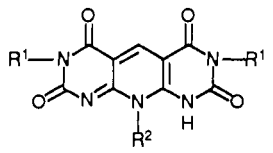
Synthesis of Bis(pyridodipyrimidines) as Autorecycling Redox Catalysts and Their Remarkable Turnover in the Oxidation of Alcohols§

Fumio Yoneda,*,† Kiyoshi Tanaka,† Hirotake Yamato,‡ Kenji Moriyama,‡ and Tomohisa Nagamatsu‡

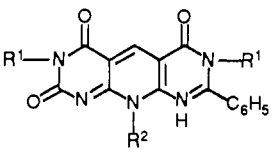
Contribution from the Faculty of Pharmaceutical Sciences, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606, Japan, and the Faculty of Pharmaceutical Sciences, Kumamoto University, Oe-honmachi, Kumamoto 862, Japan. *Received May 15, 1989*

Abstract: Bis(pyridodipyrimidines) (bis-PP's) as redox catalysts, in which two pyridodipyrimidine moieties are linked with polymethylene chains, have been synthesized by the condensation of bis(6-chloro-5-formyluracil-3-yl)alkanes with 6-alkylaminouracils. These bis-PP's oxidized alcohols more efficiently than monomeric pyridodipyrimidines to give the corresponding carbonyl compounds. Particularly, bis(7-methyl-10-(*n*-octyl)pyridodipyrimidin-3-yl)decane (**5j**) exhibited remarkable oxidizing ability toward cyclopentanol as a turnover catalyst, and its maximum effective concentration (MEC) was determined. The MEC of **5j** was 6.7×10^{-5} mmol (59 μg)/3 mL of cyclopentanol at 115 °C, and the MEC under introduction of oxygen (5 mL of oxygen/min) was 2×10^{-4} mmol (177 μg)/3 mL of cyclopentanol at 100 °C. Apart from the chemical yield of cyclopentanone, even an amount of only 2×10^{-11} mmol (17.7 pg) of catalyst **5j** oxidized cyclopentanol to give cyclopentanone in 13300000000000% yield based on the catalyst. This implies that the turnover number of catalyst **5j** is 8.9×10^7 mol min^{-1} (mol of catalyst)$^{-1}$, which would surpass that of bovine liver catalase, although the condition is quite different.

Pyridodipyrimidines (**1**) as new NAD-type redox catalysts have been found to oxidize a variety of alcohols under neutral conditions



