[Chem. Pharm. Bull. 28(1) 142—149 (1980)]

Synthesis of 1,3-Dimethylpyrimido[4,5-*b*]quinoline-2,4(1H,3H)-diones (1,3-Dimethyl-5-deazaalloxazines) and Related Compounds *via* the Intramolecular Cycloaddition of Azahexatrienes[1)]

Sadao Nishigaki, Junko Sato, Kayoko Shimizu, Kiyoko Furukawa, Keitaro Senga,[2a)] and Fumio Yoneda[2b)]

Pharmaceutical Institute, School of Medicine, Keio University,[2a)] and Faculty of Pharmaceutical Sciences, Kumamoto University[2b)]

(Received June 22, 1979)

Heating of 6-arylamino-1,3-dimethyluracils (IIa—e) with one-carbon reagents (dimethylformamide dimethylacetal, dimethylformamide-phosphorus oxychloride, and triethyl orthoformate) afforded 1,3-dimethylpyrimido[4,5-*b*]quinoline-2,4(1H,3H)-diones (Va—e) *via* the intramolecular cycloaddition of azahexatrienes. Similarly, treatment of IIa with arylaldehydes provided 5-aryl-1,3-dimethylpyrimido[4,5-*b*]quinoline-2,4(1H,3H,5H,10H)-diones (VIIa—e), which were subsequently dehydrogenated with either thionyl chloride or diethyl azodicarboxylate to give 5-aryl-1,3-dimethylpyrimido[4,5-*b*]quinoline-2,4(1H,3H)-diones (Xa—e). The reaction of 6-arylamino-1,3-dimethyl-4-N-phenylcytosines (XIIa—c) with dimethylformamide dimethylacetal to give 4-arylimino-1,3-dimethylpyrimido[4,5-*b*]quinoline-2(1H,3H)-ones (XIIIa—c) is also described.

Keywords——6-arylamino-1,3-dimethyluracils; dimethylformamide dimethylacetal; dimethylformamide-phosphorus oxychloride; triethyl orthoformate; arylaldehydes; intramolecular cycloaddition of azahexatrienes; 1,3-dimethylpyrimido[4,5-*b*]quinoline-2,4(1H,3H)-diones; 6-arylamino-1,3-dimethyl-4-N-phenylcytosines; 4-arylimino-1,3-dimethylpyrimido[4,5-*b*]quinoline-2,4(1H,3H)-ones

The intramolecular cycloaddition of azahexatrienes has recently been shown to offer a useful synthetic route to various heterocyclic systems, *e.g.* purine,[3a-c)] pyrazolo[3,4-*d*]pyrimidine,[3a,4)] pteridine,[3b,5)] pyrimido[4,5-*e*]-*as*-triazine (6-azapteridine),[3a,c)] and pyrimido[4,5-*c*]-pyridazine.[6)] We now report a new synthesis of 1,3-dimethylpyrimido[4,5-*b*]quinoline-2,4(1H,3H)-diones (1,3-dimethyl-5-deazaalloxazines: Va—e and Xa—e) *via* the intramolecular cycloaddition of azahexatrienes by the reaction of 6-arylamino-1,3-dimethyluracils (IIa—e) with one-carbon reagents, *i.e.*, dimethylformamide dimethylacetal (DMFDMA), dimethylformamide–phosphorus oxychloride (Vilsmeier reagent), triethyl orthoformate, and arylaldehydes. In addition, we report the synthesis of 4-arylimino-1,3-dimethylpyrimido[4,5-*b*]quinoline-2(1H,3H)-ones (XIIIa—c) by the reaction of 6-arylamino-1,3-dimethyl-4-N-phenylcytosines (XIIa—c) with DMFDMA, which also involves the intramolecular cycloaddition of azahexatrienes.

