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Synthetic Studies of Azaflavonoids. II.[1] Synthesis of 6-Azaflavonoids

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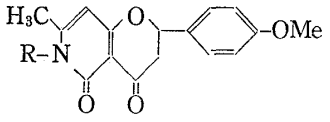
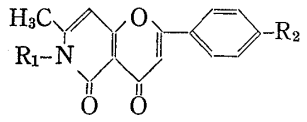
The syntheses of 5-hydroxyl-4′-methoxy-7-methyl-6-azaflavanone (Ia) and 5-hydroxy-4′-methoxy-7-methyl-6-azaflavone (IIa) from 4-hydroxy-6-methyl-2(1H)-pyridone (IVa), and the syntheses of Ib and IIb, N-methyl analogues of Ia and IIa respectively, and of IIc, N-methyl-4′-demethoxy analogue of IIa, starting with N-methyl analogue (IVb) of IVa, were described.

Keywords——flavonoids; azaflavonoids; azaflavones; azaflavanone; acid catalyzed cyclization; base catalyzed rearrangement

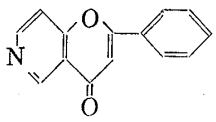
From the chemical and biological interest, the synthetic studies of 5-azaflavanones and 5-azaflavone were reported in the previous paper.[1b] In this paper the syntheses of 5-hydroxy-4′-methoxy-7-methyl-6-azaflavanone (Ia), its N-methyl analogue (Ib), 5-hydroxy-4′-methoxy-7-methyl-6-azaflavone (IIa), its N-methyl analogue (IIb), and N-methyl-4′-demethoxy analogue (IIc) are described, though 6-azaflavone itself (III) has been synthesized by French chemists.[3]



Ia: R=H
Ib: R=CH_3



IIa: R_1=H, R_2=OMe
IIb: R_1=CH_3, R_2=OMe
IIc: R_1=CH_3, R_2=H
IId: R_1=Br, R_2=OMe



III

Chart 1

4-Hydroxy-6-methyl-2(1H)-pyridone (IVa) synthesized *via* two different routes[4,5] was acetylated to 3-acetyl-4-hydroxy-6-methyl-2(1H)-pyridone (Va) with acetic anhydride in phosphorus pentoxide and polyphosphoric acid.[6] Va was treated with *p*-anisaldehyde in the presence of sodium ethoxide followed by neutralization with dilute acetic acid to give directly azaflavanone (Ia) though in poor yield. Ia melted at 288—291° and exhibited the signals due to the C_2-methine proton and C_3-methylene protons at δ 5.93 and 3.36 ppm respectively in the nuclear magnetic resonance (NMR) spectrum. To improve the yield, Va was at first derived to its benzoate, 3-acetyl-4-benzoyloxy-6-methyl-2(1H)-pyridone (VIa), followed by the treatment with *p*-anisaldehyde to give, in relatively good yield, one and the

1) *a*) A part of this work was presented at the 98th Annual Meeting of Pharmaceutical Society of Japan, April 1978 (Okayama); *b*) Preceding paper: T. Yamazaki, K. Matoba, Y. Matsuzawa, and M. Kitagawa, *Chem. Pharm. Bull.* (Tokyo), **25**, 1150 (1977).
2) Location: *Gofuku, Toyama 930, Japan.*
3) G. Lhommet, H. Sliwa, and P. Maitle, *J. Heterocyclic Chem.*, **8**, 517 (1971).
4) E. Knovenagel and A. Fries, *Chem. Ber.*, **31**, 768 (1898).
5) C. Wang, *J. Heterocyclic Chem.*, **7**, 389 (1970).
6) In the literature [N.S. Vul′-fson and G.M. Sukhotina, *Metody Poluch. Khim. Reaktivov Prep.*, **1966**, 83 [*C.A.*, **67**, 32552*f* (1967)]], Va was acetylated with acetic acid and polyphosphoric acid, but this procedure did not give the expected product.