1a



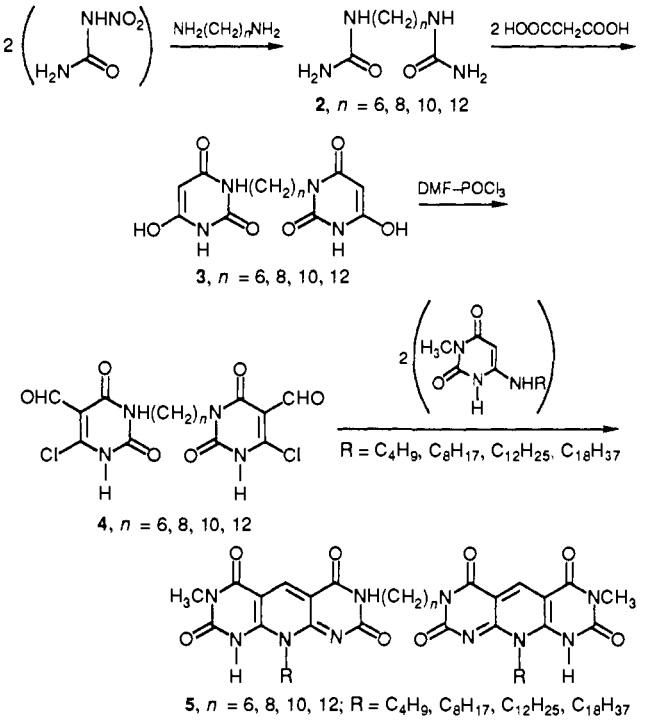
1b

to yield the corresponding carbonyl compounds, and a considerably high autorecycling turnover in the oxidation was observed.[1] In order to obtain more efficient redox organic catalysts, we have planned to manipulate the above oxidizing ability in terms of the linking of two pyridodipyrimidine moieties with polymethylene chains. Such linked bis(pyridodipyrimidine) (bis-PP) derivatives would be expected to have enhanced reactivity, because it is assumed that one pyridodipyrimidine moiety in the molecule accepts electrons to give the reduced-type pyridodipyrimidine moiety which would immediately form the intramolecular charge-transfer complex or radical pair with the other pyridodipyrimidine moiety. The formation of the intramolecular complex or radical pair must heighten the reactivity for alcohol oxidation and furthermore the sensitivity to oxygen for autorecycling turnover. There are a few examples of this type of intramolecular electron interaction in the bis-NAD and bis-flavin model reactions.[2,3] In the present paper, we describe the synthesis of a series of bis(pyridodipyrimidines) along this line and their autorecycling turnover oxidation of alcohols.

Synthesis of Bis(pyridodipyrimidines)

We have developed a new general synthetic methodology for the preparation of bis(pyridodipyrimidin-3-yl)alkanes (**5**) as one of the bis-PP's. Thus, nitrourea[4] was treated with α,ω-diaminoalkanes in boiling methanol to give the corresponding α,ω-diureidoalkanes (**2**), which were condensed with malonic acid in acetic acid-acetic anhydride[5] under reflux to afford the corresponding 3,3'-alkanediylbis(barbituric acids) (**3**). The key intermediates, **3**, thus obtained were treated with Vilsmeier reagent (DMF-$POCl_3$)[6] to give the corresponding bis(6-chloro-5-formyluracil-3-yl)alkanes (**4**), which were unstable and used for the next step without purification by recrystallization. Finally, compounds **4** were condensed with 6-(alkylamino)uracils to give rise to a variety of the respective bis(pyridodipyrimidin-3-yl)alkanes (bis-PP's, **5**; Scheme I, Table I).

Scheme I. New General Synthesis of Bis-PP's (**5**)



§ This paper is dedicated to Professor Haruaki Yajima on the occasion of his retirement from Kyoto University in March 1989.

† Kyoto University.

‡ Kumamoto University.

(1) Yoneda, F.; Yamato, H.; Ono, M. *J. Am. Chem. Soc.* **1981**, *103*, 5943-5945. This paper described the first example for the efficient autorecycling oxidation of alcohols by the coenzyme models *under neutral conditions*.

(2) Murakami, Y.; Aoyam, Y.; Kikuchi, J.; Nishida, K. *J. Am. Chem. Soc.* **1982**, *104*, 5189-5197.

(3) Yano, Y.; Ohya, E. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1227-1232.

(4) Davis, T. I.; Blanchard, K. C. *J. Am. Chem. Soc.* **1929**, *51*, 1790-1801.

(5) Stein, A.; Gregor, H. P.; Spoerri, P. E. *J. Am. Chem. Soc.* **1956**, *78*, 6185-6188.

(6) Yoneda, F. *Methods Enzymol.* **1980**, *66*, 267-277.

0002-7863/90/1512-9199$01.50/0

Table I. Bis(pyridodipyrimidin-3-yl)alkanes (5)

