

BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 973—977 (1973)

The Syntheses of Heterocyclic Compounds by the Ternary Condensation of Malononitrile, Salicylaldehyde, and Aliphatic Ketones in the Presence of Ammonium Acetate

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(Received July 28, 1972)

Various 2-amino-6-alkyl (or 5,6-dialkyl)-4-aryl-4,5-dihydronicotinonitriles (**1**) were readily prepared by the ternary condensation of malononitrile, salicylaldehyde (or 3-methoxysalicylaldehyde), and aliphatic ketones in the presence of ammonium acetate. The resulting **1** was transformed into the corresponding 3-carbamoyl derivatives (**3**) via their 2-acetamino derivatives (**2**). In addition, the reaction of **3** with acetic anhydride led to [2,3-*d*]pyridopyrimidine derivatives (**4**).

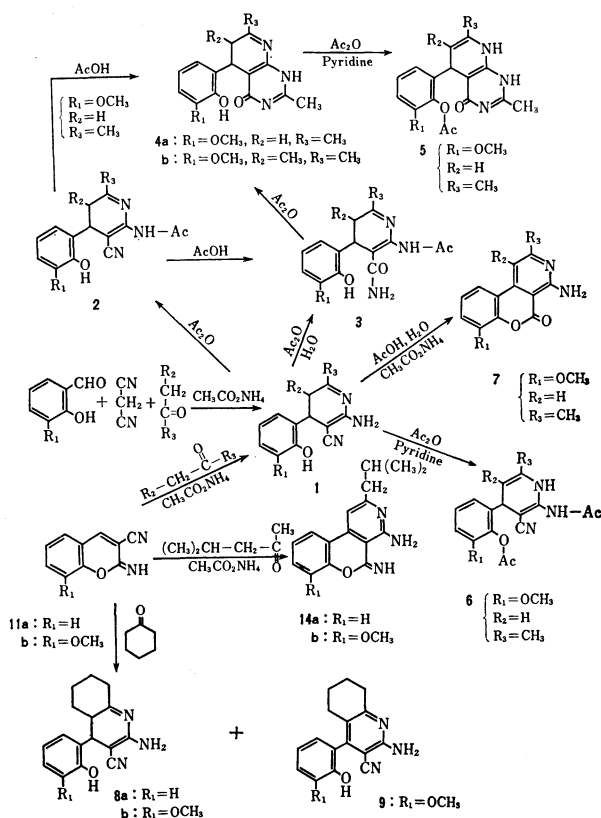
In a previous paper,¹⁾ the syntheses of benzopyranopyrido-pyrimidine and benzopyranopyridine derivatives by the ternary condensation of malononitrile, salicylaldehyde, and aromatic ketones in the presence of ammonium acetate were reported.

The present paper will deal with the syntheses of substituted 4,5-dihydronicotinonitriles (**1**), 1,4,5,6-tetrahydro-[2,3-*d*] pyridopyrimidines (**4**), and 4,4a,5,6,7,8-hexahydroquinolines (**8**) by the ternary condensation of malononitrile, salicylaldehyde (or 3-methoxysalicylaldehyde), and aliphatic ketones, *e. g.*, acetone, methyl ethyl-, methyl *n*-propyl, and diethyl ketone, and cyclohexanone in the presence of ammonium acetate.

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1) A. Sakurai, Y. Motomura, and H. Midorikawa, *J. Org. Chem.*, **37**, 1523 (1972).

