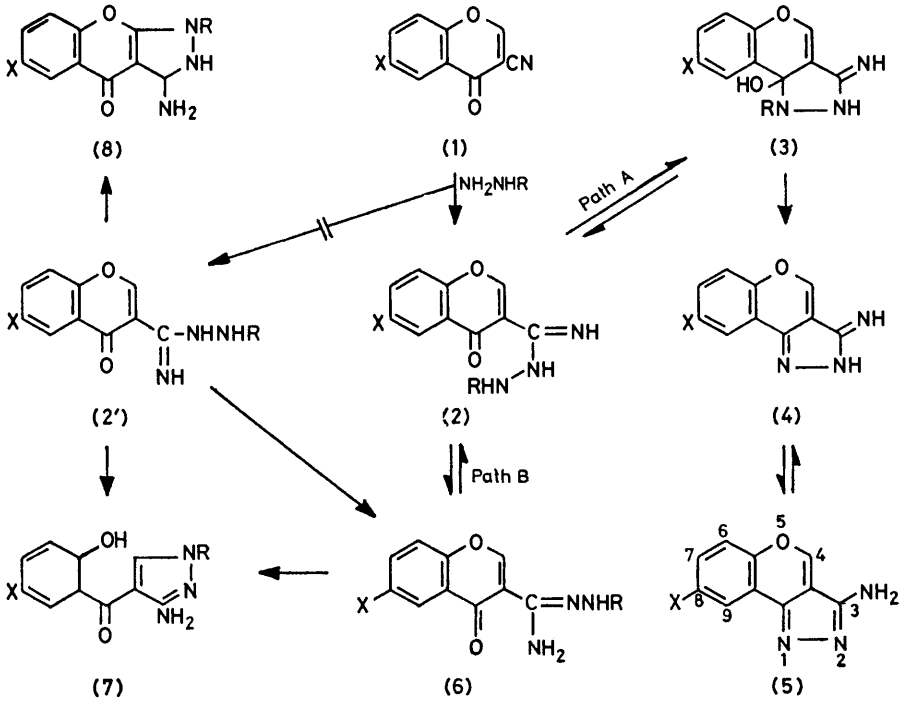
Heterocyclic Systems. Part 6.[1] Reactions of 4-Oxo-4*H*-[1]benzopyran-3-carbonitriles with Hydrazine, Phenylhydrazine, Hydroxylamine, and Some Reactive Methylene Compounds

By **Chandrakanta Ghosh,* Dilip K. SinhaRoy,** and **Kanchan K. Mukhopadhyay,** Organic Chemistry Laboratory, Department of Biochemistry, Calcutta University, Calcutta 700019, India

Hydrazine and phenylhydrazine undergo 1 : 2 addition to the carbonitrile function of 4-oxo-4*H*-[1]benzopyran-3-carbonitriles (1 ; X = H, Me, Cl, and Br) to form the iminohydrazine intermediates (2; non-isolable when R = H, and isolable when R = Ph) that further cyclise to yield 3-amino-[1]benzopyrano[4,3-*c*]pyrazoles (5) and 3-amino-4-(2-hydroxybenzoyl)-1-phenylpyrazoles (7; R = Ph) respectively. Hydroxylamine by similar 1 : 2 addition to the carbonitriles (1) gives 3-[hydroxyamino(imino)methyl]-4-oxo-4*H*-[1]benzopyrans (9), which undergo no further transformation under acidic conditions. In their reactions with the carbonitriles (1) or 4-oxo-4*H*-[1]benzopyran-3-carbaldehyde oximes (15), reactive methylene compounds such as acetylacetone, ethyl acetoacetate, diethyl malonate, and ethyl cyanoacetate in the presence of a base undergo Michael addition to the γ-pyrone system with concomitant opening of the pyrone ring and subsequent cyclisation to give benzopyrano[2,3-*b*]pyridine derivatives, (11), (12), (13), and (14), respectively.