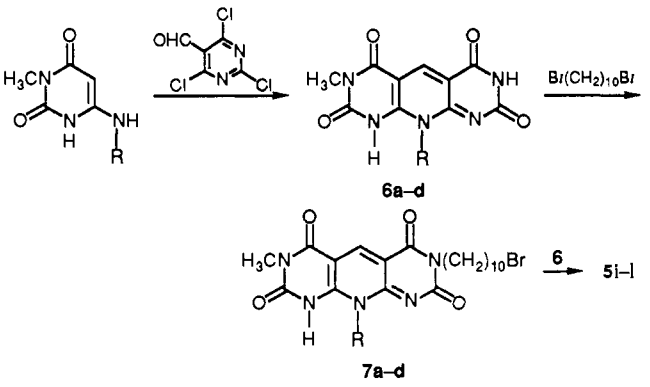
no.	n	R	mp, °C	yield, %	formula	analysis, % calcd C	calcd H	calcd N	found C	found H	found N	δ(CF_3CO_2H) for C_5-H and $C_{5'}$-H
5a	6	n-C_4H_9	206	37	$C_{34}H_{40}N_{10}O_8$	56.98	5.63	19.54	56.85	5.81	19.62	9.68 (2 H, s)
5b	6	n-C_8H_{17}	225	50	$C_{42}H_{56}N_{10}O_8$	60.85	6.81	16.90	60.81	6.71	16.88	9.76 (2 H, s)
5c	6	n-$C_{12}H_{25}$	152	18	$C_{50}H_{72}N_{10}O_8$	63.81	7.71	14.88	63.98	7.90	14.90	9.75 (2 H, s)
5d	6	n-$C_{18}H_{37}$	112	31	$C_{62}H_{96}N_{10}O_8$	67.12	8.72	12.62	67.05	8.81	12.81	9.78 (2 H, s)
5e	8	n-C_4H_9	219	22	$C_{36}H_{44}N_{10}O_8$	58.05	5.95	18.81	57.95	5.86	18.67	9.78 (2 H, s)
5f	8	n-C_8H_{17}	212	42	$C_{44}H_{60}N_{10}O_8$	61.66	7.06	16.34	61.19	7.32	16.45	9.79 (2 H, s)
5g	8	n-$C_{12}H_{25}$	166	20	$C_{52}H_{76}N_{10}O_8$	64.43	7.90	14.45	64.66	7.86	14.62	9.72 (2 H, s)
5h	8	n-$C_{18}H_{37}$	99	24	$C_{64}H_{100}N_{10}O_8$	67.57	8.86	12.31	67.32	8.68	12.08	9.77 (2 H, s)
5i	10	n-C_4H_9	145	30	$C_{38}H_{48}N_{10}O_8$	59.06	6.26	18.12	58.83	6.42	18.26	9.72 (2 H, s)
5j	10	n-C_8H_{17}	169	35	$C_{46}H_{64}N_{10}O_8$	62.42	7.29	15.83	62.04	7.05	15.73	9.72 (2 H, s)
5k	10	n-$C_{12}H_{25}$	146	40	$C_{54}H_{80}N_{10}O_8$	65.04	8.09	14.04	64.96	8.14	14.12	9.69 (2 H, s)
5l	10	n-$C_{18}H_{37}$	98	42	$C_{66}H_{104}N_{10}O_8$	68.01	8.99	12.02	67.70	8.85	12.10	9.75 (2 H, s)
5m	12	n-C_4H_9	232	20	$C_{40}H_{52}N_{10}O_8$	59.99	6.54	17.49	60.12	6.34	17.31	9.76 (2 H, s)
5n	12	n-C_8H_{17}	175	45	$C_{48}H_{68}N_{10}O_8$	63.14	7.51	15.34	63.22	7.59	15.28	9.76 (2 H, s)
5o	12	n-$C_{12}H_{25}$	195	47	$C_{56}H_{84}N_{10}O_8$	65.62	8.26	13.67	65.73	8.69	13.70	9.71 (2 H, s)
5p	12	n-$C_{18}H_{37}$	93	39	$C_{68}H_{108}N_{10}O_8$	68.42	9.12	11.73	68.51	9.06	11.67	9.72 (2 H, s)

Table II. Autorecycling Oxidation of Cyclopentanol (3 mL) by Bis(pyridodipyrimidin-3-yl)alkanes (**5a–p**) at 115 °C for 25 h

R	yield (%)[a,b] of cyclopentanone for $(CH_2)_n$ n = 6	n = 8	n = 10	n = 12
n-C_4H_9	16739 (10.6)	10666 (6.5)	11128 (6.5)	2117 (1.2)
n-C_8H_{17}	22464 (12.3)	25491 (13.5)	29325 (15.0)	31987 (15.9)
n-$C_{12}H_{25}$	10161 (4.9)	8542 (4.0)	24115 (11.0)	21227 (9.4)
n-$C_{18}H_{37}$	38378 (15.7)	39098 (15.6)	34573 (13.5)	24201 (5.4)

[a] Based on the catalyst. [b] Based on the starting cyclopentanol given in parentheses.

Scheme II. Alternative Synthesis of Bis-PP's (5)



The bis-PP's (5) can alternatively be synthesized stepwise from 3-unsubstituted pyridodipyrimidines (6). The treatment of 7-methylpyridodipyrimidines (6) with dibromodecane in HMPA in the presence of potassium carbonate gave 3-(bromodecyl)-pyridodipyrimidines (7). Compounds 7 were further condensed with the other 6 compounds in HMPA in the presence of potassium carbonate to afford the same bis-PP's (5) as above (Scheme II).