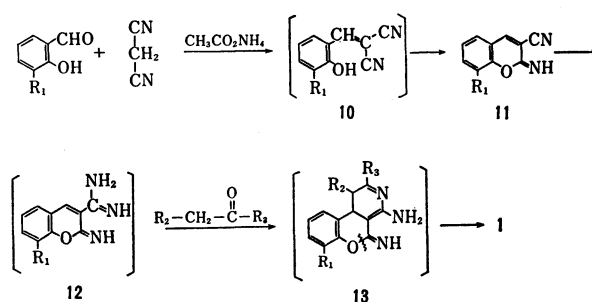
The reaction of malononitrile, 3-methoxysalicylaldehyde, and the *n*-alkyl ketone (molar ratio of 1 : 1 : 1) in the presence of ammonium acetate (1 mol or a slight excess) gave 2-amino-6-alkyl (or 5,6-dialkyl)-4-(2-hydroxy-3-methoxyphenyl)-4,5-dihydronicotinonitriles (**1**) in 13—23% yields. The subsequent treatment of the resulting **1** with acetic anhydride led to the corresponding 2-acetamino derivatives (**2**), which were then further transformed into 3-carbamoyl derivatives (**3**) by the action of acetic acid in refluxing ethanol. The further treatment of **3** with boiling acetic anhydride afforded cyclization products, such as 5-(2-hydroxy-3-methoxyphenyl)-2,7-dimethyl (or 2,6,7-trimethyl)-4-oxo-1,4,5,6-tetrahydro[2,3-*d*]pyridopyrimidines (**4**), as is indicated in Scheme 1. On the other hand, **2b** (**2**, R₁=OCH₃, R₂=H, R₃=CH₃) was converted directly to **4a** (**4**, R₁=OCH₃, R₂=H,



Scheme 1.

$R_3 = CH_3$) by treatment with acetic acid in boiling ethanol. The acetylation of **4a** with acetic anhydride in boiling pyridine afforded 5-(2-acetoxy-3-methoxyphenyl)-2,7-dimethyl-4-oxo-1,4,5,8-tetrahydro[2,3-*d*]pyridopyrimidine (**5**). The acetylation of **1b** with acetic anhydride gave **2b**, while the same reaction of **1b** with acetic anhydride-pyridine gave 2-acetamino-4-(2-acetoxy-3-methoxyphenyl)-6-methyl-1,4-dihydro-nicotinonitrile (**6**). On the other hand, when heated with acetic acid containing a few drops of water in the presence of ammonium acetate, **1b** was cyclized to 4-amino-7-methoxy-2-methyl-5-oxo-[1]benzopyrano-[3,4-*c*]pyridine (**7**),²⁾ which was proved, on the basis of the spectral studies, to be identical with that previously-reported substance obtained by the condensation of ethyl cyanoacetate, 3-methoxysalicylaldehyde, and acetone. Type 1 compounds were also obtained in 13–33% yields by the condensation of 3-cyano-coumarinimide (**11**) with *n*-alkyl ketones. The reaction of cyclohexanone with **11a** afforded 16% of 2-amino-3-cyano-4-(2-hydroxyphenyl)-4,4a,5,6,7,8-hexahydroquinoline (**8a**), while the same reaction with **11b** gave a mixture of **8b** (27%) and its 5,6,7,8-tetrahydro derivative **9** (7%) under the same reaction conditions (Scheme 1). When a methyl isoalkyl ketone such as the methyl isobutyl ketone was employed as the ketone reactant, ring-opening did not occur. For example, the condensation of **11b** with methyl isobutyl ketone afforded 4-amino-5-imino-2-isobutyl-7-methoxy-[1]benzopyrano[3,4-*c*]pyridine (**14b**), which was then hydrolyzed to the corresponding 5-oxo compound.²⁾

2) A. Sakurai, H. Midorikawa, and Y. Hashimoto, This Bulletin, **43**, 2925 (1970).



Scheme 2.

It seems reasonable to assume that the formation of **1** may be achieved by the following process. Malononitrile is first condensed with salicylaldehyde in the presence of ammonium acetate to give **10**, which is then readily converted to **11**. This is further transformed into amidine-type **12**. Then, **12** condenses with the *n*-alkyl ketone to form **13**, which immediately undergoes ring-opening to yield **1** (Scheme 2).