ALTHOUGH condensation reactions of 4-oxo-4*H*-[1]benzopyran-3-carbaldehydes have been well studied,[2-5] those of the corresponding carbonitriles are little known. The only condensation reaction of 4-oxo-4*H*-[1]benzopyran-3-carbonitriles (henceforth called chromone-3-nitriles) so far described is that with sodium azide to form 3-(1*H*-tetrazol-5-yl)chromones.[6] In view of this it seemed desirable to investigate their reactions with hydrazine, phenylhydrazine, hydroxylamine, and some reactive methylene compounds such as acetylacetone, ethyl acetoacetate, diethyl malonate, and ethyl cyanoacetate. The results of this investigation are presented here.

When an equimolar mixture of chromone-3-nitrile (1a) and hydrazine was refluxed in ethanol, 3-amino-[1]benzopyrano[4,3-*c*]pyrazole (5a) resulted. This reaction can be explained in terms of an initial 1 : 2 addition of nucleophile to the nitrile function of (1a) to give a non-isolable iminohydrazine intermediate. Such an addition is well documented in the literature.[7,8] Two orientations (2 and 2'; R = H) are possible for the intermediate, the one (2) having the two dipoles (C=O and C=NH) approximately antiparallel, being preferred to the other (2') where these dipoles are nearly parallel (Scheme 1). Three different reaction paths for (2; R = H) may be envisaged: (i) intramolecular 1 : 2 addition of the hydrazino-function to the carbonyl



SCHEME 1

TABLE 1

3-Amino-[1]benzopyrano[4,3-*c*]pyrazoles (5) and their acetates

	Pyrazole			Acetate of the pyrazole					
					τ(CDCl$_3$)				
	Mol. formula [a]	Yield (%)	M.p. (°C)	M.p.[b] (°C)	Pyrazole-H(s)	ArH(m)	–NHCO–(s)	$COCH_3$(s)	$ArCH_3$(s)
(5a)	$C_{10}H_7N_3O$	73	169	179	1.04	2.12—2.71 [c]		7.19	
(5b)	$C_{11}H_9N_3O$	64	211	171	1.07	2.13—2.70 [c]		7.17	7.57
(5c)	$C_{10}H_6ClN_3O$	71	270	220	1.03	1.94—2.60	2.70	7.20	
(5d)	$C_{10}H_6BrN_3O$	65	290 (decomp.)	234					*d*

[a] All the compounds gave correct elemental (C, H, N) analysis.* [b] Crystallised from chloroform–light petroleum. [c] Signal due to NH-proton merges with those of aromatic protons. [d] N.m.r. was not taken.

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TABLE 2

3-Amino-4-(2-hydroxybenzoyl)-1-phenylpyrazoles (7; R = Ph) and their precursors (2; R = Ph)

	Iminohydrazine (2; R = Ph)	Pyrazoles (7; R = Ph)							
					τ(CDCl$_3$)				
	M.p. (°C)	Mol. formula [a]	Yield [b]	M.p.[c]	ArOH(s)	Pyrazole-H(s)	ArH(m)	NH_2(br s)	$ArCH_3$(s)
a	252	$C_{16}H_{13}N_3O_2$	59	144	–1.28	2.11	2.21—3.10	3.99	
b	249	$C_{17}H_{15}N_3O_2$	55	151	–1.57	2.06	2.34—3.11	3.97	7.68
c	265 (decomp.)	$C_{16}H_{12}ClN_3O_2$	62	185	–1.57	2.00	2.07—3.00	3.95	
d	273 (decomp.)	$C_{16}H_{12}BrN_3O_2$	65	198	–1.68	1.61	2.05—3.00	3.97	

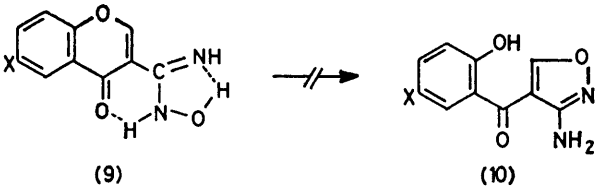
[a] All the compounds gave correct elemental analysis; see asterisked footnote to Table 1. [b] Based on chromone-3-nitrile (1). [c] Crystallised from either chloroform or chloroform–light petroleum.

