Synthesis of new pyrido[2,3-*d*]pyrimidine derivatives by three-component condensation of 5-acetyl-4-aminopyrimidines, cyclohexane-1,3-diones, and orthocarboxylic acid esters*

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A three-component condensation of 5-acetyl-4-aminopyrimidine derivatives with dimedone (or cyclohexane-1,3-dione) and triethyl orthoacetate (or triethyl orthopropionate) gave derivatives of 7-(1,3-dioxocyclohex-2-ylidene)-7,8-dihydropyrido[2,3-*d*]pyrimidine. These heterocyclic compounds containing the enamino ketone fragment can form boron chelates under the action of butoxy(diphenyl)borane.

Key words: 2,6-disubstituted 5-acetyl-4-aminopyrimidines, cyclohexane-1,3-diones, triethyl orthoacetate, triethyl orthopropionate, three-component condensation, 7-(1,3-dioxocyclohex-2-ylidene)-7,8-dihydropyrido[2,3-*d*]pyrimidines and their diphenylboron complexes.

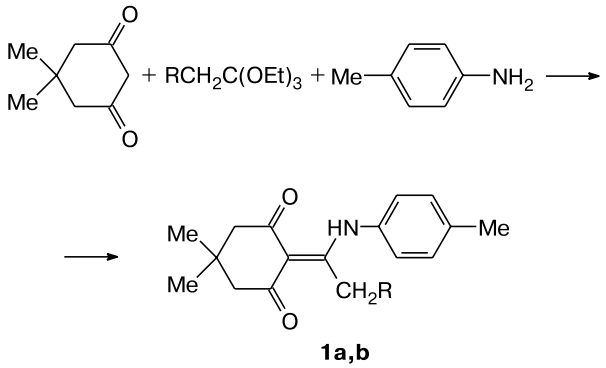
Easily accessible derivatives of 5-acetyl-4-aminopyrimidine (AAP)[1—3] can be effectively used for the design of the pyrido[2,3-*d*]pyrimidine system. Earlier, we have obtained substituted pyrido[2,3-*d*]pyrimidin-5(8*H*)-ones[2,4] by reactions of AAP with amide acetals and 5-oxo-5,8-dihydropyrido[2,3-*d*]pyrimidine-7-carboxylates[3] by condensation of AAP with diethyl oxalate. Heating of AAP with alkyl β-oxo carboxylates gives the corresponding 6-acylpyrido[2,3-*d*]pyrimidin-7(8*H*)-ones and that with ethyl malonate yields ethyl 7-oxo-7,8-dihydropyrido[2,3-*d*]pyrimidine-6-carboxylates.[5]

In the present work, we proposed a new approach to the synthesis of pyrido[2,3-*d*]pyrimidines *via* three-component "one-pot" condensation of AAP with dimedone (or cyclohexane-1,3-dione) and trialkyl orthoacetate and trialkyl orthopropionate.

Three-component condensation of cyclohexane-1,3-diones with trialkyl orthoformate and aromatic amines is known to produce 2-arylaminomethylenecyclohexanediones,[6] which are potential ligands for preparation of metal chelate complexes.[7] However, it has been reported that analogous reactions with trialkyl orthoacetates and trialkyl orthopropionates do not yield the corresponding enaminones.[8]

Contrary to those data, we found that refluxing of a mixture of dimedone, triethyl orthoacetate (or triethyl orthopropionate), and *p*-toluidine afford compounds **1a,b**. According to ^{1}H NMR and IR spectroscopic data, they are structurally analogous to the condensation products obtained from triethyl orthoformate (Scheme 1).

Scheme 1



1a,b

R = H (**a**), Me (**b**)

This result suggests that amines of the AAP type can be employed for the synthesis of the corresponding *N*-substituted aminopyrimidines whose intramolecular cyclization can afford pyrido[2,3-*d*]pyrimidine derivatives.

It turned out that reactions between 1,3-diketones **2** and **3**, orthoesters **4** and **5**, and aminopyrimidines **6a—c** in boiling xylene without any catalysts give the corresponding 7-(1,3-dioxocyclohex-2-ylidene)-7,8-dihydropyrido[2,3-*d*]pyrimidines (**7a—f**) (Scheme 2).