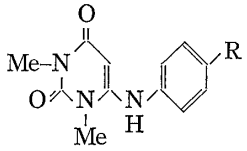
The requisite starting materials (IIa—e and XIIa—c) were prepared by the nucleophilic displacement of 6-chloro-1,3-dimethyluracil (I)[7)] or 6-chloro-1,3-dimethyl-4-N-phenylcytosine

1) A part of this work has been reported in a preliminary form: K. Senga, K. Shimizu, S. Nishigaki, and F. Yoneda, *Heterocycles*, **6**, 1361 (1977).
2) Location: *a*) *35, Shinanomachi, Shinjuku-ku, Tokyo 160, Japan*; *b*) *5-1, Oe-honmachi, Kumamoto 862, Japan.*
3) *a*) F. Yoneda, M. Higuchi, and T. Nagamatsu, *J. Am. Chem. Soc.*, **96**, 5607 (1974); *b*) F. Yoneda, M. Higuchi, and M. Kawamura, *Heterocycles*, **4**, 1659 (1976); *c*) F. Yoneda and M. Higuchi, *Chem. Pharm. Bull.*, **25**, 2794 (1977).
4) F. Yoneda, T. Nagamatsu, T. Nagamura, and K. Senga, *J. Chem. Soc. Perkin I*, **1977**, 765.
5) F. Yoneda and M. Higuchi, *J. Chem. Soc. Perkin I*, **1977**, 1336.
6) K. Senga, J. Sato, Y. Kanamori, M. Ichiba, S. Nishigaki, M. Noguchi, and F. Yoneda, *J. Heterocycl. Chem.*, **15**, 781 (1978).
7) W. Pfleiderer and K.-H. Schündehütte, *Ann. Chem.*, **612**, 158 (1958).

(XI),[8] respectively, with the appropriate arylamines according to the reported procedures[8,9] (Tables I and II).

Heating of IIa with excess DMFDMA at 95° for 1 hr afforded a 60% yield of 1,3-dimethylpyrimido[4,5-*b*]quinoline-2,4(1H,3H)-dione (Va), which was isolated by concentration of the reaction mixture and addition of ethanol. The structure of Va was readily established from the analytical and spectral data. In particular, the nuclear magnetic resonance (NMR)

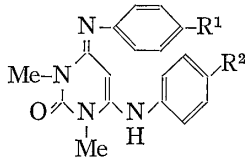
Table I. 6-Arylamino-1,3-dimethyluracils



Compd. No.	R	mp (°C)	Yield (%)	Formula	Analysis (%) Calcd (Found) C	H	N	IR (Nujol) cm^{-1} (CO)	(NH)
IIa	H	190—192[a,b]	87	$C_{12}H_{13}N_3O_2$	62.32 (62.18	5.67 5.65	18.17 18.33)	1700	3270
IIb	OMe	188—190[a,c]	91	$C_{13}H_{15}N_3O_3$	59.76 (59.86	5.79 5.84	16.08 16.15)	1690	3210
IIc	Br	217—219[a]	97	$C_{12}H_{12}BrN_3O_2$	46.46 (46.29	3.90 3.91	13.55 13.60)	1710	3240
IId	Cl	210—212[a,d]	81	$C_{12}H_{12}ClN_3O_2$	54.24 (54.27	4.56 4.55	15.82 15.70)	1705	3210
IIe	NO_2	270—272[e]	48	$C_{12}H_{12}N_4O_4$	52.17 (52.38	4.38 4.33	20.28 20.53)	1690	3220

a) Recrystallized from EtOH.
b) Lit.[9] mp 186.5—187°.
c) Lit. mp 243° (F. Yoneda, S. Matsumoto, Y. Sakuma, and S. Fukazawa, *J. Chem. Soc. Perkin I*, **1975**, 1907).
d) Lit.[9] mp 212—214°.
e) Recrystallized from DMF.

Table II. 6-Arylamino-1,3-dimethyl-4-N-phenylcytosines



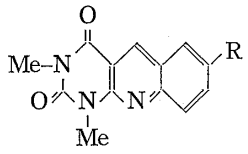
Compd. No.	R^1	R^2	mp (°C)[a]	Yield (%)	Formula	Analysis (%) Calcd (Found) C	H	N	IR (Nujol) cm^{-1} (CO)	(NH)
XIIa	H	H	179—181	52	$C_{18}H_{18}N_4O$	70.56 (70.54	5.92 5.82	18.29 18.37)	1655	3290
XIIb	H	OMe	151—151.5	60	$C_{19}H_{20}N_4O_2$	67.84 (67.91	5.99 5.95	16.66 16.92)	1655	3280
XIIc	H	Br	155—155.5	46	$C_{18}H_{17}BrN_4O$	56.11 (55.87	4.46 4.44	14.54 14.82)	1655	3300

a) All compounds were recrystallized from EtOH–H_2O.