group with subsequent water elimination to give the aminopyrazole (5) *via* its tautomeric form (4) (Path A); (ii) reaction *via* the amidohydrazone (6; R = H) which would ultimately lead to the pyrazole (7; R = H) (Path B); and (iii) isomerisation to (2′; R = H) which would lead either to the benzoylpyrazole (7; R = H) directly or *via* the amidohydrazone (6; R = H) (intramolecular 1 : 4 addition of the hydrazino-function to the γ-pyrone system followed by opening of the pyrone ring [4-6,9,10]), or to the pyrazolone (8; R = H) (intramolecular 1 : 4 addition of the hydrazino-function to the α,β-unsaturated imine and subsequent hydrogen shift) or its dehydrogenated product [by aerial oxidation of (8; R = H)]. However since the reaction of chromone-3-nitrile (1a) with hydrazine gave only the pyrazole (5a) (73% yield) it may be assumed that both the barrier to the formation of the iminohydrazine in orientation (2′) [or to the isomerisation (2)→(2′)] and the activation energy for the process shown in Path (B) are higher than that involved in the alternative Path (A).

The product obtained by allowing (1a) and hydrazine to react may exist either as (4a) or (5a). Its n.m.r. spectrum τ[$(CD_3)_2SO$] 0.40 (1 H, br s, =NH, exchangeable with D_2O), 1.46 (1 H, br s, NH), 2.16 (1 H, s, 4-H), and 2.63 (4 H, m, ArH) indicates that in Me_2SO the compound exists exclusively in the tautomeric form [4a] although on acetylation it gave the acetate of the aminopyrazole (5a). Various 8-substituted 3-amino-[1]benzopyrano-[4,3-*c*]pyrazoles (5; R = H) were synthesised, and they are tabulated in Table 1.

When chromone-3-nitrile (1a) was treated with phenylhydrazine, a high-melting intermediate having no i.r. absorption above 3 210 cm^{-1} (absence of NH_2) was obtained. This intermediate, assigned structure (2a; R = Ph), on prolonged refluxing in ethanol both in the presence and absence of an acid catalyst afforded the pyrazole (7a; R = Ph) exclusively. The formation of this compound can also be explained by the reaction sequence proposed in Scheme 1. The intermediate iminohydrazine (2a; R = Ph) cannot follow Path (A) since there would be severe steric crowding at the benzylic centre as a result of a change from sp^2 to sp^3 hybridisation, and if the intermediate (3a; R = Ph) is formed at all, it cannot collapse to any stable heterocyclic system and, rather, it reverts to the iminohydrazine (2a; R = Ph). The exclusive formation of the aminopyrazole (7a; R = Ph) indicates that the iminohydrazine (2a; R = Ph) on refluxing tautomerises to the amidohydrazone (6a; R = Ph), the latter rearranging to the product (7a; R = Ph). The different aminopyrazoles (7) synthesised are listed in Table 2.

Hydroxylamine hydrochloride underwent similar 1 : 2 addition to the nitrile function of (1) to give the iminohydroximes (9) which were stabilised as a result of double chelation and, thereby, resisted an anticipated



(9) (10)

transformation into the oxazoles (10). When refluxed with acetic anhydride in pyridine, each of the hydroximes (9) gave a complex mixture which was not further investigated.

Next, we were interested to see how the chromone-

TABLE 3

3-Acetyl-2-methyl-[1]benzopyrano[2,3-*b*]pyridin-5-ones *

	Mol. formula	Yield (%) from the Nitrile (1)	Yield (%) from the Hydroxime (15)	M.p. (°C)	τ(CDCl$_3$) Pyridine-H(s)	ArH(m)	$COCH_3$(s)	2-Methyl(s)	$ArCH_3$(s)
(11a)	$C_{15}H_{11}NO_3$	80	67	218	1.03	1.72—2.63	7.17	7.37	
(11b)	$C_{16}H_{13}NO_3$ ‡	85	65	194—198	1.00	1.90—2.75	7.10	7.30	7.53
(11c)	$C_{15}H_{10}ClNO_3$	81	71	242—245	1.03	1.73—2.40	7.13	7.30	
(11d)	$C_{15}H_{10}BrNO_3$	78	68	195	1.02	1.60—2.53	7.13	7.30	

* $\nu_{max.}$(Nujol) *ca.* 1 680 (aryl methyl ketone) and 1 655 cm^{-1} (pyrone C=O); all the compounds gave correct elemental analysis; see asterisked footnote to Table 1. ‡ Mass spec.: *m/e* 267 (25%, M^+), 252 (100, $M - CH_3$), 224 (50, $M - CH_3 - CO$), and 196 (25, $M - CH_3 - 2CO$).