In the IR spectra of **1**, **2**, and **8**, $C\equiv N$ stretching bands were shifted to lower frequencies at 2160–2150 cm^{-1} (**1**), 2170 cm^{-1} (**2**), and 2170–2140 cm^{-1} (**8**) respectively, whereas the stretching bands of **6** and **9** appeared at 2200 cm^{-1} . The NMR spectra of **1a–e** in $(CD_3)_2SO$ showed a methyl singlet due to three protons in the 1.5–1.7 ppm region. In addition, **1c** (from methyl ethyl ketone) gave a methyl doublet, centered at 0.98 ppm, due to three protons. These NMR data suggest that the methylene group adjacent to the carbonyl group of the ketones, such as the methyl ethyl-, methyl *n*-propyl-, and diethyl ketone, is involved in this cyclization. The structural assignment of **1**, therefore, was based on the above spectral data and the fact that **1b** gave the expected compound, **7**. The IR spectrum of **3a** (obtained when **2b** was heated with acetic acid in ethanol) gave no absorption band due to a $C\equiv N$ stretching, but new bands appeared at 3440, 3350, 3320, and 3180 cm^{-1} . In the spectrum of **4a**, however, the primary amino stretching bands disappeared and only the absorption at 3310 cm^{-1} was observed in this region. The NMR spectrum in CF_3CO_2H revealed two singlets, at 2.0 and 2.8 ppm, due to three protons. The former was assigned to a methyl proton at the 7-position by means of a NMR comparison of the methyl protons in **1b**, **2b**, and **3a** (Tables 1, 2, and 3). The latter signal, therefore, was assigned to a methyl proton of the 2-position. The NMR spectrum in $(CD_3)_2SO$ of **5** (derived from **4a**) gave a new methyl singlet at 2.24 ppm, and the IR spectrum showed a new absorption band at 1755 cm^{-1} attributable to acetoxy carbonyl. These observations show that the hydroxy group of **3a** is independent of the cyclization to **4a**. The NMR spectrum of **5** exhibited signals of methine doublets at 4.24 and 4.62 ppm, each corresponding to one proton, but no signal for the methylene group was observed in Compound **4a**. This suggests that compound **5** is predominantly in the 1,4,5,8-tetrahydro form rather than in the 1,4,5,6-tetrahydro form of [2,3-*d*]pyridopyrimidine. Similarly, **6** (derived from **1b**) is predominantly in the 1,4-dihydro form of ni-

TABLE 1. SUBSTITUTED 2-AMINO-4-ARYL-4,5-DIHYDRONICOTINONITRILES (1)

Compd	R ₁	R ₂	R ₃	Mp, °C	Yield, %	IR (KBr), cm ⁻¹			NMR δ (ppm) ^{b)}			
						νNH ₂	OH	νC≡N	CH ₃	CH	NH ₂	
1a	H	H	CH ₃	226–229 (decomp.)	8	3420, 3350, 3340, 3220		2160				
1b	OCH ₃	H	CH ₃	250–253 (decomp.)	23	3430, 3360, 3320, 3230		2150	1.66 (s, 3H)	1.92 (d, 2H)	3.4 (t, 1H)	5.28 (s, 2H)
1c	OCH ₃	CH ₃	CH ₃	233–236 (decomp.)	17	3470, 3340, 3210		2150	0.98 (d, 3H) 1.56 (s, 3H)		1.8–2.1 (m, 1H) 3.08 (d, 1H)	5.26 (s, 2H)
1d	OCH ₃	C ₂ H ₅	CH ₃	232–235 (decomp.)	28 ^{a)}	3450, 3350, 3220		2160				
1e	OCH ₃	n-C ₃ H ₇	CH ₃	217–219 (decomp.)	13 ^{a)}	3450, 3370, 3340, 3210		2160				
1f	OCH ₃	CH ₃	C ₂ H ₅	236–238 (decomp.)	17	3450, 3340, 3330, 3220		2160	0.96 (d, 3H) 1.0 (t, 3H)	1.87 (q, 2H) ^{c)}	1.8–2.1 (m, 1H) 3.1 (d, 1H)	5.31 (s, 2H)

a) Yield based on **11b**. b) Parts per million downfield from tetramethylsilane in (CD₃)₂SO; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet c) Overlapped with CH (δ 1.8–2.1), 3H.