same azaflavanone obtained above. Trials to isolate azachalcone, 4-hydroxy-3-(4-methoxybenzylidene)acetyl-6-methyl-2(1H)-pyridone (VIIa), and its sodium salt, were unsuccessful, but its formation was suggested from the NMR spectrum of the crude product in trifluoroacetic acid (TFA) solution (other solvents tried did not dissolve I, VII and their derivatives). Thus the spectrum exhibited the signals at δ 2.80, 6.67, 7.20, 7.80, and 8.30 ppm due to C_6-methyl protons, C_5 proton, vinylic protons, and benzene aromatic protons (A_2B_2 type) of VIIa respectively, together with those due to the protons of Ia, but signals associated with VIIa disappeared after about ten minutes.

Next we tried to synthesize Ib, N-methyl analogue of Ia. 3-Acetyl-1,6-dimethyl-4-hydroxy-2(1H)-pyridone (Vb) synthesized after the same manner as Va, was directly treated with *p*-anisaldehyde not *via* 3-acetyl-4-benzoyloxy-1,6-dimethyl-2(1H)-pyridone (VIb) in the presence of sodium ethoxide to give a chalcone, 1,6-dimethyl-4-hydroxy-3-(4-methoxybenzylidene)acetyl-2(1H)-pyridone (VIIb), as expected. The chalcone was supposed to have cyclized to flavanone, Ib, judging from the NMR spectrum measured after 2.5 hr in TFA–dueteriochloroform (2: 3). Thus it exhibited a quartet signal due to the C_2-methine proton at δ 5.82 ppm and a multiplet due to the C_3-methylene protons at δ 3.33 ppm. However, trials to isolate Ib failed. Such phenomena are parallel with those found in 2-(4-methoxybenzylidene)-acetyl-3-hydroxy-pyridine (VIII) reported in our previous paper,[1b] and it is suggested that the hydrogen bond between C_4-carbonyl and C_5-hydroxy groups plays an important role in the stabilization of the flavanone, Ia. Thus the isolation of Ib was not successful, but VIIb could be cyclized oxidatively to IIb, N-methyl analogue of IIa, as follows: VIIb was treated with palladium acetate in the presence of sodium ethoxide[7] to give IIb though in poor yield. IIb exhibited a carbonyl band at 1670 cm^{-1} in the infrared (IR) spectrum, a singlet signal due to the C_3 proton at δ 7.01 ppm in the NMR spectrum, and two absorption maxima at 325 and 302 nm in the ultra violet (UV) spectrum.

On the other hand, IIa and N-methyl-4′-demethoxy analogue (IIc) of IIa were synthesized by the dehydrogenation of Ia and by the rearrangement of VIb respectively. At first the oxidation of Ia was tried. However, trials using the oxidative reagents such as PCl_5,[8] chloranil,[9] and palladium black[10] failed. But with N-bromosuccinimide (NBS), the conversion of Ia to IIa was successful; Ia was treated with NBS in the presence of benzoylperoxide to give IIa and a large amount of IId, N-bromo analogue of IIa. The physical data obtained from IIa were similar to those from IIb and the magnesium-hydrochloric acid test (flavone test) was positive. IId exhibited a carbonyl band at 1700 cm^{-1} in the IR spectrum, no signals except those due to vinylic methyl protons and methoxy protons at higher field than δ 6.00 ppm in the NMR spectrum, and the similar absorption maxima with those obtained in IIa in the UV spectra. The flavone test was positive, too. The reduction of IId to IIa was unsuccessful. IId afforded Ia instead of IIa with zinc in acetic acid though in poor yield, and also resisted catalytic reduction.

Next the synthesis of IIc by the rearrangement of VIb will be mentioned. VIb was treated with sodium hydride in benzene[1b] to give benzoyl 1,6-dimethyl-2,4-dihydroxy-3-pyridoyl methane (IX), which exhibited several absorption peaks between 1580 and 1690 cm^{-1} in the IR spectrum and a singlet signal at δ 6.86 ppm due to a vinylic proton of the enolized IX in the NMR spectrum. IX thus obtained was cyclized with sodium acetate in acetic acid to give IIc, which exhibited a singlet signal due to C_3 proton at δ 7.18 ppm in the NMR spectrum and two absorption maxima at 327 and 278 nm in the UV spectrum. The flavone test was positive, too. On the other hand, trials to obtain N-demethyl analogue of IIc by the similar rearrangement failed.