TABLE 4

Ethyl 2-methyl-5-oxo-5*H*-[1]benzopyrano[2,3-*b*]pyridine-3-carboxylates *

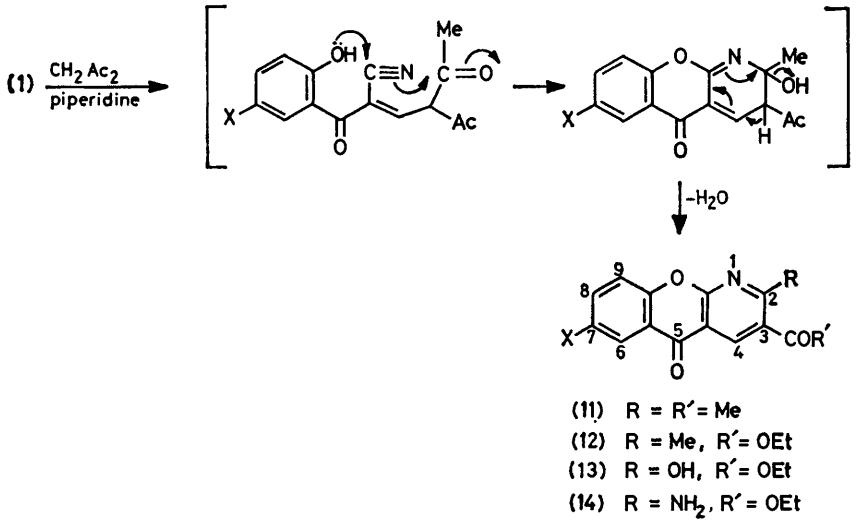
	Mol. formula	Yield (%) from the Nitrile (1)	Yield (%) from the Hydroxime (15)	M.p. (°C)	τ(CDCl$_3$) Pyridine-H(s)	ArH(m)	CH_2CH_3 (q)	2-Methyl (s)	CH_2CH_3 (t)	$ArCH_3$ (s)
(12a)	$C_{16}H_{13}NO_4$	63	49	162	0.80	1.64—2.70	5.60	7.07	8.57	
(12b)	$C_{17}H_{15}NO_4$	63	51	170	0.81	1.62—2.71	5.57	7.07	8.56	7.54
(12c)	$C_{16}H_{12}ClNO_4$	65	47	169	0.83	1.70—2.80	5.60	7.05	8.57	
(12d)	$C_{16}H_{12}BrNO_4$	68	53	194	0.83	1.74—2.78	5.58	7.06	8.55	

* $\nu_{max.}$(Nujol) *ca.* 1 715 (ester carbonyl), and 1 655 cm^{-1} (pyrone carbonyl); all the compounds gave correct elemental analysis; see asterisked footnote to Table 1.