8) K. Senga, F. Yoneda, and S. Nishigaki, *J. Org. Chem.*, **36**, 1829 (1971).
9) H. Goldner, G. Dietz, and E. Carstens, *Ann. Chem.*, **694**, 142 (1966).

spectrum (DMSO-d_6) showed three sharp singlets at δ 3.33 (N–Me), 3.63 (N–Me), and 9.40 (C^5–H) as well as a multiplet at δ 7.33—8.33 (C^{6-9}–4H). In accord with the above result, the reactions of other 6-arylamino-1,3-dimethyluracils (IIb—e) with DMFDMA provided 35—63% yields of the corresponding 1,3-dimethylpyrimido[4,5-*b*]quinoline-2,4(1H,3H)-diones (Vb—e). The compounds Va—d could also be obtained in 43—91% yields by refluxing IIa—d with the Vilsmeier reagent in benzene for 30 min. Alternatively, refluxing IIa—e with triethyl orthoformate in dimethylformamide for 1 hr gave 42—87% yields of Va—e; however, attempted cyclization of IIa with triethyl orthoacetate or triethyl orthopropionate under the same conditions to give 5-alkyl-1,3-dimethylpyrimido[4,5-*b*]quinoline-2,4(1H,3H)-diones resulted in the recovery of the starting material (Table III).

Table III. 1,3-Dimethylpyrimido[4,5-*b*]quinoline-2,4-(1H, 3H)-diones



Compd. No.	R	mp (°C)[a]	Yield (%) A[b]	B[c]	C[d]	Formula	Analysis (%) Calcd (Found) C	H	N	IR (Nujol) cm^{-1} (CO)	
Va	H	211—212	60	91	68	$C_{13}H_{11}N_3O_2$	64.72 (64.61	4.60 4.57	17.42 17.46)	1650	1705
Vb	OMe	273—274	63	43	65	$C_{14}H_{13}N_3O_3$	61.98 (61.69	4.83 4.77	15.49 15.36)	1650	1705
Vc	Br	275	56	50	69	$C_{13}H_{10}BrN_3O_2$	48.77 (48.84	3.15 3.25	13.13 13.34)	1655	1715
Vd	Cl	270	62	81	42	$C_{13}H_{10}ClN_3O_2$	56.62 (56.44	3.66 3.68	15.24 15.43)	1655	1710
Ve	NO_2	300	35	—	87	$C_{13}H_{10}N_4O_4$	54.55 (54.58	3.52 3.58	19.58 19.86)	1675	1730

a) All compounds were recrystallized from DMF.
b) Cyclization with dimethylformamide dimethylacetal.
c) Cyclization with the Vilsmeier reagent.
d) Cyclization with triethyl orthoformate.

The reaction of IIa—e with DMFDMA or the Vilsmeier reagent leading to Va—e was presumably initiated by the formation of a 5-N,N-dimethylaminomethylene intermediate (III), which possesses an azahexatriene-type structure. This could undergo intramolecular cyclization through valence isomerization and subsequent aromatization of IV by the loss of dimethylamine. Analogously, the reaction of IIa—e with triethyl orthoformate can be explained in the same way (the N,N-dimethylamino groups of the intermediates (III and IV) are replaced by ethoxy groups). In this case, the aromatization of IV to Va—e proceeds by the elimination of ethanol (Chart 1).

Although the introduction of an alkyl substituent at the 5 position of Va was unsuccessful, heating of IIa with excess benzaldehyde at 180° for 5 hr, followed by dilution with ethanol caused the separation of 1,3-dimethyl-5-phenylpyrimido[4,5-*b*]quinoline-2,4(1H,3H, 5H,10H)-dione (VIIa) in 50% yield. The characterization of VIIa was based on the following evidence. The analytical and mass spectral data established the molecular formula as $C_{19}H_{17}N_3O_2$. The infrared (IR) spectrum exhibited a secondary amino absorption band at 3240 cm^{-1}, while the NMR spectrum (DMSO-d_6) showed three sharp singlets at δ 3.13 (N–Me), 3.53 (N–Me), and 5.17 (C^5–H), a multiplet at δ 6.77—7.50 (C_6H_5 and C^{6-9}–4H), and a deuterium oxide-exchangeable broad singlet at δ 9.17 (NH). Similarly, the reaction of IIa with other