Oxidation of Alcohols with Bis-PP's (5)

All of the bis-PP's (5) oxidized alcohols more efficiently than the corresponding monomeric pyridodipyrimidines (1), as was expected.[7] Table II shows the relationship between the length of the 3,3′ chain or the 10- and 10′-alkyl groups and the reactivity in the autorecycling oxidation of cyclopentanol. On the average, decane (n = 10) has turned out to be the best among the 3,3′ chains (n = 6, 8, 10, 12). Table III shows the autorecycling

(7) Compounds 5 oxidized effectively almost all kinds of alcohols, such as allylic and benzylic alcohols and aliphatic secondary alcohols, while they oxidized poorly aliphatic primary alcohols, such as octyl alcohol. In this paper, we chose cyclopentanol, which was most resistant against air oxidation among the aliphatic secondary alcohols, for detailed experiments.

Table III. Autorecycling Oxidation of Cyclopentanol (3 mL) by Bis(pyridoidpyrimidin-3-yl)decanes (5i–l) at 115 °C for 25 **h**

no.	R	yield (%) of cyclopentanone catalyst = 7.5 mg	catalyst = 15 mg
5i	n-C_4H_9	21171[a] (6.2)[b]	11128[a] (6.5)[b]
5j	n-C_8H_{17}	58190 (14.9)	29325 (15.0)
5k	n-$C_{12}H_{25}$	41184 (9.4)	24115 (11.0)
5l	n-$C_{18}H_{37}$	60513 (13.4)	34573 (13.5)

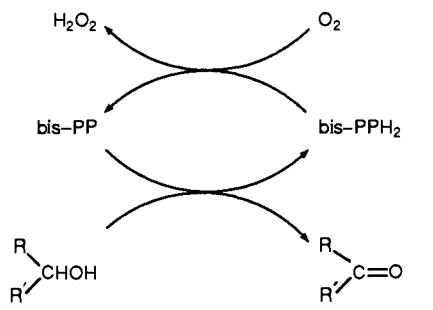
[a] Based on the catalyst. [b] Based on the starting cyclopentanol.

Table IV. Autorecycling Oxidation of *l*-Menthol and *dl*-Menthol (each 3 g) by Bis(pyridodipyrimidin-3-yl)decanes (5i–l) (15 mg) at 120 °C for 25 h

no.	R	yield (%) of products *l*-menthone	*dl*-menthone
5i	n-C_4H_9	trace	trace
5j	n-C_8H_{17}	12527[a] (11.1)[b]	21985[a] (19.4)[b]
5k	n-$C_{12}H_{25}$	trace	8337 (6.5)
5l	n-$C_{18}H_{37}$	30616 (20.5)	37052 (23.8)

[a] Based on the catalyst. [b] Based on the starting *l*- and *dl*-menthol.

Scheme III



oxidation of cyclopentanol by the bis-PP's (5i–l) fixed with a decane chain. As seen from the table, the bis-PP (**5j**) bearing an n-octyl group at the 10 and 10′ positions exhibited the best oxidizing ability. The yields of cyclopentanone based on the amount of starting cyclopentanol (3 mL) were almost the same with the use of 15 or 7.5 mg of the catalyst. However, the turnover number, which corresponds to the oxidation yield based on the catalsyt, increased with 7.5 mg of the catalyst. This suggests that 7.5 mg or less of the bis-PP's acted efficiently as a turnover catalyst under these conditions. This phenomenon means that the bis-PP's oxidized cyclopentanol rapidly and the bis-PP's themselves were reduced to dihydro-bis-PP's, which, however, are oxidized slowly to the original bis-PP's by adventitious air. The concentration of the dissolved oxygen may be crucial for the autorecycling of the catalyst (Scheme III).