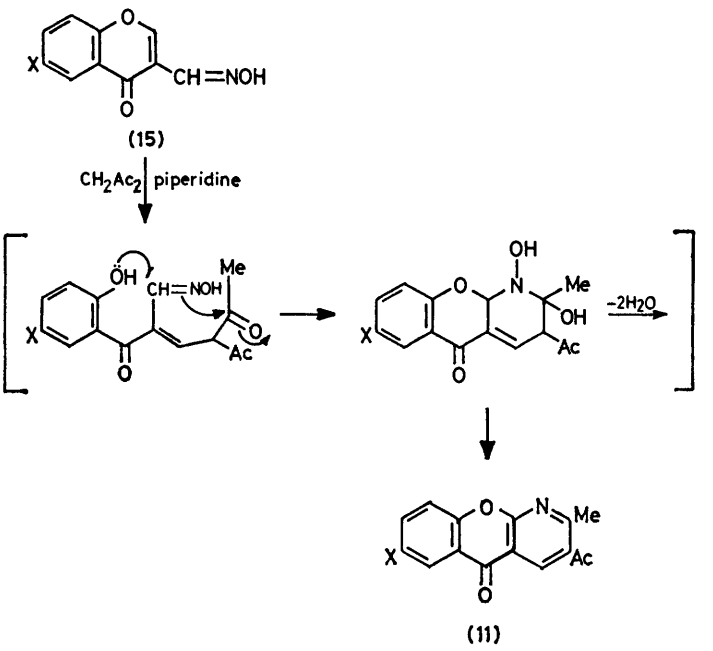
3-nitriles (1) would behave towards reactive methylene compounds. Reaction of the nitrile (1a) with acetylacetone in the presence of piperidine afforded the [1]benzopyrano[2,3-*b*]pyridinone (11a). Structure (11) was assigned to the compound on the basis of spectral evidence (see Experimental section and Table 3), which was corroborated by preparation of an authentic specimen.[11] The mechanism for the formation of the pyridinone (11a) from the nitrile (1a) is depicted in Scheme 2. Acetylacetone undergoes Michael addition to the α,β-unsaturated ketone (1a) with concomitant opening of the pyrone ring giving an intermediate which further undergoes double cyclisation (probably concerted) yielding the pyridine (11a).

Ethyl acetoacetate underwent similar reaction with the chromone-nitriles (1) yielding the 5*H*-[1]benzopyrano[2,3-*b*]pyridine-3-carboxylates (12) (Table 4); the other possible products, namely 3-acetyl-2-hydroxy-5-oxo-5*H*-[1]benzopyrano[2,3-*b*]pyridines were not obtained. Diethyl malonate and ethyl cyanoacetate on condensation with chromone-3-nitriles (1) gave respectively the esters (13) and the corresponding 2-amino-products (14), identical with their respective condensation products (obtained in poor yield) from the appropriate 4*H*-[1]benzopyran-3-carbaldehydes.[11] Identity, though shown for only one representative member (a) of each series (11)—(14) in the Experimental section, is applicable for all other substituted pyridines.

Later, it was found that the oximes (15) on condensation with the reactive methylene compounds considered here gave the same products as were obtained from the corresponding chromone-3-nitriles (1). The mechanism of this condensation, with acetylacetone as a representative case, is depicted in Scheme 3. The chromone-3-nitriles (1) are generally prepared from the oximes (15),[12,13] so the use of the latter (15) for preparing benzopyranopyridines (11)—(14) shortens the route.



SCHEME 2



SCHEME 3

EXPERIMENTAL

I.r. spectra were recorded with a Beckmann IR-20A, n.m.r. spectra with a Varian EM-390 90 MHz, and mass spectra with a Hitachi RMU-6L spectrometer at 70 eV by using a direct inlet system. M.p.s were taken for samples in open capillaries. Light petroleum refers to the fraction b.p. 40—60 °C.

4-Oxo-4H-[1]benzopyran-3-carbonitriles (1a—d).—These compounds were prepared in 70—80% yield by refluxing equimolar quantities of the appropriate 4-oxo-4*H*-[1]benzopyran-3-carbaldehyde [4,12] and hydroxylamine hydrochloride in ethanol in the presence of concentrated hydrochloric acid.[6,13]

3-Amino[1]benzopyrano[4,3-c]pyrazoles (5a—d).—To a refluxing solution of chromone-3-nitrile (1) (0.003 mol) in ethanol (20 ml) was added a mixture of hydrazine hydrochloride (0.32 g, 0.003 mol) and sodium acetate (1.0 g) dissolved in the minimum amount of water. The reaction mixture was further refluxed for 2 h, cooled, and the precipitated pyrazole (5) filtered off and crystallised from dimethylformamide (see Table 1). The pyrazole (5a) had m.p. 169 °C, *m/e* 185 (100%, M^+), 156 (27, $M - N_2H$),[14] and 129 (17, $M - N_2H - HCN$). The pyrazoles (5) on acetylation with acetic anhydride–pyridine afforded the corresponding *acetates* (5; $NHCOCH_3$ in place of NH_2) (Table 1).