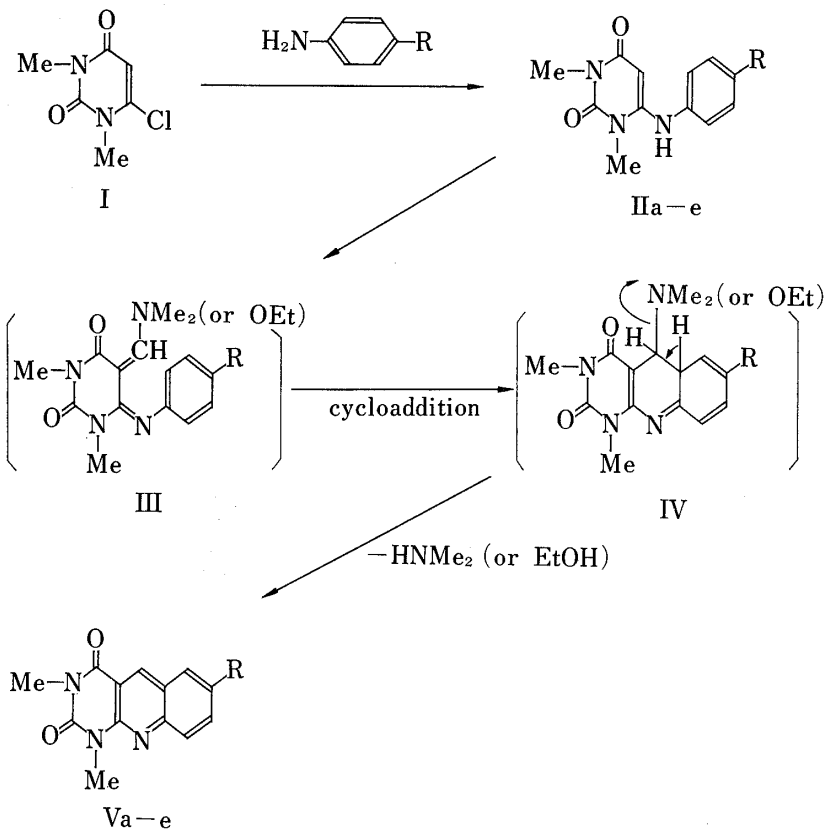
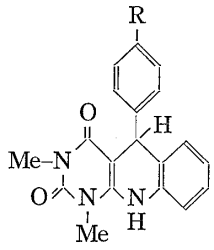


Chart 1

TABLE IV. 5-Aryl-1,3-dimethylpyrimido[4,5-*b*]quinoline-2,4(1H,3H,5H,10H)-diones

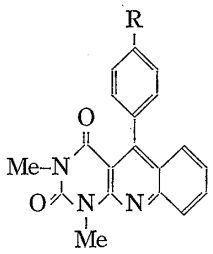


Compd. No.	R	mp (°C)	Yield (%)	Formula	Analysis (%) Calcd (Found) C	H	N	IR (Nujol) cm^{-1} (CO)	(NH)
VIIa	H	>300[a]	50	$C_{19}H_{17}N_3O_2$	71.45 (71.27	5.37 5.36	13.16 13.36)	1690	3240
VIIb	Me	228—231[b]	24	$C_{20}H_{19}N_3O_2$	72.05 (71.91	5.74 5.44	12.61 12.39)	1690	3240
VIIc	OMe	254—256[a]	49	$C_{20}H_{19}N_3O_3$	68.75 (68.56	5.48 5.32	12.03 11.86)	1690	3260
VIId	Br	>300[a]	37	$C_{19}H_{16}BrN_3O_2$	57.30 (57.31	4.05 4.02	10.55 10.55)	1700	3260
VIIe	Cl	299—300[a]	34	$C_{19}H_{16}ClN_3O_2$	64.50 (64.30	4.56 4.56	11.88 11.97)	1695	3240

a) Recrystallized from EtOH–DMF.
b) Recrystallized from EtOH.

arylaldehydes yielded 24—49% yields of the corresponding 5-aryl-1,3-dimethylpyrimido[4,5-*b*]quinoline-2,4(1H,3H,5H,10H)-diones (VIIb—e)(Table IV). The dehydrogenation of VIIa—e to 5-aryl-1,3-dimethylpyrimido[4,5-*b*]quinoline-2,4(1H,3H)-diones (Xa—e) was achieved in 61—89% yields by refluxing with thionyl chloride for 15 min. Alternatively, heating of the appropriate VIIa—e with diethyl azodicarboxylate at 160° for 15 min furnished 70—90% yields of the corresponding Xa—e (Table V).