Obviously, the reaction intermediates vinylaminopyrimidines (**VAP**) are similar to compounds **1** and readily

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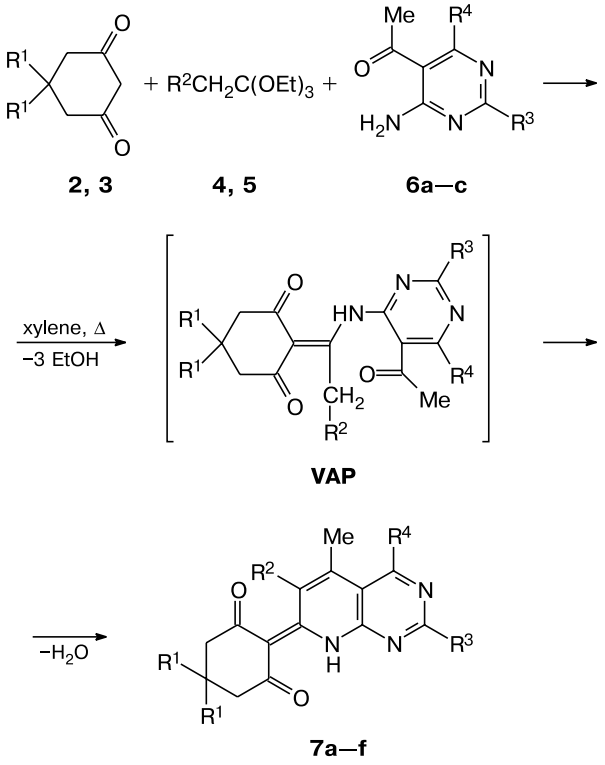
Scheme 2



R^1 = Me (**2**), H (**3**); R^2 = H (**4**), Me (**5**)

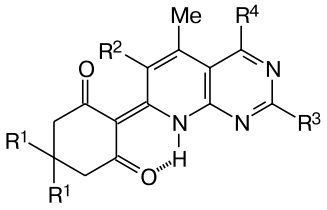
Compound	R^1	R^2	Compound	R^3	R^4
7a	Me	H	**6a**, **7a**	Ph	Me
7b	Me	H	**6b**, **7b**	Ph	SMe
7c	Me	H	**6c**, **7c**	4-ClC_6H_4	Me
7d	H	H	**7d**	Ph	Me
7e	Me	Me	**7e**	Ph	Me
7f	Me	Me	**7f**	Ph	SMe

undergo *in situ* intramolecular cyclization; the closure of the pyridine ring involves the methyl (methylene) group of the alkylidene fragment and the carbonyl group of the acetyl fragment.

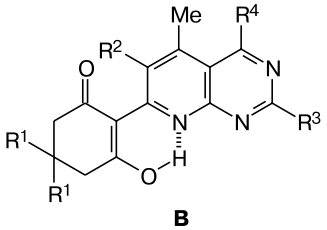
Yellow compounds **7** crystallized upon cooling of the reaction mixture and were easily isolated. Compounds **7** are soluble in $CHCl_3$ and well crystallize from benzene or toluene but they are poorly soluble in ethanol, acetone, and DMSO.

The structures of the pyridopyrimidines obtained were confirmed by spectroscopic data. Their mass spectra contain molecular ion peaks (Table 1). The ^{1}H NMR spectra of compounds **7a**—**d** in $CDCl_3$ show a characteristic singlet at δ ~9.0 for the H(6) atom of the bicyclic system. Instead of this signal, the spectra of pyridopyrimidine derivatives **7e,f** contain a singlet at δ 2.2 for the methyl group (Table 2). A comparatively narrow low-field signal appears at δ 16.9 for heterocycles **7a**—**d**; its position remains virtually the same in the spectra recorded in DMSO-d_6. Obviously, this proton is involved in intramolecular hydrogen bonding (IHB), which was confirmed by IR spectra in KBr or $CHCl_3$ (broad absorption over 3200—2800 cm^{-1} overlapping with the ν(CH) bands).

For compounds **7**, we should choose between tautomeric structures **A** (with the aminovinylic fragment and the IHB N—H...O) and **B** (with the imino enol fragment and the IHB O—H...N).