7) A. Kasahara, T. Izumi, and M. Ooshima, *Bull. Chem. Soc. Japan*, **47**, 2526 (1974).
8) F. Cramev and G.H. Elschnig, *Chem. Ber.*, **89**, 1 (1956).
9) R.T. Annolel and C.J. Collins, *J. Am. Chem. Soc.*, **61**, 1407 (1931).
10) J. Massicot, *Compt. rend.*, **240**, 94 (1955) [*C.A.*, **50**, 979*h* (1956)].

The orientation in the flavonoids synthesized as above was suggested from the previous studies on the reaction of IVa with hydrazine[11] or 1,6-dimethyl-4-hydroxy-2(1H) pyridone (IVb) with diazomethane,[12] respectively. The authors examined also the reaction product of Vb and diazomethane. In this case the sole product isolated was 2-acetyl-1,6-dimethyl-4-methoxy-2(1H)-pyridone (X), which exhibited an absorption maximum at 313 nm in the UV spectrum. This wave length is coincident with the calculation[12] and supports the orientation of the ring closure.

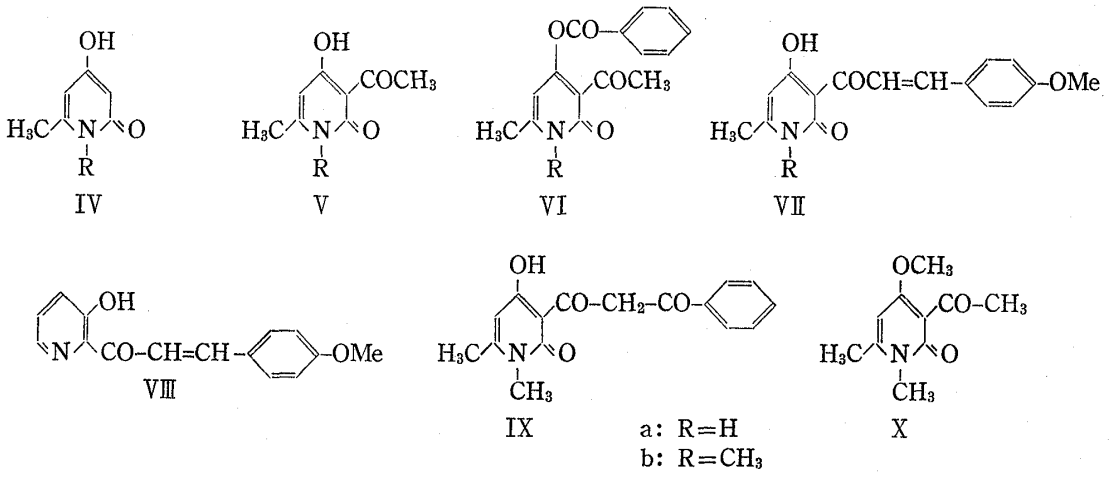


Chart 2

Experimental

All the melting points taken on a Kofler Block and the boiling points were uncorrected. The following equipments were used: IR spectra, Hitachi Grating Infra Red 215 Spectrometer; UV spectra, Hitachi 124 Spectrophotometer; NMR spectra, JEOL C-60H Spectrometer with tetramethylsilane as an internal reference; Mass spectra (MS), JEOL TMS-01SG (75 eV, direct inlet system). For column chromatography, silica gel (Wako gel C-200) was used. The abbreviations used to demonstrate coupling pattern in NMR spectra are as follows; singlet-s, doublet-d, triplet-t, quartet-q, multiplet-m, broad-br. All the solvents were evaporated under reduced pressure.