Table V. 5-Aryl-1,3-dimethylpyrimido[4,5-*b*]quinoline-2,4(1H,3H)-diones



Compd. No.	R	mp (°C)[a]	Yield (%) A[b]	Yield (%) B[c]	Formula	Analysis (%) Calcd (Found) C	H	N	IR (Nujol) cm^{-1} (CO)	
Xa	H	261—264	89	90	$C_{19}H_{15}N_3O_2$	71.91 (71.67	4.76 4.73	13.24 13.14)	1660	1710
Xb	Me	236—237	73	70	$C_{20}H_{17}N_3O_2$	72.49 (72.27	5.17 5.17	12.68 12.58)	1660	1710
Xc	OMe	262—264	70	75	$C_{20}H_{17}N_3O_3$	69.15 (69.06	4.93 4.98	12.10 11.93)	1660	1705
Xd	Br	255—256	61	87	$C_{19}H_{14}BrN_3O_2$	57.55 (57.32	3.54 3.79	10.61 10.32)	1655	1710
Xe	Cl	286	62	70	$C_{19}H_{14}ClN_3O_2$	64.87 (64.88	4.01 3.96	11.94 12.20)	1655	1710

a) All compounds were recrystallized from EtOH–DMF.
b) Oxidation with thionyl chloride.
c) Oxidation with diethyl azodicarboxylate.

The reaction of IIa with arylaldehydes to give VIIa—e can be rationalized by assuming the initial formation of the 5-benzylidene intermediate (VI), followed by intramolecular cyclization via valence isomerization. The dehydrogenation of VIIa—e with thionyl chloride[10] to Xa—e probably proceeds through the N-sulfinyl chloride intermediate (VIII) and subsequent aromatization accompanied by the loss of hydrogen chloride and sulfur monoxide. On the other hand, the dehydrogenation of VIIa—e with diethyl azodicarboxylate[11] to give Xa—e would involve the intermediacy of the N-(1,2-dicarboethoxyhydrazino) derivative (IX), which undergoes aromatization by the elimination of diethyl hydrazodicarboxylate (Chart 2).

In connection with the successful synthesis of Va—e by the reactions of IIa—e with DMFDMA, we also investigated the following reactions. Thus, treatment of XIIa or XIIc with excess DMFDMA at 160° for 1.5 hr gave 15 and 10% yields of 1,3-dimethyl-4-phenyliminopyrimido[4,5-*b*]quinoline-2(1H,3H)-one (XIIIa) and 4-(*p*-bromophenyl)imino-1,3-dimethylpyrimido[4,5-*b*]quinoline-2(1H,3H)-one (XIIIc), respectively, as the only isolatable products. The structures of XIIIa and XIIIc were readily confirmed by their quantitative conversion

10) Thionyl chloride is known to be a strong dehydrogenation agent: For example, K. Senga, Y. Kanamori, and S. Nishigaki, *Chem. Pharm. Bull.*, **26**, 3240 (1978).
11) Diethyl azodicarboxylate is known to be a strong hydrogen acceptor: F. Yoneda, M. Higuchi, K. Mori, K. Senga, Y. Kanamori, K. Shimizu, and S. Nishigaki, *Chem. Pharm. Bull.*, **26**, 2905 (1978) and references cited therein.