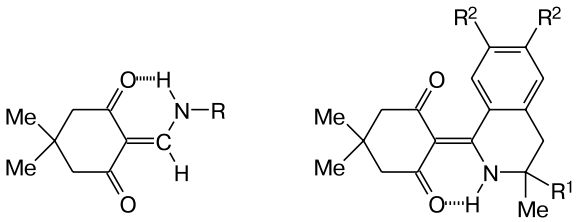


A



B

It is known that 2-aminomethylenedimedones **8** in the crystalline state and in solutions exist as aminovinyl ketones stabilized by the IHB N—H...O (see Ref. 9 and references therein). An analogous structure has been assigned to 1,2,3,4-tetrahydroisoquinoline derivatives **9** (see Refs 10 and 11).



8 **9**

8: R = Me, Ph, COPh; **9:** R^1 = H, Me; R^2 = H, OMe, Me

Although compounds **8** and **9** are structurally similar to pyrido[2,3-*d*]pyrimidine derivatives **7**, it should be taken into account that stabilization of tautomer **B** of the latter can also be contributed by aromatization of the bicyclic fragment, which is impossible, *e.g.*, for tetrahydroisoquinolines **9**.

However, spectroscopic data provide evidence for aminovinylic structure **A** in solutions, at least for compounds **7a**—**d**. For instance, in the ^{13}C NMR spectrum of compound **7a**, the chemical shifts of the signals for two carbonyl groups are close (δ 196.6 and 199.9), which agrees

Table 1. Yields, melting points, elemental analysis data, and mass spectra of compounds **7a—f** and **10—12**

Compound	Yield (%)	M.p. /°C	Found / Calculated (%)*			Molecular formula	MS, m/z (I_{rel} (%))
			C	H	N		
7a	61	276—277	73.63 73.97	6.31 6.21	11.07 11.25	$C_{23}H_{23}N_3O_2$	373 $[M]^+$ (100), 289 (21), 276 (74), 275 (69)
7b	50	296—297	67.98 68.12	5.88 5.72	10.27 10.36	$C_{23}H_{23}N_3O_2S$	405 $[M]^+$ (100), 390 $[M - Me]^+$ (20), 308 (34), 307 (18), 292 (27)
7c	38	274—275	67.50 67.72	5.54 5.44	10.30 10.30	$C_{23}H_{22}ClN_3O_2$	407 $[M]^+$ (100), 323 (22), 309 (91)
7d	40	274—275	72.76 73.03	5.63 5.54	11.87 12.17	$C_{21}H_{19}N_3O_2$	345 $[M]^+$ (100), 289 (42), 276 (94), 275 (81)
7e	42	289—290	74.58 74.39	6.45 6.50	10.64 10.85	$C_{24}H_{25}N_3O_2$	387 $[M]^+$ (12), 372 $[M - Me]^+$ (59), 370 $[M - OH]^+$ (100), 316 (57), 290 (28), 260 (45)
7f	32	259—260	69.12 68.71	6.12 6.01	9.84 10.02	$C_{24}H_{25}N_3O_2S$	419 $[M]^+$ (17), 404 $[M - Me]^+$ (66), 402 $[M - OH]^+$ (100), 348 (22), 306 (31)
10	64	210—211	78.26 78.21	6.16 6.00	7.89 7.82	$C_{35}H_{32}BN_3O_2$	537 $[M]^+$ (8), 460 $[M - Ph]^+$ (100)
11	64	234—235	77.48 77.80	5.59 5.54	8.27 8.25	$C_{33}H_{28}BN_3O_2$	509 $[M]^+$ (0.6), 432 $[M - Ph]^+$ (25), 119 (75), 93 (100)
12	71	259—260	78.56 78.40	6.37 6.21	7.90 7.62	$C_{36}H_{34}BN_3O_2$	551 $[M]^+$ (4), 474 $[M - Ph]^+$ (60), 78 (100)

* Found/calculated (%): S, 7.60/7.91 (**7b**); Cl, 8.71/8.69 (**7c**); S, 7.42/7.64 (**7f**); B, 1.94/2.01 (**10**); B, 1.92/2.12 (**11**); B, 1.85/1.96 (**12**).

well with data for aminomethylene diketones **8** (see Ref. 9) and tetrahydroisoquinolines **9** (see Ref. 10).

The chemical shifts of the signals for the CH_2 groups of the cyclohexane ring (Table 3) are also virtually the same as the corresponding chemical shifts for compounds **9** (see Ref. 10) and the dioxo form of dimedone (δ 54.1; *cf.* δ 46.2 for the enol tautomer[12]).