3-Acetyl-4-hydroxy-6-methyl-2(1H)-pyridone (Va)——To a suspension of PPA (37.5 ml), P_2O_5 (about 20 g), and acetic anhydride (7.5 ml), 4-hydroxy-6-methyl-2(1H)-pyridone (IVa, 1.5 g)[4,5] was added portionwise. After warmed at 120° for 6 hr with stirring, the mixture was poured into ice-water to give precipitation, which was filtered and recrystallized from EtOH. 1.14 g (yield: 56.9%). mp 238—253° (sublim.) (Lit[6] mp 259.5—260.5°). IR (Nujol) cm^{-1}: ν_{NH} 3180, $\nu_{C=O}$ 1680, 1625. NMR (CF_3COOH) δ: 2.37 and 2.67 (each 3H, s, $-COCH_3$ and C_6-CH_3), 6.50 (1H, s, C_5-H).

3-Acetyl-4-benzoyloxy-6-methyl-2(1H)-pyridone (VIa)——A mixture of Va (1.2 g, 7.2 mmol) and benzoylchloride (2.03 g, 14.4 mmol) in pyridine was warmed for a minute on a water bath and stirred at room temperature. After 2 days, the reaction mixture was warmed further 1 hr on a water bath. By a small amount of water, an excess reagent was decomposed. After removal of the solvent, the residue was dissolved in $CHCl_3$. The organic layer was washed with 10% HCl, sat. $NaHCO_3$, and sat. NaCl solution, and dried over $MgSO_4$. The residue obtained after removal of the solvent was recrystallized from EtOH. 0.92 g (47.0%). mp 212—213°. IR (Nujol) cm^{-1}: $\nu_{C=O}$ 1750, 1668. NMR (CF_3COOH) δ: 2.50 and 2.83 (each 3H, s, C_6-CH_3 and $-COCH_3$), 6.46 (1H, s, C_5-H), 7.30—8.30 (5H, m, benzene aromatic H). *Anal.* Calcd. for $C_{15}H_{13}NO_4$: C, 66.42; H, 4.80; N, 5.17. Found: C, 66.44; H, 4.53; N, 5.35.

5-Hydroxy-7-methyl-4′-methoxy-6-azaflavanone (Ia)——a) To an ethanolic solution of Va (0.5 g, 3 mmol) and *p*-anisaldehyde (0.6 g, 4.5 mmol), NaOEt [prepared from Na (0.25 g, 9 mmol)] in EtOH was added. The mixture was stirred for 4 days at room temperature. The filtrate separated from insoluble material (Va, 0.2 g) was concentrated and the residue was neutralized with 10% HCl solution to give yellow crystals, which were recrystallized from EtOH. 0.15 g (yield: 17.6%). mp 288—291°. IR (Nujol) cm^{-1}: $\nu_{C=O}$ 1673, 1628. NMR (CF_3COOH) δ: 2.67 (3H, s, C_7-CH_3), 3.36 (2H, m, $>CH_2$), 4.07 (3H, s, -OMe), 5.97 (1H, m, >CH-), 6.83 (1H, s, C_8-H), 7.16 and 7.56 (each 2H, d, J=8.5 Hz, benzene aromatic H). *Anal.* Calcd. for $C_{16}H_{15}NO_4$:

11) E. Bisagni, C. Ducrocq, and A. Civier, *Tetrahedron*, **32**, 1383 (1976).
12) H.J. den Hertog and D.J. Buurman, *Rec. Trav. Chim.*, **75**, 257 (1956) [*C.A.*, **50**, 12044*i* (1956)].

C, 67.40; H, 5.26; N, 4.91. Found: C, 67.63; H, 5.55; N, 5.20. MS *m/e*: 285 (M^+, base peak), 270 ($M-CH_3$, 88.0%).

b) Under the conditions similar to those described in a), VIa gave Ia in a yield of 87.6%.