3-Amino-4-(2-hydroxybenzoyl)-1-phenylpyrazoles (7; R = Ph).—The experimental procedure for the preparation of the pyrazole (7a) is described here as a representative case. A mixture of chromone-3-carbonitrile (1a) (0.21 g, 0.001 2 mol) and phenylhydrazine (0.13 g, 0.001 2 mol) was refluxed in ethanol (30 ml) for 6 h. A portion of ethanol was distilled off, and the mixture cooled when fine yellow crystals of the *iminohydrazine* (2a; R = Ph) (0.31 g, 91%), m.p. 252 °C (ethanol), $\nu_{max.}$(KBr) 3 210, 1 640, 1 600sh, and 1 530 cm^{-1}, separated out. This iminohydrazine (0.31 g) was refluxed with 20% sulphuric acid (20 ml) and ethanol (15 ml) for 10 h. Most of the ethanol was distilled out and the reaction mixture was then cooled and neutralised with a saturated solution of sodium carbonate. The precipitated solid was collected, dried, and recrystallised from chloroform (charcoal) to yield the *aminopyrazole* (7a; R = Ph) (0.20 g, 65%) as light yellow needles, m.p. 144 °C, *m/e* 279 (100%, M^+), 186 (22, $M - C_6H_4OH$), 159 (90, $M - C_7H_4O_2$), and 121 (52, HOC_6H_4CO). It gave a violet colour with ferric chloride solution. On refluxing with acetic anhydride in the presence of fused sodium acetate it afforded a *triacetate* (7a; R = Ph, OAc in place of OH, and NAc_2 in place of NH_2), m.p. 136—137 °C (chloroform–light petroleum), $\tau(CDCl_3)$ 2.28 (1 H, s, pyrazole-H), 2.30—3.00 (9 H, m, ArH), 7.78 (6 H, s, NAc_2), and 7.87 (3 H, s, Ac). The above triacetate on refluxing in aqueous methanol afforded a *diacetate* (7a; R = Ph, OAc in place of OH, and NHAc in place of NH_2), m.p. 141 °C ($CHCl_3$), identical with that obtained by acylating the aminopyrazole (7a; R = Ph) with acetic anhydride–pyridine. This diacetate had $\tau(CDCl_3)$ 1.97 (1 H, br s, N*H*Ac), 2.26 (1 H, s, pyrazole-H), 2.32—3.16 (9 H, m, ArH), 7.67 (3 H, s, $NHCOCH_3$), and 7.82 (3 H, s, OAc). The other pyrazoles (7b—d) prepared similarly from the nitriles (1b—d) are listed in Table 2.

3-[Hydroxyamino(imino)methyl]-4-oxo-4H-[1]benzopyran (9).—Chromone-3-nitrile (1a) (1.28 g, 0.007 5 mol) and hydroxylamine hydrochloride (0.52 g, 0.007 5 mol) were refluxed together in ethanol (40 ml) for 4 h. A saturated aqueous solution of sodium acetate (2.0 g) was then added to the mixture, which was then further refluxed for 2 h. A portion of alcohol was distilled out, the reaction mixture diluted with water, and the deposited solid was filtered off and crystallised from ethanol to give fine *crystals* of (9a) (0.60 g, 39%), m.p. 263 °C (Found: C, 58.65; H, 4.2; N, 13.5; M^+, 204. $C_{10}H_8N_2O_3$ requires C, 58.82; H, 3.92; N, 13.92%; M^+, 204), $\nu_{max.}$(KBr) 3 335, 3 240, 3 090, 1 662, 1 640, and 1 600 cm^{-1}; $\tau[(CD_3)_2SO]$ −0.50 (1 H, br s, NHO*H*, exchangeable with D_2O), 0.37br (1 H, s, N*H*OH), 0.99 (1 H, br s, =NH, exchangeable), 1.93 (1 H, dd, *J* 8, 2 Hz, ArH *ortho* to carbonyl), and 2.07—2.73 (4 H, m,

ArH + 2-H); *m/e* 204 (27%, M^+), 171 (100, $M - NH_2OH$), and 144 (19, $M - NH_2OH - HCN$).