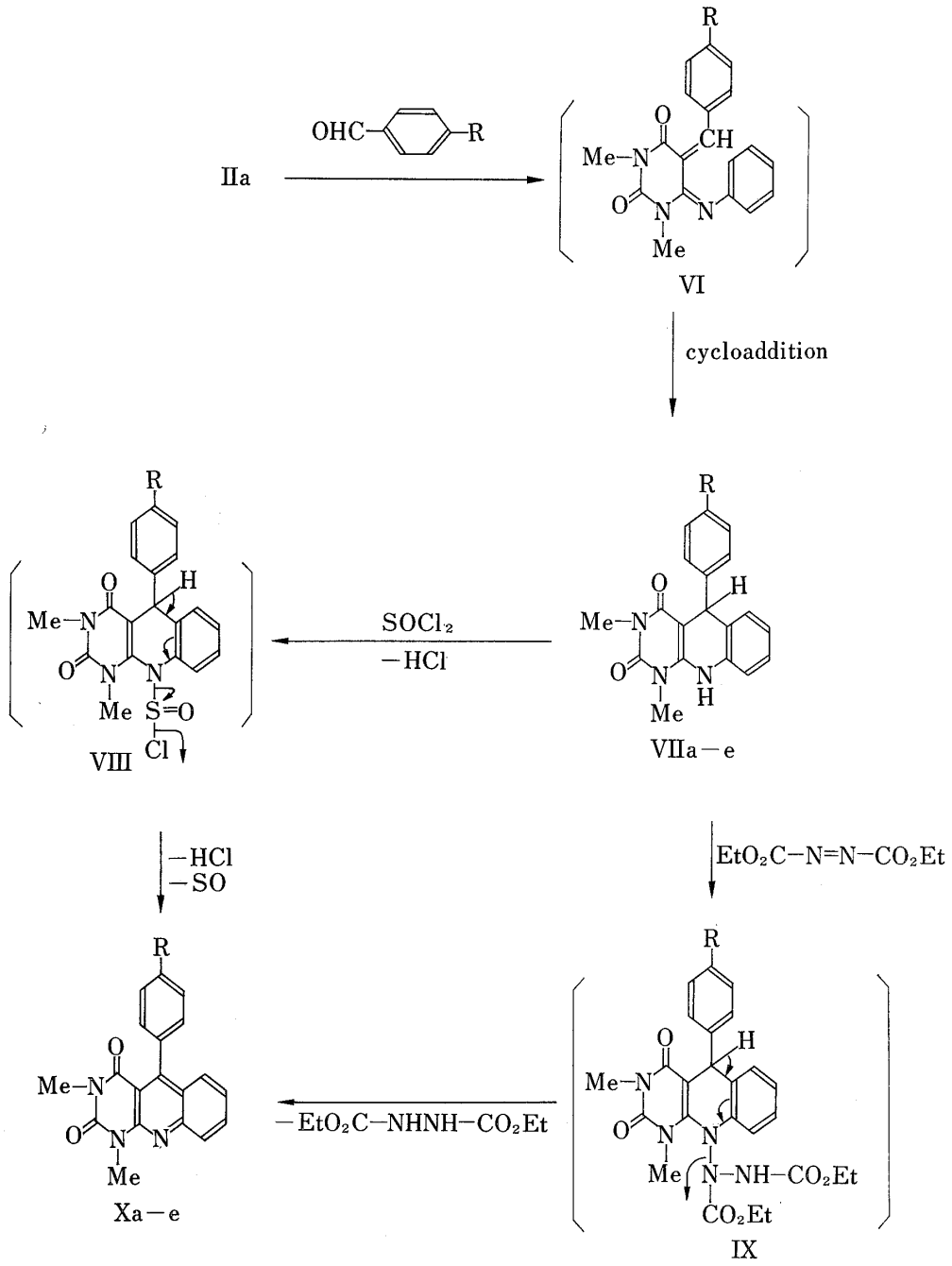
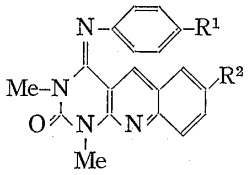


Chart 2

to Va using hot concentrated hydrochloric acid. In contrast, the reaction of XIIb with DMFDMA under the same conditions afforded a 5% yield of 7-methoxy-1,3-dimethyl-4-phenyliminopyrimido[4,5-*b*]quinoline-2(1H,3H)-one (XIIIb), which, upon heating with concentrated hydrochloric acid, yielded Vb quantitatively (Table VI). In addition, refluxing of 3-methyl-6-(N-methylanilino)uracil (XIV)[12] with DMFDMA at 160° for 30 min provided a 55% yield of 1,3-dimethyl-6-(N-methylanilino)uracil (XV), and none of the expected 3,10-dimethylpyrimido[4,5-*b*]quinoline-2,4(3H,10H)-dione could be isolated (Chart 3).

12) F. Yoneda, Y. Sakuma, M. Ichiba, and K. Shinomura, *J. Am. Chem. Soc.*, **98**, 830 (1976).

Table VI. 4-Arylimino-1,3-dimethylpyrimido[4,5-*b*]quinoline-2(1H,3H)-ones



Compd. No.	R^1	R^2	mp (°C)[a]	Yield (%)	Formula	Analysis (%) Calcd (Found) C	H	N	IR (Nujol) cm^{-1} (CO)
XIIIa	H	H	224—225	15	$C_{19}H_{16}N_4O$	72.13 (71.84	5.10 5.07	17.71 17.64)	1690
XIIIb	H	OMe	243—244	5	$C_{20}H_{18}N_4O_2$	69.35 (69.06	5.24 5.20	16.18 15.97)	1685
XIIIc	Br	H	230—231	10	$C_{19}H_{15}BrN_4O$	57.73 (57.46	3.83 3.79	14.14 13.92)	1690

a) All compounds were recrystallized from EtOH.