3-Acetyl-1,6-dimethyl-4-hydroxy-2(1H)-pyridone (Vb)——Under the conditions similar to those described in the preparation of Va, 1,6-dimethyl-4-hydroxy-2(1H)-pyridone (IVb)[5] gave Vb in a yield of 37.0%. It was recrystallized from hot water. Pale yellow needles. mp 130—132°. IR (Nujol) cm^{-1}: $\nu_{C=O}$ 1615—1670. NMR (CF_3COOH) δ: 2.80 and 3.05 (each 3H, s, $-COCH_3$ and C_6-CH_3), 3.93 (3H, s, $>N-CH_3$), 6.98 (1H, s, C_5-H). *Anal.* Calcd. for $C_9H_{11}NO_3$: C, 59.67; H, 6.08; N, 7.73. Found: C, 59.96; H, 6.20; N, 7.54.

1,6-Dimethyl-4-hydroxy-3-(4-methoxybenzylidene)acetyl-2(1H)-pyridone (VIIb)——Under the conditions similar to those described in the transformation to Ia from Va, Vb gave VIIb instead of the corresponding flavanone, in a yield of 44.8%. VIIb recrystallized from EtOH was yellow needle. mp 156—158° IR (Nujol) cm^{-1}: $\nu_{C=O}$ 1628, 1605. NMR ($CDCl_3$) δ: 2.36 (3H, s, C_6-CH_3), 3.47 (3H, s, $>N-CH_3$), 3.85 (3H, s, -OMe), 5.91 (1H, s, C_5-H), 6.90 and 7.60 (each 2H, d, $J=9$ Hz, benzene aromatic H), 7.75 and 8.35 (each 1H, d, $J=15$ Hz, vinylic H), 16.51 (1H, s, phenolic OH). UV λ_{max}^{EtOH} nm (ε): 383 (23700), 206 (30800). *Anal.* Calcd. for $C_{17}H_{17}NO_4$: C, 68.23; H, 5.68; N, 4.68. Found: C, 68.39; H, 5.91; N, 4.61.

N-Methyl Analogue (Ib) of Ia——VIIb was dissolved in CF_3COOH–$CDCl_3$ (2: 3) in NMR sample tube and the temporal change was observed as follows: 31% conversion for 15 min, 61.6% conversion for 47 min, 73.7% conversion for 90 min, 90.0% conversion for 155 min, and complete conversion about 20 hr. The spectrum measured at the end of the reaction was as follows: δ 2.68 ppm (3H, s, C_7-CH_3), 3.36 (2H, m, $>CH_2$), 3.80 and 3.84 (each 3H, s, $>N-CH_3$ and -OMe), 5.80 (1H, d.d, $J=11$ and 6 Hz, >CH-), 6.85 (1H, s, C_3-H), 7.06 and 7.40 (each 2H, d, $J=9$ Hz, benzene aromatic H).

3-Acetyl-4-benzoyloxy-1,6-dimethyl-2(1H)-pyridone (VIb)——Under the conditions similar to those described in the preparation of VIa, VIb was synthesized from Vb in a yield of 58.6%. VIb: yellow oil. IR (film) cm^{-1}: $\nu_{C=O}$ 1740, ν1560—1700. NMR ($CDCl_3$) δ: 2.28 and 2.56 (each 3H, s, $-COCH_3$ and C_6-CH_3), 3.43 (3H, s, $>N-CH_3$), 6.05 (1H, s, C_5-H), 7.50 (3H, m, aromatic H), 8.03 (2H, m, aromatic H). MS *m/e*: 285 (M^+, 38.4%), 166 ($M-C_6H_5COO$, base peak).