TABLE 2. SUBSTITUTED 2-ACETAMINO-4-ARYL-4,5-DIHYDRONICOTINONITRILES (2)

Compd	R ₁	R ₂	R ₃	Mp, °C	Yield, %	IR (KBr), cm ⁻¹			NMR δ (ppm) ^{a)}			
						νNH	OH	νC≡N	CH ₃	CH	OH	NH
2a	H	H	CH ₃	206–208	69							
2b	OCH ₃	H	CH ₃	210–213	90	3290, 3230	2170	1690	1.7 (s, 3H) 1.96 (s, 3H)	1.9–2.1 (d, 2H) ^{b)}	3.6 (t, 1H)	8.42 (s, 1H)
2c	OCH ₃	C ₂ H ₅	CH ₃	205–207	78	3290, 3220	2170	1690	1.0 (t, 3H) 1.63 (s, 3H) 1.95 (s, 3H)	1.5–2.0 (CH ₃ and CH, 3H)	3.5 (d, 1H)	8.33 (br, 1H)

a) Parts per million downfield from tetramethylsilane in (CD₃)₂SO; s, singlet; d, doublet; t, triplet; br, broad. b) Overlapped with CH₃ (δ 1.96), 5H.

TABLE 3. SUBSTITUTED 2-ACETAMINO-4-ARYL-3-CARBAMOYL-4,5-DIHYDROPYRIDINES (3)

Compd	R ₁	R ₂	R ₃	Mp, °C	Yield, %	IR (KBr), cm ⁻¹			NMR δ (ppm) ^{b)}			
						νNH ₂	NH	OH	CH ₃	CH	NH ₂	OH
3a	OCH ₃	H	CH ₃	254–256 (decomp.)	59	3440, 3350, 3320, 3180		1660	1.7 (s, 3H) 1.98 (s, 2H)	4.05 (t, 1H)	7.03 (br, 2H)	9.03 (s, 1H)
3b	OCH ₃	CH ₃	CH ₃	266–268 (decomp.)	67	3420, 3350, 3310, 3170		1660	0.95 (d, 3H) 1.64 (s, 3H) 2.0 (s, 3H)	2–2.2 (m, 1H) 3.82 (d, 1H)	7.1 (br, 2H)	9.0 (s, 1H)
3c	OCH ₃	C ₂ H ₅	CH ₃	242–245 (decomp.)	48							
3d	OCH ₃	CH ₃	C ₂ H ₅	238–240 (decomp.)	41	3430, 3350, 3300, 3170		1660				

a) Yield based on **1**. b) Parts per million downfield from tetramethylsilane in (CD₃)₂SO; s, singlet; d, doublet; t, triplet; br, broad. In **3a** spectrum, δCH₂ 1.8–2.1 ppm, overlapped with CH₃ (δ 1.98), 5H.

cotinonitrile, judging from the NMR spectrum, which has methine doublets at 4.27 and 4.43 ppm, each corresponding to one proton. On the other hand, the IR spectra of the compound, **14**, obtained by the condensation of **11** with methyl isobutyl ketone gave no absorption attributable to a C=N group, and the NMR spectra showed no signal for the methyl singlet observed in Compound **1**—**6**, as has been mentioned above. This shows that the methyl group adjacent to the ketone carbonyl was involved in this cyclization.

Experimental

All the melting points are uncorrected. The IR spectra were determined by means of potassium bromide pellets. The NMR spectra were determined in deuteriodimethylsulfoxide or trifluoroacetic acid at 100 MHz, using tetramethylsilane as the internal standard. The chemical shifts are reported as parts per million downfield from TMS.

Reaction of Malononitrile, 3-Methoxysalicylaldehyde (or Salicylaldehyde), and n-Alkyl Ketones. A mixture of malononitrile (0.06 mol), aldehyde (0.06 mol), ketone (0.06 mol), and ammonium acetate (0.06—0.07 mol) in ethanol (30 ml) was refluxed for 1 hr. The pale yellow crystals which precipitated during the reaction were collected and washed with hot ethanol. Recrystallization from dimethyl sulfoxide-ethanol gave **1a**—**c** and **1f**. The experimental results and spectral data are summarized in Table 1.