The choice of the right tautomeric structure of compounds **7e,f** obtained from triethyl orthopropionate was more difficult. The signals at δ ~16.2 in their ^1H NMR spectra ($CDCl_3$) are noticeably broader than the signals for NH in heterocycles **7a—d**; in DMSO-d_6, those signals do not appear at all. The singlets for two CH_2 groups of the cyclohexane ring coincide (see Table 2). The ^{13}C NMR spectra also suggest that the C atoms of both the methylene and carbonyl groups are equivalent (*e.g.*, their values for compound **7e** are δ 51.8 and 195.4, respectively; see Table 3).

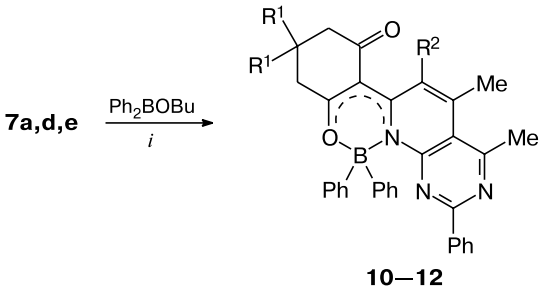
Apparently, the IHB in heterocycles **7e,f** is very unstable because of the steric effect of the methyl group in position 6 of the pyridopyrimidine system, which distorts the plane of the H-chelate ring. This facilitates cleavage of the hydrogen bond, lowers the order of the C=C bond, and decreases the energy barrier to rotation about it; consequently, the signals in the ^1H and ^{13}C NMR spectra are averaged.

The changes in the low-temperature ^1H and ^{13}C NMR spectra also confirmed the instability of the IHB in compounds **7e,f**. For instance, in the ^1H NMR spectrum of pyridopyrimidine **7e** in $CDCl_3$ at −50 °C, although the signal for NH at δ 16.2 becomes narrower, neither ^1H nor ^{13}C NMR spectra show double sets of the signals for the CH_2 and C=O groups.

Pyrido[2,3-*d*]pyrimidine derivatives **7** should exhibit chelating properties because of the presence of the enamino ketone fragment with the IHB.

Indeed, refluxing of compounds **7a,d,e** with butoxy(diphenyl)borane in toluene gave chelate complexes **10—12** (Scheme 3).

Scheme 3



10—12

	10	**11**	**12**
R^1	Me	H	Me
R^2	H	H	Me

i. Toluene, refluxing.

Chelate complexes **10—12** are yellow crystalline solids and are well soluble in most organic solvents but light

Table 2. ^{1}H NMR spectra of compounds **7a—f** and **10—12**

Compound	Solvent	δ, *J*/Hz					
		4-Me (s, 3 H)	5-Me (s, 3 H)	CH_2CO	NH (br.s, 1 H)	Ar	Other signals
7a	$CDCl_3$	3.10	2.88	2.48, 2.56 (both s, 2 H each)	16.88	7.52 (m, 3 H); 8.60 (m, 2 H)	1.12 (s, 6 H, CMe_2); 9.02 (s, 1 H, H(6))
	DMSO-d_6	3.10	2.87	2.46, 2.50 (both s, 2 H each)	16.90	7.60 (m, 3 H); 8.50 (m, 2 H)	1.07 (s, 6 H, CMe_2); 8.88 (s, 1 H, H(6))
7b	$CDCl_3$	—	2.95	2.49, 2.58 (both s, 2 H each)	16.96	7.52 (m, 3 H); 8.60 (m, 2 H)	1.12 (s, 6 H, CMe_2); 2.82 (s, 3 H, SMe), 8.98 (s, 1 H, H(6))
7c	$CDCl_3$	3.10	2.88	2.50, 2.58 (both s, 2 H each)	16.89	7.49 (d, 2 H, J = 7.5); 8.52 (d, 2 H, J = 7.5)	1.12 (s, 6 H, CMe_2); 9.02 (s, 1 H, H(6))
7d	$CDCl_3$	3.09	2.85	2.62, 2.68 (both m, 2 H each)	16.87	7.55 (m, 3 H); 8.60 (m, 2 H)	2.01 (m, 2 H, CH_2); 8.98 (s, 1 H, H(6))
7e	$CDCl_3$	3.12	2.82	2.53 (s, 4 H)	16.19[a]	7.52 (m, 3 H); 8.61 (m, 2 H)	1.18 (s, 6 H, CMe_2); 2.19 (s, 3 H, 6-Me)
	DMSO-d_6	3.18	2.85	2.45 (s, 4 H)	—[b]	7.60 (m, 3 H); 8.55 (m, 2 H)	1.15 (s, 6 H, CMe_2); 2.18 (s, 3 H, 6-Me)
7f	$CDCl_3$	—	2.98	2.53 (s, 4 H)	16.22[a]	7.52 (m, 3 H); 8.61 (m, 2 H)	1.18 (s, 6 H, CMe_2); 2.85 (s, 3 H, SMe); 2.19 (s, 3 H, 6-Me)
10	$CDCl_3$	3.10	2.97	2.47, 2.70 (both s, 2 H each)	—	7.08—7.22 (m, 7 H); 7.25 (m, 2 H); 7.40 (m, 4 H); 7.78 (m, 2 H)	1.12 (s, 6 H, CMe_2); 8.94 (s, 1 H, H(6))
11	$CDCl_3$	3.10	2.98	2.60, 2.80 (both m, 2 H each)	—	7.04—7.20 (m, 7 H); 7.25 (m, 2 H); 7.34 (m, 4 H); 7.79 (m, 2 H)	2.03 (m, 2 H, CH_2); 8.82 (s, 1 H, H(6))
12[c]	$CDCl_3$	3.12	2.91	2.40 (s, 4 H)	—	7.00—7.60 (m, 13 H); 7.82 (m, 2 H)	1.20 (s, 6 H, CMe_2); 2.40 (s, 3 H, 6-Me)