Table V. α,ω-Diureidoalkanes (**2**)

					analysis, %					
					calcd			found		
no.	*n*	mp, °C	yield, %	formula	C	H	N	C	H	N
2a	6	211	49	$C_8H_{18}N_4O_2$	47.50	8.97	27.70	47.31	8.73	27.51
2b	8	193	80	$C_{10}H_{22}N_4O_2$	52.15	9.63	24.33	51.98	9.56	24.15
2c	10	196	93	$C_{12}H_{26}N_4O_2$	55.78	10.14	21.69	55.56	10.33	21.50
2d	12	185	80	$C_{14}H_{30}N_4O_2$	58.71	10.56	19.56	58.63	10.70	19.63

Table VI. 3,3′-Alkanediylbis(barbituric acids) (**3**)

					analyis, %					
					calcd			found		
no.	*n*	mp, °C	yield, %	formula	C	H	N	C	H	N
3a	6	160	66	$C_{14}H_{18}N_4O_6$	49.70	5.36	16.56	49.70	5.11	17.43
3b	8	147	45	$C_{16}H_{22}N_4O_6$	52.45	6.05	15.29	52.11	5.86	15.16
3c	10	128	50	$C_{18}H_{26}N_4O_6$	54.81	6.64	14.21	54.64	6.56	14.36
3d	12	113	65	$C_{20}H_{30}N_4O_6$	56.86	7.16	13.26	56.81	7.45	13.05

In the meantime, the bis-PP's (**5i–l**) oxidized *l*-menthol and *dl*-menthol to give *l*-menthone and *dl*-menthone, respectively (Table IV). Of unusual interest is the fact that the oxidation yields changed drastically according to the length of the 10- and 10′-alkyl groups and furthermore, *dl*-menthol was oxidized in higher yield than *l*-menthol. At the moment, it is not clear why the difference in 10- and 10′-alkyl substituents has a big effect on the oxidative ability of the bis-PP's (**5i–l**) toward menthols. Moreover, it is interesting to note that the bis-PP's appear to have a sign of chiral discrimination toward the chiral substrate. This phenomenon would be closely related to an approach and interaction of the substrate to the bis-PP's. However, in order to elucidate the chiral discrimination of the bis-PP's, much more work is necessary.

Maximum Effective Concentration as a New Expression Mode for the Efficiency of the Catalysts

On the basis of the above experiments, bis(7-methyl-10-(*n*-octyl)pyridodipyrimidin-3-yl)decane (**5j**) was selected as the catalyst for further experiments, and its maximum effective concentration (MEC) has been determined for the oxidation of cyclopentanol at 115 °C for 25 h (Figure 1). When the use of the catalyst increased, the oxidation yield increased up to a use of 6.7×10^{-5} mmol of the catalyst, after which the use of even more catalyst did not raise the yield of cyclopentanone. Therefore, 6.7×10^{-5} mmol (59 μg)/3 mL of cyclopentanol is considered to be the MEC for this catalyst under those conditions. At this point, the yield of cyclopentanone was 6970000% based on the catalyst, which means that this catalyst recycled 69 700 times. The yield based on the starting cyclopentanol was about 13%. Under these conditions, the above amount of compound **5j** acted efficiently as a turnover catalyst without waste of the catalyst.

Taking into consideration that dissolved oxygen affects the yields of the products, 5 mL of oxygen/min was introduced to the reaction mixture at 100 °C. In this case also, the yield of cyclopentanone increased up to a use of 2×10^{-4} mmol (177 μg) of catalyst **5j** toward 3 mL of cyclopentanol, which can be considered its MEC under aerobic conditions. This was about three times the MEC under the conditions without introduction of oxygen. The yield of cyclopentanone was about 50% based on the starting cyclopentanol (Figure 2).

Apart from the chemical yield of cyclopentanone, even an amount of only 2×10^{-11} mmol (17.7 pg) of catalyst **5j** oxidized cyclopentanol to give cyclopentanone in 13300000000000% yield based on the catalyst. This means that the turnover number of catalyst **5j** is 8.9×10^7 mol min^{-1} (mol of catalyst)$^{-1}$. This turnover number would surpass that of bovine liver catalase (2.8×10^6 mol min^{-1} (mol of catalyst)$^{-1}$),[8] although the condition is quite different.

(8) Walsh, C. *Enzymatic Reaction Mechanisms*, W. H. Freeman and Co.: San Francisco, 1979; p 489.