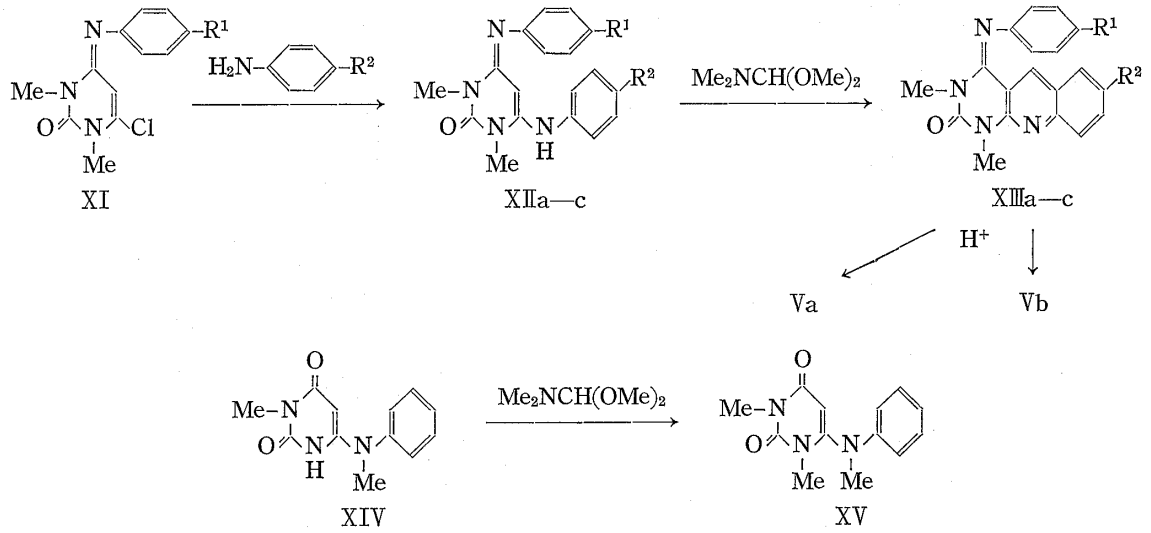


Chart 3

Experimental[13]

6-Arylamino-1,3-dimethyluracils (IIa—e) (Table I)——A mixture of 6-chloro-1,3-dimethyluracil (I)[7] (0.87 g, 0.005 mol) and an appropriate arylamine (0.01 mol) was heated at 180° for 3 hr. The reaction mixture was triturated with a mixture of ether and H_2O. The insoluble material was filtered and recrystallized to give the corresponding IIa—e.

6-Arylamino-1,3-dimethyl-4-N-phenylcytosines (XIIa—c) (Table II)——A mixture of 6-chloro-1,3-dimethyl-4-N-phenylcytosine (XI)[8] (1.25 g, 0.005 mol) and an appropriate arylamine (0.01 mol) was heated at 180° for 3 hr. The reaction mixture was dissolved in EtOH and made basic with 28% NH_3. The precipitates were filtered, washed with H_2O, dried, and recrystallized to give the corresponding XIIa—c.

13) Melting points were taken on a YANACO micro hot-stage melting point apparatus and are uncorrected. IR spectra were recorded on a JASCO IR-E spectrophotometer from samples mulled in Nujol. NMR spectra were determined at 60 MHz with a Varian T-60 spectrometer using tetramethylsilane as internal standard. Mass spectra were obtained on a JEOL JMS-D 300 spectrometer with a direct inlet system at 70 eV.

1,3-Dimethylpyrimido[4,5-*b*]quinoline-2,4(1H,3H)-diones (Va—e) (Table III)——Method A: A mixture of the appropriate IIa—e (0.001 mol) and dimethylformamide dimethylacetal (DMFDMA: 0.357 g, 0.003 mol) was heated at 95° for 1.5 hr. The reaction mixture was concentrated *in vacuo* and the residue was covered with EtOH. The insoluble material was filtered, washed with EtOH, and recrystallized to give the corresponding Va—e.

