkaline with

1 N $NaHCO_3$ and concentrated under reduced pressure to remove excess formamide. The residue was dissolved in $CHCl_3$ and purified by SiO_2 column chromatography, eluting with AcOEt. Recrystallization from C_6H_6 gave colorless needles. Yield 1.30 g. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3540, 3400, 1711. NMR ($CDCl_3$) ppm: 2.56 (6H, s), 7.15 (1H, s), 6.59 (1H, broad), 7.90 (1H, broad). This compound was identical with an authentic specimen.[6b]

4-Methyl-6-phenylpyrimidine-2-carboxamide (VIIb)——4-Methyl-6-phenylpyrimidine (1.70 g, 0.01 mol) was allowed to react with formamide according to the general procedure. The reaction mixture was diluted with H_2O and extracted with AcOEt. The crude product was purified by Al_2O_3 column chromatography, eluting with AcOEt. Recrystallization from C_6H_6 gave colorless needles. Yield 0.83 g. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3540, 3400, 1700. NMR ($CDCl_3$) ppm: 2.72 (3H, s), 7.17—7.93 (5H, m), 8.00—8.50 (3H, m).

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