Found: C, 68.76; H, 5.79; N, 18.65%. Calcd for $C_{13}H_{13}N_3O$ (**1a**): C, 68.70; H, 5.77; N, 18.49%. Found: C, 65.54; H, 5.65; N, 16.60%. Calcd for $C_{14}H_{15}N_3O_2$ (**1b**): C, 65.35; H, 5.88; N, 16.33%. Found: C, 66.47; H, 6.35; N, 15.55%. Calcd for $C_{15}H_{17}N_3O_2$ (**1c**): C, 66.40; H, 6.32; N, 15.49%. Found: C, 67.05; H, 6.86; N, 14.43%. Calcd for $C_{16}H_{19}N_3O_2$ (**1f**): C, 67.34; H, 6.71; N, 14.73%.

Reaction of 8-Methoxy-3-cyanocoumarinimide (11b**)¹¹ and n-Alkyl Ketones.** A mixture of **11b** (0.02 mol), ketone (0.02 mol), and ammonium acetate (0.04 mol) in ethanol (20 ml) was refluxed for 0.5 hr. After the mixture had cooled, the resulting precipitate was collected and recrystallized from ethanol-dimethyl sulfoxide to afford **1d** and **1e** (Table 1).

Found: C, 67.26; H, 6.48; N, 14.48%. Calcd for $C_{16}H_{19}N_3O_2$ (**1d**): C, 67.34; H, 6.71; N, 14.73%. Found: C, 67.82; H, 7.15; N, 13.82%. Calcd for $C_{17}H_{21}N_3O_2$ (**1e**): C, 68.20; H, 7.07; N, 14.04%.

Formation of **2 by the Reaction of **1** and Acetic Anhydride.** Acetic anhydride (15—18 ml) was added to **1** (0.02 mol) and heated for a few minutes. Pale yellow crystals thereupon began to separate from the solution (Table 2).

Found: C, 66.74; H, 5.59; N, 15.65%. Calcd for $C_{15}H_{15}N_3O_2$ (**2a**): C, 66.90; H, 5.61; N, 15.61%. Found: C, 64.08; H, 5.73; N, 14.15%. Calcd for $C_{16}H_{17}N_3O_3$ (**2b**): C, 64.20; H, 5.72; N, 14.04%. Found: C, 66.04; H, 6.51; N, 12.72%. Calcd for $C_{18}H_{21}O_3N_3$ (**2c**): C, 66.03; H, 6.47; N, 12.84%.

Formation of **3 by the Reaction of **1** with Acetic Anhydride and Water.** Acetic anhydride (5—8 ml) was added to **1** (4 mmol), and the mixture was heated for a few minutes. After cooling, a few drops of water were added to the reaction mixture; a crystalline precipitate was thus formed. Recrystallization from acetic acid-ethanol afforded colorless crystals (Table 3).

Found: C, 60.41; H, 5.96; N, 13.15%. Calcd for $C_{16}H_{19}N_3O_4$ (**3a**): C, 60.55; H, 6.04; N, 13.24%. Found: C, 61.62; H, 6.39; N, 12.55%. Calcd for $C_{17}H_{21}N_3O_4$ (**3b**): C, 61.62; H, 6.39; N, 12.68%. Found: C, 62.81; H,

6.47; N, 12.26%. Calcd for $C_{18}H_{23}N_3O_4$ (**3c**): C, 62.59; H, 6.71; N, 12.17%. Found: C, 62.36; H, 6.68; N, 12.04%. Calcd for $C_{18}H_{23}N_3O_4$ (**3d**): C, 62.59; H, 6.71; N, 12.17%.

Formation of **4a by the Reaction of **3a** and Acetic Anhydride.** Acetic anhydride (3 ml) was added to **3a** (1 mmol) and heated for 0.5 hr. After the mixture had cooled, the deposited crystals were collected and recrystallized from dimethyl sulfoxide-ethanol to afford white crystals (mp 276—278°C (decomp.)) in a 63% yield; ν_{max}^{KBr} 3310 (NH), 1650 cm^{-1} (C=O); NMR (CF_3CO_2H) 2.0, 2.8 (CH_3 , singlet, 3H each), 3.97 (OCH_3 , singlet, 3H), 2.35 (CH_2 , doublet, 2H), 4.55 (CH, triplet, 1H), 7.7—8.2 ppm (NH, broad, 1H).