(9) Goldner, H.; Dietz, G.; Carstens, E. *Liebigs Ann. Chem.* **1966**, *691*, 142–158.

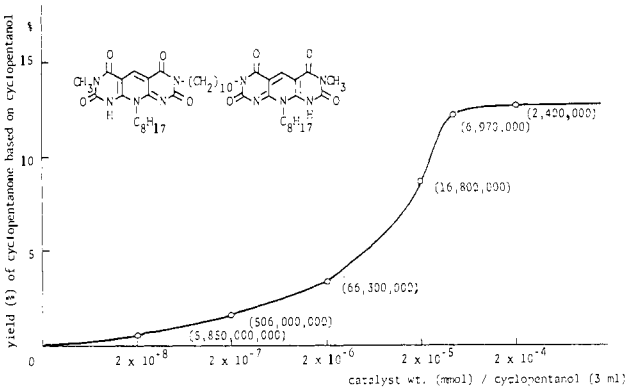


Figure 1. Autorecycling oxidation of cyclopentanol by various amounts of compound **5j** at 115 °C for 25 h. The numbers in parentheses show the yield based on the catalyst.

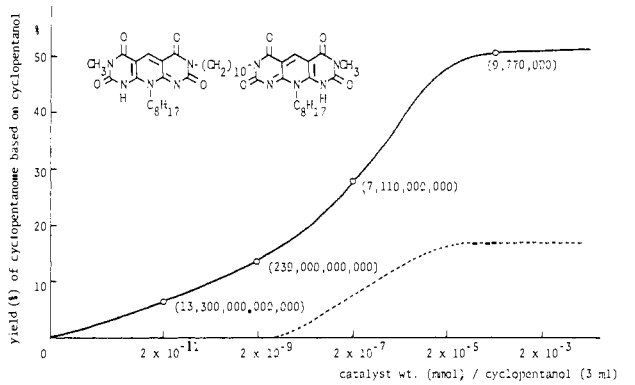


Figure 2. Autorecycling oxidation of cyclopentanol by various amounts of compound **5j** at 100 °C for 25 h under introduction of oxygen (5 mL/min): (—) under introduction of O_2; (- - -) without introduction of O_2. The numbers in parentheses show the yield based on the catalyst.

Experimental Section

All melting points were determined on a Yanagimoto hot-stage apparatus and are uncorrected. The IR spectra were obtained on a Jasco IRA-1 spectrometer and the ^1H NMR spectra on a JEOL JNM 3H-60 spectrometer (tetramethylsilane as internal standard).

α,ω-Diureidoalkanes (2a–d). General Procedure. A mixture of nitrourea (0.2 mol) and α,ω-diaminoalkane (0.1 mol) in methanol (100 mL) was refluxed for 1 h. The reaction mixture was evaporated to dryness, and the residue was recrystallized from water to give colorless needles (Table V).

3,3′-Alkanedlylbis(barbituric acids) (3a–d). General Procedure. α,ω-Diureidoalkane (**2**; 0.1 mol) and malonic acid (0.2 mol) were added to a mixture of acetic acid (100 mL) and acetic anhydride (30 mL), and the mixture was heated at 90 °C for 3 h. After cooling, the reaction mixture was evaporated in vacuo, and the residue was triturated in a

Table VII. 6-(Alkylamino)-3-methyluracils[1,9]

compd	R	mp, °C	yield, %	formula	analysis, % calcd C	calcd H	calcd N	found C	found H	found N
a	n-C_4H_9[9]	244	72	$C_9H_{15}N_3O_2$	54.80	7.67	21.31	54.71	7.80	21.22
b	n-C_8H_{17}	214	84	$C_{13}H_{23}N_3O_2$	61.63	9.15	16.59	61.59	9.24	16.36
c	n-$C_{12}H_{25}$	213	92	$C_{17}H_{31}N_3O_2$	65.98	10.10	13.58	66.22	10.23	13.41
d	n-$C_{18}H_{37}$	193	83	$C_{23}H_{43}N_3O_2$	70.18	11.01	10.68	70.49	11.27	10.72