[a] The very wide, nonintegrable signal.
[b] Not observed.
[c] The spectrum also shows the signals for ligand **7e** (according to the integral signal intensity, its percentage is ~20%).

petroleum. Complexes **10** and **11** obtained from ligands **7a,d** can be stored in air and in solutions for a long period of time, while complex **12** partially decomposes even in freshly prepared solutions ($CDCl_3$, C_6D_6), releasing the free ligand. Its content rapidly increases with time (^{1}H NMR data). This is in full agreement with the aforesaid assumption that the IHB in bidentate ligand **7e** is weakened (in other words, the H-chelate ring is unstable) by the steric effect of the methyl group.

The mass spectra of compounds **10—12** contain low-intensity molecular ion peaks and intense peaks of the $[M - Ph]^+$ ions (see Table 1). In accordance with the chelate structure, their ^{11}B NMR spectra show signals due to tetracoordinated boron. Interestingly, in the ^{1}H NMR spectra of chelates **10—12**, the signals for the *ortho*-protons of the phenyl group bound to the pyrimidine ring are substantially shifted upfield compared to the starting pyridopyrimidine derivatives (from δ ~8.60 in ligands **7** to δ ~7.80 in chelates **10—12**; see Table 2). The intense band at 1540 cm^{-1} in the IR spectra of chelates **10** and **11** in $CHCl_3$ or KBr, which is absent from the spectra of the free ligands (Table 4), is probably due to delocalization of the π-electrons in the boron chelate ring.

Thus, the proposed three-component condensation can be actually regarded as an equivalent of the Friedlaender reaction of AAP with 2-acylcyclohexane-1,3-diones. Nevertheless, our attempts to obtain compound **7a** by refluxing pyrimidine **6a** with 2-acetyldimedone in *p*-xylene were unsuccessful.

Experimental

^{1}H NMR spectra were recorded on a Bruker WM-250 instrument; ^{13}C and ^{11}B NMR spectra, on a Bruker AC-200 instrument; low-temperature ^{1}H and ^{13}C NMR spectra (−50 °C) and 2D NMR spectra ({^{1}H—^{13}C} HSQC and HMBC techniques), on a Bruker DRX-500 instrument. IR spectra were recorded on a Specord-M80 instrument. Mass spectra were re-