Benzoyl 1,6-dimethyl-4-hydroxy-2-oxo-3-pyridoyl Methane (IX) and N-Methyl-4′-demethoxy Analogue (IIc) of IIa——A suspension of VIb (2.4 g, 8.4 mmol) and NaH (50% in oil, 2.48 g, 51.7 mmol) in benzene was refluxed under nitrogen for 7 hr. After an excess of NaH was decomposed with EtOH, the reaction mixture was poured onto ice. The aqueous layer was acidified with AcOH and extracted with $CHCl_3$. The organic layer, washed with sat. NaCl, was dried over $MgSO_4$. The residue obtained after removal of the solvent was fractionated by silica gel column chromatography. From benzene fraction, IX was obtained and recrystallized from benzene. 0.6 g (yield: 25.0%). mp 168—172°. IR (Nujol) cm^{-1}: ν 1580—1690. NMR ($CDCl_3$-CF_3COOH) δ: 2.58 (3H, s, C_6-CH_3), 3.76 (3H, s, $>N-CH_3$), 6.16 (1H, s, C_5-H), 6.86 (1H, br.s, $-C\underline{H}=C(OH)-$), 7.10—8.00 (5H, m, aromatic H). *Anal.* Calcd. for $C_{16}H_{15}NO_4$: C, 67.37; H, 5.26; N, 4.91. Found: C, 67.24; H, 5.50; N, 4.83. From benzene–ether (9: 1) fraction, Vb (0.15 g) was recovered. Furthermore, from the $CHCl_3$–EtOH (9: 1) fraction, IIc was obtained. It was recrystallized from benzene. 30 mg (2.2%). mp 260—263°. IR (Nujol) cm^{-1}: $\nu_{C=O}$ 1680, ν1600. UV λ_{max}^{EtOH} nm (ε): 327 (17400), 278 (16900). NMR ($CDCl_3$-CF_3COOH) δ: 2.85 (3H, s, C_7-CH_3), 3.92 (3H, s, $>N-CH_3$), 7.18 (1H, s, C_8-H), 7.56 (1H, s, C_3-H), 7.79 (3H, br.s, aromatic H), 8.08 (2H, br.s, aromatic H). MS *m/e*: 267 (M^+, base peak), 239 (M-CO, 74.7%). *Anal.* Calcd. for $C_{16}H_{13}NO_3$: C, 71.90; H, 4.90; N, 5.24. Found: C, 71.73; H, 5.17; N, 5.33.

IIc from IX——A solution of IX (0.3 g) and NaOAc (0.3 g) in glacial AcOH (25 ml) was refluxed for 6 hr. After removal of AcOH, the residue was basified with aqueous NH_3, and extracted with $CHCl_3$. The organic layer was washed with 10% HCl and water, and then dried over $MgSO_4$. After removal of the solvent, a crystalline mass was obtained and recrystallized from EtOH. mp 259—262°. 153 mg (Yield: 54.4%). Its IR spectrum was identical with that of IIc obtained from VIb.

5-Hydroxy-4′-methoxy-7-methyl-6-azaflavone (IIa) and Its N-Bromo Analogue (IId)——A $CHCl_3$ solution of Ia (0.5 g, 1.8 mmol), NBS (0.37 g, 2.1 mmole), and benzoyl peroxide (0.05 g, 0.2 mmol) was refluxed for 2 days. After the reaction mixture was cooled, the precipitation was collected by filtration. It was identified with a mixture of Ia (0.1 g, 20%) and IId (0.2 g, 30.8%). IId was fractionally recrystallized from EtOH. IId: mp 301—303°. The Beilstein test and flavone test were positive. IR (Nujol) cm^{-1}: $\nu_{C=O}$ 1700, ν1608. UV λ_{max}^{EtOH} nm: 332, 303 (sh.), 205. NMR (CF_3COOH) δ: 2.77 (3H, s, C_7-CH_3), 4.07 (3H, s, -OMe), 7.10 (1H, s, C_8-H), 7.20 (1H, s, C_3-H), 7.43 and 8.20 (each 2H, d, $J=9$ Hz, aromatic H). MS *m/e*: 363 ($M+2$, 25.8%), 361 (M^+, 21.3%), 283 (M+1–Br, base peak), 255 (M+1–Br–CO, 37.1%), 240 (M+1–Br–CO–CH_3, 22.1%). The filtrate was concentrated and fractionated by silica gel column chromatography. IIa was eluted by $CHCl_3$ and recrystallized from EtOH. mp 130—132°. 0.1 g (Yield: 19.8%). The flavone test was positive. IR (Nujol) cm^{-1}: $\nu_{C=O}$ 1665. UV λ_{max}^{EtOH} nm: 333, 254, 222 (sh.), 205. NMR (CF_3COOH) δ: 2.91 (3H, s, C_7-CH_3), 4.07 (3H, s, -OMe), 7.16 (1H, s, C_8-H), 7.32 (1H, s, C_3-H), 7.24 and 8.05 (each 2H, d, $J=9$ Hz, aromatic H). MS *m/e*: 283 (M^+, base peak), 268 ($M-CH_3$, 6.4%), 255 (M—CO, 9.5%), 240 ($M-CH_3$—CO, 15.9%). *Anal.* Calcd. for $C_{16}H_{13}NO_4$: C, 67.84; H, 4.59; N, 4.95. Found: C, 67.97; H, 4.38; N, 4.81.