Table VIII. 3-Methylpyridodipyrimidines (6)

no.	R	mp, °C	yield, %	formula	analysis, % calcd C	calcd H	calcd N	found C	found H	found N	$\delta(CF_3CO_2H)$ for C_5–H
6a	n-C_4H_9	>340	87	$C_{14}H_{15}N_5O_4$	52.99	4.77	22.07	53.25	4.92	21.90	9.60 (1 H, s)
6b	n-C_8H_{17}	298	64	$C_{18}H_{23}N_5O_4$	57.90	6.21	18.76	57.92	6.44	19.24	9.50 (1 H, s)
6c	n-$C_{12}H_{25}$	285	76	$C_{22}H_{31}N_5O_4$	61.52	7.28	16.31	61.24	7.22	16.60	9.68 (1 H, s)
6d	n-$C_{18}H_{37}$	280	94	$C_{28}H_{43}N_5O_4$	65.47	8.44	13.64	65.11	8.12	13.50	9.50 (1 H, s)

Table IX. 3-(Bromodecyl)-7-methylpyridodipyrimidines (7)

no.	R	mp, °C	yield, %	formula	analysis, % calcd C	calcd H	calcd N	found C	found H	found N	$\delta(CF_3CO_2H)$ for C_5–H
7a	n-C_4H_9	128	52	$C_{24}H_{34}BrN_5O_4$	53.73	6.39	13.05	53.39	6.14	12.82	9.79 (1 H, s)
7b	n-C_8H_{17}	125	50	$C_{28}H_{42}BrN_5O_4$	56.75	7.14	11.82	56.44	7.39	11.73	9.76 (1 H, s)
7c	n-$C_{12}H_{25}$	120	54	$C_{32}H_{50}BrN_5O_4$	59.25	7.77	10.80	59.39	7.83	11.05	9.76 (1 H, s)
7c	n-$C_{18}H_{37}$	115	40	$C_{38}H_{62}BrN_5O_4$	62.28	8.73	9.56	62.83	8.42	9.86	9.68 (1 H, s)

small amount of ethanol to precipitate white powder as crude product. Recrystallization from ethanol gave colorless microcrystalline powder (Table VI).

Bis(pyridodipyrimidin-3-yl)alkanes (5a–p). General Procedure. 3,3′-Alkanediylbis(barbituric acid) (**3**; 2.5 mmol) was added to Vilsmeier reagent prepared from DMF (3 mL) and $POCl_3$ (50 mL), and the mixture was heated at 90 °C for 5 h. After reaction, $POCl_3$ was evaporated under reduced pressure, and the residue was treated with ice water to precipitate crude bis(6-chloro-5-formyluracil-3-yl)alkanes (**4**). They were filtered off, dried over P_2O_5, and used for the next step without purification because of their instability. The compounds **4** (1.5 mmol) and appropriate 6-(alkylamino)-3-methyluracil (1.5 mmol) were added to DMF (20 mL), and the mixture was heated at 90 °C for 5 h. The reaction mixture was evaporated in vacuo, and the residue was recrystallized from acetic acid to give yellow microcrystalline powder (Table I).

6-(Alkylamino)-3-methyluracils. General Procedure. 6-Chloro-3-methyluracil (1.61 g, 10 mmol) and alkylamine (22 mmol) were added to 1-butanol (25 mL), and the mixture was refluxed for 5 h. After cooling, the precipitated crystals were collected by filtration, washed with water, and recrystallized from ethanol to give colorless microcrystalline powder (Table VII).

10-Alkyl-3-methylpyrido[2,3-*d*;6,5-*d*′]dipyrimidine-2,4,6,8-(3*H*,10*H*,7*H*,9*H*)-tetrones (6a–d). General Procedure. 6-(Alkylamino)-3-methyluracil (4.64 mmol) and 2,4,6-trichloropyrimidine-5-carbaldehyde[6] (0.98 g, 4.64 mmol) were added to DMF (20 mL), and the mixture was stirred for 3 h at room temperature. After the reaction, the precipitated crystals were collected by filtration and recrystallized from DMF to give yellow microcrystalline powder (Table VIII).