Table 3. ^{13}C NMR spectra of compounds **7a** and **7e** in $CDCl_3$

Assignment	δ, *J*/Hz	
	7a*	**7e**
4-Me	27.51	28.65 (q, ^1J = 128.8)
5-Me, 6-Me	25.20	20.31, 20.66 (both q, ^1J = 129.0)
C<u>Me</u>$_2$	28.33	28.59 (m) (q, ^1J = 128.8)
<u>C</u>Me$_2$	30.22	30.69 (m)
CH_2	52.47, 53.78	51.75 (t, ^1J = 127.0)
OC—<u>C</u>—CO	103.47	107.20 (s)
C(4a)	114.66	115.48 (m)
C(6)	123.72	131.62 (m)
Ph	128.54, 129.02, 131.69, 136.22	128.56, 128.83, 131.64, 135.91
C(5)	149.04	147.93 (m)
C(8a)	152.31	149.77 (s)
C(7)	155.50	158.22 (q, ^3J = 4.4)
C(2)	163.30	162.32 (t, ^3J = 3.0)
C(4)	166.95	167.05 (q, ^2J = 6.4)
CO	196.62, 199.86	195.35 (t, ^2J = 6.4)

* The assignment of the signals in the ^{13}C NMR spectrum was confirmed by 2D NMR spectra ({^1H—^{13}C} HSQC and HMBC experiments).

corded on a Kratos MS-30 instrument (EI, 70 eV, ionization chamber temperature 250 °C, direct inlet probe).

Pyrimidines **6a** (see Ref. 1), **6b** (see Ref. 2), and **6c** (see Ref. 3) were prepared according to known procedures.

5,5-Dimethyl-2-[1-(4-tolylamino)ethylidene]cyclohexane-1,3-dione (1a). A mixture of dimedone (0.56 g, 4 mmol), *p*-toluidine (0.428 g, 4 mmol), and triethyl orthoacetate (1.5 mL, 8.2 mmol) was refluxed for 8 h and cooled to 20 °C. Rubbing along the flask walls gave crystallization of the product. The precipitate that formed was filtered off and washed with light petroleum (5 mL). The yield of compound **1a** was 0.63 g (58%), m.p. 139—140 °C. Found (%): C, 75.04; H, 7.80; N, 5.25. $C_{17}H_{21}NO_2$. Calculated (%): C, 75.25; H, 7.80; N, 5.16. IR ($CHCl_3$), ν/cm^{-1}: 1640 (CO), 1560 (C=C). ^1H NMR ($CDCl_3$), δ: 1.08 (s, 6 H, CMe_2); 2.37 (s, 3 H, Me); 2.39 (s, 2 H, CH_2); 2.47 (s, 2 H, CH_2); 2.50 (s, 3 H, Me); 7.02, 7.21 (both d, 2 H each, C_6H_4, *J* = 7.5 Hz); 14.91 (br.s, 1 H, NH).

5,5-Dimethyl-2-[1-(4-tolylamino)propylidene]cyclohexane-1,3-dione (1b) was obtained analogously from dimedone, *p*-toluidine, and triethyl orthopropionate. The yield was 44%, m.p. 132—133 °C. Found (%): C, 75.48; H, 8.34; N, 4.89. $C_{18}H_{23}NO_2$. Calculated (%): C, 75.76; H, 8.12; N, 4.91. IR ($CHCl_3$), ν/cm^{-1}: 1644 (CO); 1560 (C=C). ^1H NMR ($CDCl_3$), δ: 1.08 (s, 6 H, CMe_2); 1.10 (t, 3 H, <u>CH_3</u>CH_2, *J* = 6.8 Hz); 2.38 (s, 5 H, CH_2, Me); 2.48 (s, 2 H, CH_2); 2.95 (q, 2 H, CH_3<u>CH_2</u>, *J* = 6.8 Hz); 7.03, 7.21 (both d, 2 H each, C_6H_4, *J* = 7.5 Hz); 14.90 (br.s, 1 H, NH).

Table 4. Vibrational frequencies in the IR spectra of compounds **7a—f** and **10—12** in the 1700—1500 cm^{-1} range

Compound	Recording conditions	ν/cm^{-1}
7a	$CHCl_3$	1636, 1602, 1556
	KBr	1638, 1600, 1556
7b	$CHCl_3$	1636, 1596, 1552, 1544 sh
7c	$CHCl_3$	1640, 1600, 1556
7d	$CHCl_3$	1636, 1600, 1556
7e	$CHCl_3$	1628, 1584 sh, 1576, 1552, 1544 sh
	KBr	1636, 1625, 1584, 1576, 1552, 1544
7f	$CHCl_3$	1624, 1580, 1552, 1528
10	$CHCl_3$	1650 sh, 1644, 1604, 1568, 1540
	KBr	1650 sh, 1644, 1600, 1564, 1540
11	KBr	1644, 1604, 1564, 1540
12	KBr	1652, 1572, 1536, 1516