Method B: Vilsmeier reagent prepared from dimethylformamide (0.11 g, 0.0015 mol) and phosphorus oxychloride (0.23 g, 0.0015 mol) was added dropwise to a suspension of the appropriate IIa—d (0.0005 mol) in dry benzene (2 ml). The mixture was refluxed for 30 min. The resulting solution was concentrated *in vacuo* and the residue was triturated with 5% NH_3. The insoluble material was filtered, washed well with H_2O, dried, and recrystallized to give the corresponding Va—d, identical in all respects with the compounds prepared by Method A.

Method C: A solution of the appropriate IIa—e (0.0005 mol) in a mixture of triethyl orthoformate (0.3 g, 0.002 mol) and dimethylformamide (1.5 ml) was refluxed for 1 hr. The reaction mixture was concentrated *in vacuo* and the residue was covered with EtOH. The insoluble material was filtered, washed with EtOH, and recrystallized to give the corresponding Va—e, identical in all respects with the compounds obtained by Method A.

5-Aryl-1,3-dimethylpyrimido[4,5-*b*]quinoline-2,4(1H,3H,5H,10H)-diones (VIIa—e) (Table IV)——A mixture of IIa (0.12 g, 0.0005 mol) and an appropriate arylaldehyde (0.0015 mol) was heated at 180° for 5 hr and the reaction mixture was triturated with EtOH. The insoluble material was filtered, washed with EtOH, and recrystallized to give the corresponding VIIa—e.

5-Aryl-1,3-dimethylpyrimido[4,5-*b*]quinoline-2,4(1H,3H)-diones (Xa—e) (Table V)——Method A: A suspension of the appropriate VIIa—e (0.0005 mol) in thionyl chloride (3 ml) was refluxed for 15 min. The reaction mixture was concentrated *in vacuo* and the residue was triturated with 5% NH_3. The insoluble material was filtered, washed well with H_2O, dried, and recrystallized to give the corresponding Xa—e.

Method B: A mixture of the appropriate VIIa—e (0.0003 mol) and diethyl azodicarboxylate (0.21 g, 0.0012 mol) was heated at 160° for 15 min and the reaction mixture was triturated with EtOH. The insoluble material was filtered, washed with hot EtOH, and recrystallized to give the corresponding Xa—c, identical in all respects with the compounds prepared by Method A.

4-Arylimino-1,3-dimethylpyrimido[4,5-*b*]quinoline-2(1H,3H)-ones (XIIIa—c) (Table VI)——A mixture of the appropriate XIIa—c (0.001 mol) and DMFDMA (0.6 g, 0.005 mol) was heated at 160° for 1.5 hr. The reaction mixture was concentrated *in vacuo* and the residue was covered with EtOH. The insoluble material was filtered, washed with EtOH, and recrystallized to give the corresponding XIIIa—c.

Acid Hydrolysis of XIIIa—c——A suspension of the appropriate XIIIa—c (0.0005 mol) in 35% HCl (3 ml) was heated at 95° for 30 min. The precipitates were filtered, washed well with H_2O, dried, and recrystallized from dimethylformamide to give Va or Vb, identical in all respects with the compounds prepared by the reaction of IIa or IIb with DMFDMA.

1,3-Dimethyl-6-(N-methylanilino)uracil (XV)——A mixture of 3-methyl-6-(N-methylanilino)uracil (XIV)[12] (0.462 g, 0.002 mol) and DMFDMA (0.36 g, 0.003 mol) was refluxed at 160° for 30 min. The reaction mixture was concentrated *in vacuo* and the residue was covered with ether. The insoluble material was filtered and recrystallized from H_2O to give XV (0.265 g, 55%), mp 104°. *Anal.* Calcd. for $C_{13}H_{15}N_3O_2$: C, 63.66; H, 6.16; N, 17.13. Found: C, 63.40; H, 6.12; N, 17.34. IR cm^{-1}: 1645, 1690 (CO). NMR ($CDCl_3$) δ: 3.00 (s, 3H, N–Me), 3.23 (s, 3H, N–Me), 3.36 (s, 3H, N–Me), 5.50 (s, 1H, C^5–H), 6.66—7.66 (m, 5H, C_6H_5). MS *m/e*: 245 (M^+).

Acknowledgement The authors are grateful to Mr. Katsuhiko Nagahara of Kitasato University for NMR spectroscopy and elemental analyses, and to Dr. Kenji Ishii and Mr. Takafumi Harada of Keio University for determining mass spectra.