Found: C, 64.21; H, 5.86; N, 13.89%. Calcd for $C_{16}H_{17}N_3O_3$: C, 64.20; H, 5.72; N, 14.04%.

Similarly, the same reaction with **3b** gave **4b** (mp 273—274°C (decomp.)) in a 72% yield; NMR (CF_3CO_2H) peaks at 1.15 (CH_3 , doublet, 3H), 1.92, 2.8 (CH_3 , singlet, 3H each), 3.97 (OCH_3 , singlet, 3H), 2.4—2.7 (CH, multiplet, 1H), 4.25 (CH, doublet, 1H), 7.5—8.2 ppm (NH, broad, 1H).

Found: C, 64.99; H, 6.11; N, 13.09%. Calcd for $C_{17}H_{19}N_3O_3$: C, 65.16; H, 6.11; N, 13.41%.

5-(2-Acetoxy-3-methoxyphenyl)-2,7-dimethyl-4-oxo-1,4,5,8-tetrahydro[2,3-d]pyridopyrimidine (5**).** A mixture of **4a** (1.1 g) and acetic anhydride (5 ml) in pyridine (4 ml) was heated for 2 hr. When the reaction mixture was then left to stand overnight, pale yellow crystals were obtained. Recrystallization from ethanol gave 0.7 g of colorless needles (mp 225—227°C); ν_{max}^{KBr} 3360 (NH), 1755, 1660 cm^{-1} (C=O);

NMR spectrum ($DMSO-d_6$) gave signals at 1.64, 2.16 (CH_3 , singlet, 3H each), 2.24 (O-Ac, singlet, 3H), 3.72 (OCH_3 , singlet, 3H), 4.24, 4.62 (CH, doublet, 1H each), 8.5, 11.59 ppm (NH, singlet, 1H each).

Found: C, 63.20; H, 5.73; N, 12.42%. Calcd for $C_{18}H_{19}N_3O_4$: C, 63.33; H, 5.61; N, 12.31%.

2-Acetamino-4-(2-acetoxy-3-methoxyphenyl)-6-methyl-1,4-dihydro-nicotinonitrile (6**).** To a solution of **1b** (0.8 g) dissolved in pyridine (3 ml), acetic anhydride (3 ml) was added,

after which the mixture was heated for 5 min. After the mixture had then been allowed to stand at room temperature, the resulting precipitate was washed with dilute methanol and recrystallized from ethanol-dimethyl sulfoxide to afford 0.5 g of colorless crystals (mp 224—227°C); NMR ($DMSO-d_6$) 1.66 (6- CH_3 , singlet, 3H), 2.0 (NH-Ac, singlet, 3H), 2.28 (O-Ac, singlet, 3H), 3.76 (OCH_3 , singlet, 3H), 4.27, 4.43 (CH, doublet, 1H each), 8.68, 9.9 ppm (NH, singlet, 1H each); ν_{max}^{KBr} 3260, 3220 (NH), 2200 (C=N), 1760 (O-Ac), 1690 cm^{-1} (NH-Ac).

Found: C, 63.13; H, 5.62; N, 12.22%. Calcd for $C_{18}H_{19}N_3O_4$: C, 63.33; H, 5.61; N, 12.31%.

Reaction of **1b and Acetic Acid.** A mixture of **1b** (0.4 g), acetic acid (5 ml), water (1 ml), and ammonium acetate (1 g) was refluxed for 1 hr. The pale yellow crystals which were thus precipitated were collected and recrystallized from ethanol-dimethyl sulfoxide to give 0.2 g of 4-amino-7-methoxy-2-methyl-5-oxo-[1]benzopyrano[3,4-c]pyridine (**7**) (mp 230—232°C).²⁾ This compound was proved by IR spectral studies to be identical with that obtained by the condensation of ethyl cyanoacetate, 3-methoxysalicylaldehyde, and acetone in the presence of ammonium acetate.