10-Alkyl-3-(10-bromodecyl)-7-methylpyrido[2,3-*d*;6,5-*d*′]dipyrimidine-2,4,6,8(3*H*,10*H*,7*H*,9*H*)-tetrones (7a–d). General Procedure. Compounds **6** (0.35 g, 0.478 mmol), 1,10-dibromodecane (0.36 g, 0.973 mmol), and potassium carbonate (0.77 g, 1.947 mmol) were added to HMPA (5 mL), and the mixture was heated at 100 °C for 5 h under stirring. The reaction mixture was neutralized with acetic acid and diluted with a small amount of water and extracted with ether. The ether extracts were evaporated to dryness, and the residue was diluted with a small amount of water to precipitate crystals, which were filtered off and recrystallized from ethanol to give yellow microcrystalline powder (Table IX).

Bis(pyridodipyrimidin-3-yl)alkanes (5i–l). General Procedure. Compounds **7** (0.35 g, 0.478 mmol), compounds **6** (0.277 g, 0.478 mmol), and potassium carbonate (0.1 g, 0.716 mmol) were added to HMPA (5 mL), and the mixture was heated at 100 °C for 5 h under stirring. After the reaction, the mixture was neutralized with acetic acid, diluted with a small amount of water, and extracted with ether. The ether extracts were evaporated to dryness, and the residue was diluted with a small amount of water to precipitate crystals, which were collected by filtration. Recrystallization from acetic acid gave a yellow microcrystalline powder of compounds **5i–l** in 40–50% yield based on compounds **6**. The products thus obtained were identical in all respects with the authentic samples prepared by the former method.

General Procedure for Alcohol Oxidation. A mixture of the catalyst **5** (15 mg) in an appropriate alcohol (3 mL or 3 g) was stirred in a flask joined with a refluxing condenser at an appropriate temperature. The reaction mixture was analyzed by gas chromatography. Furthermore the reaction mixture was diluted with ether and filtered. The filtrate was treated with a 2 N HCl solution of 2,4-dinitrophenylhydrazine to give the 2,4-dinitrophenylhydrazone of the corresponding carbonyl compound, which was filtered off, dried, and weighed.

Registry No. **2a**, 2188-09-2; **2b**, 93227-42-0; **2c**, 6968-52-1; **2d**, 24667-86-5; **3a**, 123463-93-4; **3b**, 123463-94-5; **3c**, 123463-95-6; **3d**, 123463-96-7; **5a**, 94590-72-4; **5b**, 94561-91-8; **5c**, 94590-75-7; **5d**, 94566-50-4; **5e**, 94590-73-5; **5f**, 94561-92-9; **5g**, 94566-49-1; **5h**, 94566-51-5; **5i**, 94561-90-7; **5j**, 94561-93-0; **5k**, 94561-95-2; **5l**, 94561-89-4; **5m**, 94590-74-6; **5n**, 94561-94-1; **5o**, 94561-96-3; **5p**, 94566-52-6; **6a**, 87624-52-0; **6b**, 87624-43-9; **6c**, 87624-53-1; **6d**, 87624-54-2; **7a**, 123464-01-7; **7b**, 123464-02-8; **7c**, 123464-03-9; **7d**, 94589-14-7; $NH_2CONHNO_2$, 556-89-8; $NH_2(CH_2)_6NH_2$, 124-09-4; $NH_2(CH_2)_8NH_2$, 373-44-4; $NH_2(CH_2)_{10}NH_2$, 646-25-3; $NH_2(CH_2)_{12}NH_2$, 2783-17-7; $CH_2(CO_2H)_2$, 141-82-2; $BuNH_2$, 109-73-9; $CH_3(CH_2)_7NH_2$, 111-86-4; $CH_3(CH_2)_{11}NH_2$, 124-22-1; $CH_3(CH_2)_{17}NH_2$, 124-30-1; $Br(CH_2)_{10}Br$, 4101-68-2; 6-(butylamino)-3-methyluracil, 123463-97-8; 6-(octylamino)-3-methyluracil, 123463-98-9; 6-(dodecylamino)-3-methyluracil, 123463-99-0; 6-(octadecylamino)-3-methyluracil, 123464-00-6; 6-chloro-3-methyluracil, 4318-56-3; 2,4,6-trichloropyrimidine-5-carbaldehyde, 50270-27-4; cyclopentanol, 96-41-3; cyclopentanone, 120-92-3; L-methanol, 2216-51-5; DL-menthol, 15356-70-4; L-menthone, 14073-97-3; DL-menthone, 1074-95-9.