Compounds (9b—d) prepared similarly in 40—50% yield had m.p.s 265, 278 (decomp.), and 290 °C (decomp.), respectively.

3-Acetyl-2-methyl-[1]*benzopyrano*[2,3-b]*pyridin-5-ones* (11).—Chromone-3-nitrile (1) or chromone-3-carbaldehyde oxime (15) (0.01 mol) and acetylacetone (1.0 g, 0.01 mol) were refluxed together in ethanol (40 ml) containing piperidine (1.0 ml) for 4 h. On cooling and dilution of the reaction mixture with water the *pyridine* (11) was obtained. This was crystallised from chloroform–light petroleum (see Table 3).

Authentic Samples of 3-Acetyl-2-methyl-[1]*benzopyrano*-[2,3-b]*pyridin-5-one* (11a).—A mixture of 2-amino-4-oxo-4*H*-[1]benzopyran-3-carbaldehyde [11] (1.85 g, 0.01 mol), acetylacetone (1.0 g, 0.01 mol), and piperidine (1.0 ml) was refluxed in ethanol (60 ml) for 8 h. Work-up gave the *pyridine* (11a) (0.61 g, 24%), m.p. 218 °C (chloroform–light petroleum).

*Ethyl 2-Methyl-5-oxo-*5H-[1]*benzopyrano*[2,3-b]*pyridine-3-carboxylates* (12).—A mixture of chromone-3-nitrile (1) or chromone-3-carbaldehyde oxime (15) (0.01 mol) and ethyl acetoacetate (1.30 g, 0.01 mol) and piperidine (1—2 ml) was refluxed in ethanol (40 ml) for 4 h, cooled, and diluted with water to give the *product* (12) which was crystallised from chloroform–light petroleum (see Table 4).

When 2-amino-3-formylchromone was similarly condensed with ethyl acetoacetate, the *pyridine* (12a) was obtained in 16% yield.

*Ethyl 2-Hydroxy-5-oxo-*5H-[1]*benzopyrano*[2,3-b]*pyridine-3-carboxylates* (13).—These compounds were prepared in 30—50% yield by refluxing an equimolar mixture of the chromone-nitriles (1) or the oximes (15) and diethyl malonate in ethanol containing piperidine. The *pyridine* (13a) had m.p. and mixed m.p. 238—240 °C (ethanol). The pyridines (13b—d) had m.p.s 244, 285, and 309 °C, respectively.

*Ethyl 2-Amino-5-oxo-*5H-[1]*benzopyrano*[2,3-b]*pyridine-3-carboxylates* (14).—These compounds were prepared in 40—55% yield by the same procedure as described for the pyridines (13) with diethyl malonate replaced by ethyl cyanoacetate. The *pyridine* (14a) had m.p. and mixed m.p. 235—236 °C (ethanol) (Found: C, 63.2; H, 3.9; N, 9.8%. $C_{15}H_{12}N_2O_4$ requires C, 63.36; H, 4.26; N, 9.85%), $\nu_{max.}$(KBr) 1 695 (ester carbonyl) and 1 655 cm^{-1} (pyrone carbonyl). The other pyridines (14b—d) of this series had m.p. 265, 270, and 300—303 °C, respectively.

*Authentic Samples of Ethyl 2-Hydroxy- and 2-Amino-5-oxo-*5H-[1]*benzopyrano*[2,3-b]*pyridine-3-carboxylates*, (13a) *and* (14a).—These compounds were prepared by the same procedure as adopted for the preparation of the authentic sample (11a), acetylacetone being replaced by diethyl malonate and ethyl cyanoacetate, respectively. The *pyridine* (13a) (yield 21%) had m.p. 237—240 °C (lit.,[11] m.p. 239—242 °C) and the *pyridine* (14a) (yield 35%) had m.p. 235—236 °C (lit.,[11] m.p. 235—236 °C).

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