7-(5,5-Dimethyl-1,3-dioxocyclohex-2-ylidene)-4,5-dimethyl-2-phenyl- (7a), 7-(5,5-dimethyl-1,3-dioxocyclohex-2-ylidene)-5-methyl-4-methylthio-2-phenyl- (7b), 2-(4-chlorophenyl)-7-(5,5-dimethyl-1,3-dioxocyclohex-2-ylidene)-4,5-dimethyl- (7c), and 7-(1,3-dioxocyclohex-2-ylidene)-4,5-dimethyl-2-phenyl-7,8-dihydropyrido[2,3-*d*]pyrimidines (7d) (general procedure). A mixture of an appropriate pyrimidine **6a—c** (1.2 mmol), dimedone **2** or cyclohexane-1,3-dione **3** (2.4 mmol), and triethyl orthoacetate **4** (3.6 mmol) was refluxed in *p*-xylene (5 mL) for 4—5 h and then cooled to 20 °C. The precipitate that formed was filtered off and washed with light petroleum (10 mL) to give pyridopyrimidines **7a—d** as yellow crystals. The yields, melting points, elemental analysis data, and mass spectra of the compounds obtained are given in Table 1 and their ^1H NMR spectra are given in Table 2. The ^{13}C NMR spectrum of compound **7a** is presented in Table 3. IR spectra are given in Table 4.

7-(5,5-Dimethyl-1,3-dioxocyclohex-2-ylidene)-4,5,6-trimethyl-2-phenyl-7,8-dihydropyrido[2,3-*d*]pyrimidine (7e) and 7-(5,5-dimethyl-1,3-dioxocyclohex-2-ylidene)-5,6-dimethyl-4-methylthio-2-phenyl-7,8-dihydropyrido[2,3-*d*]pyrimidine (7f). A mixture of an appropriate pyrimidine **6a,b** (1.3 mmol), dimedone **2** (2.6 mmol), and triethyl orthopropionate **5** (3.9 mmol) was refluxed in *p*-xylene (6 mL) for 2.5 h and cooled to 20 °C. Recrystallization of the precipitate from benzene gave compounds **7e,f** as yellow crystals (see Tables 1—4).

Pyridopyrimidine diphenylboron chelate 7a (10). A mixture of pyridopyrimidine **7a** (0.1 g, 0.27 mmol) and butoxy(diphenyl)borane (0.25 mL, 1.07 mmol) was refluxed in toluene (3 mL) for 10 h. The solvent and BuOH were removed *in vacuo*. Chelate **10** was extracted from the residue with boiling light petroleum (4×10 mL), the extract was cooled to 20 °C, and the resulting precipitate was filtered off. The yield of chelate **10** was 0.089 g (64%), a yellow powder. ^{11}B NMR ($CHCl_3$), δ: 6.8 (see also Tables 1, 2, 4).

Pyridopyrimidine diphenylboron chelate 7d (11). A mixture of pyridopyrimidine **7d** (0.1 g, 0.29 mmol) and butoxy(diphe-

nyl)borane (0.28 mL, 1.17 mmol) was refluxed in toluene (4 mL) for 9 h. The solvent and BuOH were removed *in vacuo*. Chelate **11** was extracted from the residue with boiling benzene—light petroleum (1 : 2, 30 mL). The extract was concentrated *in vacuo* and the residue was washed with light petroleum (20 mL). The yield of chelate **11** was 0.096 g (64%). ^{11}B NMR ($CHCl_3$), δ: 7.6 (see also Tables 1, 2, 4).

Pyridopyrimidine diphenylboron chelate 7e (12). A mixture of pyridopyrimidine **7e** (0.1 g, 0.26 mmol) and butoxy(diphenyl)borane (0.25 mL, 1.0 mmol) was refluxed in toluene (4 mL) for 6 h and then cooled to 20 °C. The product was precipitated with light petroleum (5 mL), filtered off, and washed with light petroleum (10 mL). The yield of chelate **12** was 0.10 g (71%), a yellow powder. ^{11}B NMR ($CHCl_3$), δ: 5.4 (see also Tables 1, 2, 4).

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