Reduction of IId——To a solution of IId (0.1 g) in AcOH (10 ml), Zn-dust (0.2 g) was added under ice-cooling and with stirring, and the reaction mixture was stirred at room temperature for 1 hr. After removal

of the insoluble materials, the filtrate was concentrated and the residue was fractionated by silica gel column chromatography. The compound eluted by $CHCl_3$–EtOH (9: 1) was identified with Ia (0.03 g).

N-Methyl Analogue (IIb) of IIa——To a solution of VIIb (0.4 g, 1.3 mmol) and NaOEt (0.07 g, 1.3 mmol) in benzene (5 ml) and EtOH (10 ml), palladium acetate (0.62 g, 2.7 mmole) in EtOH (12 ml) was added under stirring at room temperature. After refluxed for 17 hr, the reaction mixture was filtered. The organic layer was washed with water and dried over $MgSO_4$. The solvent was removed to give a crystalline mass, which was recrystallized from EtOH. IIb: 37 mg (9.2%). mp 307—308°. IR (Nujol) cm^{-1}: $\nu_{C=O}$ 1670, 1615. UV λ_{max}^{EtOH} nm(ε): 325 (20,900), 302 (15,900). NMR (CF_3COOH-$CDCl_3$) δ: 2.73 (3H, s, C_7-CH_3), 3.80 (3H, s, >N-CH_3), 4.00 (3H, s, -OMe), 7.01 (1H, s, C_8-H), 7.10 (1H, s, C_3-H), 7.29 and 8.10 (each 2H, d, $J=9$ Hz, aromatic H). MS *m/e*: 297 (M^+, base peak), 269 (M−CO, 34.3%), 254 (M−CO−CH_3, 32.9%). *Anal.* Calcd. for $C_{17}H_{15}NO_4$: C, 68.69; H, 5.05; N, 4.71. Found: C, 68.57; H, 5.09; N, 4.48. From the mother liquor, VIIb (148 mg, 37%) was recovered.

3-Acetyl-1,6-dimethyl-4-methoxy-2(1H)-pyridone (X)——An excess of CH_2N_2 etherate was added dropwise to a suspension of Vb in ether–MeOH. After stood overnight at room temperature, the reaction mixture was concentrated and fractionated by silica gel column chromatography. X was eluted by $CHCl_3$ and recrystallized from benzene. mp 160—163°. 0.5 (30.9%). IR (Nujol) cm^{-1}; $\nu_{C=O}$ 1695, 1635, $\nu_{C=C}$ 1580. UV λ_{max}^{EtOH} nm(ε): 312 (7300) (Calcd.[12] 308 nm), 213 (21800). NMR ($CDCl_3$) δ: 2.46 and 2.51 (each 3H, s, -$COCH_3$ and C_6-CH_3), 3.51 (3H, s, C_5-H), MS *m/e*: 195 (M^+, base peak), 180 (M−CH_3, 76.3%). *Anal.* Calcd. for $C_{10}H_{13}NO_3$: C, 61.54; H, 6.67; N, 7.18. Found: C, 61.31; H, 6.80; N, 7.01.

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