Reaction of **11 and Cyclohexanone.** To a mixture of **11a**¹⁾ (2.38 g, 0.014 mol) and cyclohexanone (1.37 g, 0.014 mol) in ethanol (10 ml), ammonium acetate (2 g, 0.026 mol) was added. After having been refluxed for 1 hr, the reaction mixture afforded 0.6 g (16%) of 2-amino-3-cyano-4-(2-hydroxyphenyl)-4,4a,5,6,7,8-hexahydroquinoline (**8a**).

(mp 223—225°C (decomp.)); $\nu_{\text{max}}^{\text{KBr}}$ 3440, 3350, 3220 (NH₂, OH), 2140 cm⁻¹ (C≡N).

Found: C, 71.89; H, 6.26; N, 15.98%. Calcd for C₁₆-H₁₇N₃O: C, 71.88; H, 6.41; N, 15.72%.

When **11b** was used instead of **11a**, the condensation afforded 27% of **8b** (mp 230—233°C (decomp.)) and 7% of 2-amino-3-cyano-4-(2-hydroxy-3-methoxyphenyl)-5,6,7,8-tetrahydroquinoline (**9**) (mp 241—244°C); $\nu_{\text{max}}^{\text{KBr}}$ 3470, 3370, 3220 (NH₂, OH), 2200 cm⁻¹ (C≡N).

Found: C, 68.99; H, 5.46; N, 14.58%. Calcd for C₁₇-H₁₇N₃O₂: C, 69.13; H, 5.80; N, 14.23%.

The IR spectrum (KBr) of **8b** gave bands at 3440, 3340, 3220 (NH₂, OH), and 2170 cm⁻¹ (C≡N).

Found: C, 68.53; H, 6.42; N, 14.19%. Calcd for C₁₇-H₁₉N₃O₂: C, 68.66; H, 6.44; N, 14.13%.

Reaction of 11 and Methyl Isobutyl Ketone. To a mixture of **11b** (3 g, 0.015 mol) and methyl isobutyl ketone (1.8 g, 0.018 mol) in ethanol (10 ml), ammonium acetate (2.31 g, 0.03 mol) was added, and the mixture was refluxed for 1 hr. This mixture afforded 1 g (22%) of **14b** (mp 180—182°C); $\nu_{\text{max}}^{\text{KBr}}$ 3300, 3130 (NH₂, NH), 1645 cm⁻¹ (C=N); NMR (CF₃CO₂H) peaks at 1.15 (CH₃, doublet, 6H), 2.05—2.55 (CH, multiplet, 1H), 2.95 (CH₂, doublet, 2H), 4.13 (OCH₃, singlet, 3H).

Found: C, 68.90; H, 6.48; N, 14.02%. Calcd for C₁₇-

H₁₉N₃O₂: C, 68.66; H, 6.44; N, 14.13%.

When **11a** was used instead of **11b**, the condensation afforded 18% of **14a** (mp 184—186°C); $\nu_{\text{max}}^{\text{KBr}}$ 3295; 3125 (NH₂, NH), 1645 cm⁻¹ (C=N).

Found: C, 71.84; H, 6.35; N, 15.44%. Calcd for C₁₆-H₁₇N₃O: C, 71.88; H, 6.41; N, 15.72%.

Reaction of 14b and Hydrochloric Acid. To a solution of **14b** (0.2 g) suspended in ethanol (7 ml), hydrochloric acid (3 ml) was added. After the reaction mixture has then been refluxed for 1 hr, a crystalline precipitate was yielded. Recrystallization from ethanol gave 0.1 g of 4-amino-2-isobutyl-7-methoxy-5-oxo-[1]benzopyrano[3,4-*c*]pyridine (mp 196—197°C).²⁾ This compound was identified with that obtained by the reaction of ethyl cyanoacetate, 3-methoxy-salicylaldehyde, and methyl isobutyl ketone by a study of their IR spectra.

The authors wish to express their thanks to Dr. Taro Hayashi and Dr. Tatsuo Takeshima for their kind advice. Thanks are also due to Dr. Haruo Homma and his staff for their microanalyses, to Mr. Jun Uzawa for his measurements of the NMR spectra, and to Mr. Hironori Ogawa for his measurements of the IR spectra.