Benzopyrans. Part 42 [1]. Reactions of 4-Oxo-4*H*-1-benzopyran-3-carbaldehyde with Some Active Methylene Compounds in the Presence of Ammonia

Chandra Kanta Ghosh*[a], Anirban Ray[a] and Amarendra Patra[b]

[a] Organic Chemistry Laboratory, Department of Biochemistry, Calcutta University, Calcutta-700019, India
[b] Department of Pure Chemistry, Calcutta University, Calcutta-700009, India

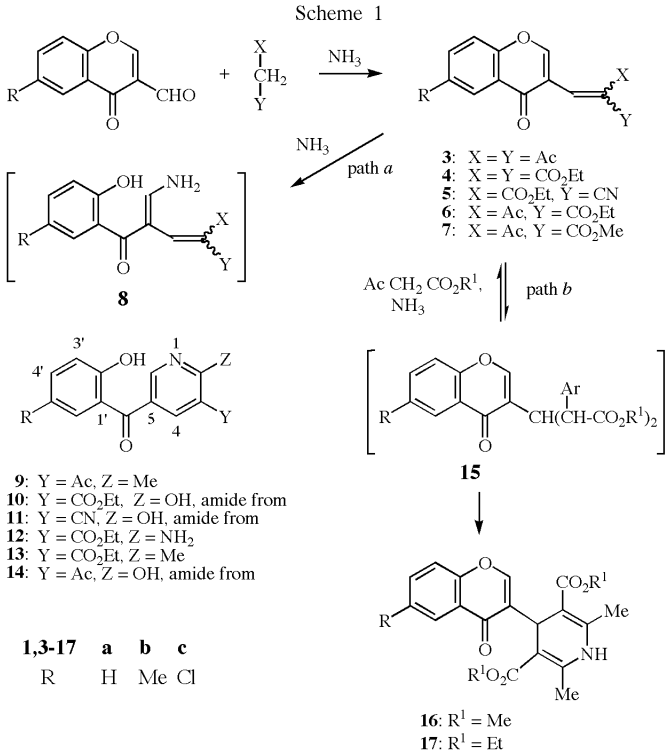
Received January 24, 2001

The title aldehyde **1** in the presence of ammonia gives the pyridine derivatives **9-11** respectively with acetylacetone, diethyl malonate and ethyl cyanoacetate, and ethyl (or methyl)-1-benzopyrano[4,3-*b*]pyridine-3-carboxylate **22** (or **23**) with ethyl (or methyl) acetoacetate. Acetylacetone pretreated with ammonia condenses with **1** giving the fused pyridine **24**. Ammonia converts the ester **6** to the pyridine **13** or **14**. Chromic acid oxidation of **22** and **23** affords the coumarinopyridines **25** and **26**, respectively.

J. Heterocyclic Chem., **38**, 1459 (2001).

The title aldehyde **1** condenses readily in the presence of a base with active methylene compounds [2]. When a mixture of **1**, acetylacetone (**2**, X = Y = Ac) and ammonium acetate is refluxed in ethanol, the initial condensate **3** undergoes nucleophilic attack by ammonia at its pyran 2-position with concomitant opening of the pyran ring, the resultant intermediate **8** (X = Y = Ac) cyclising to the pyridine **9** (Scheme 1 – path *a*) [3]. When refluxed with methyl acetoacetate and liquor ammonia in methanol, the aldehyde function of **1** is involved in the Hantzsch pyridine synthesis so as to form the 1,4-dihydropyridine **16** evidently *via* the Michael adduct **15** (R^1 = Me) of the initial condensate **7** and methyl acetoacetate (Scheme 1 – path *b*) [4]; neither the pyridine **13** (CO_2Me in place of CO_2Et) nor **14** anticipated to arise by the mechanism as depicted in path *a* is formed. These two conflicting reports [3,4] prompted us to record herein our findings on the condensation of the title aldehyde **1** with acetylacetone, diethyl malonate, ethyl cyanoacetate and ethyl as well as methyl acetoacetate in the presence of liquor ammonia.

Scheme 1



The aldehyde **1a** when refluxed with excess acetylacetone in a mixture of ethanol and liquor ammonia afforded the pyridine **9a**. Thus in the presence of either ammonia or ammonium acetate as the source of ammonia, the reaction between **1** and acetylacetone follows the same course as depicted in Scheme 1 – path *a*. Under similar conditions **1** gave **10** with diethyl malonate and **11** (Tables 1 and 2) in complete exclusion of **12** with ethyl cyanoacetate *via* the intermediates **4** and **5**, respectively. It is relevant to mention here that 3-cyanopyridone **11** and the corresponding amide also result from the pyridine mediated condensation of **1** with cyanoacetamide [5]. In contrast, ethyl acetoacetate (**2**, X = Ac, Y = CO_2Et) with **1** under reflux in ethanol containing liquor ammonia gave neither the pyridine **13** (or **14**) (Scheme 1 – path *a*) nor the dihydropyridine **17** (path *b*); the benzopyranopyridine **22** (Tables 3 and 4), identical with that derived from **1** and ethyl β-aminocrotonate (**18**), was the sole product. Formation of 5-hydroxy-5*H*-1-benzopyrano[4,3-*b*]pyridines analogous to **22-24** by treating **1** with various acyclic [6,7] as well as carbocyclic [7] enamines is well known.

Under the present experimental conditions ammonia can only generate from diethyl malonate and ethyl cyanoacetate the corresponding carbanions which condense with the aldehyde **1** and the resultant condensates **4** and **5** on further reaction with ammonia give the pyridines **10** and **11**, respectively (Scheme 1 – path *a*). Under similar conditions ammonia can generate the corresponding carbanions from acetylacetone and ethyl as well as methyl acetoacetate or add to their ketone functionality to form respectively the enamines **20**, **18** and **19** (Scheme 2). The methylene group of acetylacetone being highly active, the generation of the corresponding carbanion by ammonia predominates over the formation of the enamine **20**; hence treatment of **1** with acetylacetone in the presence of ammonia

Table 1

3-Ethoxycarbonyl-, 3-Cyano- and 3-Acetyl-5-(2-hydroxybenzoyl)pyridin-2-one (**10**, **11** and **14**) and Ethyl 2-Methyl-5-(2-hydroxybenzoyl)pyridine-3-carboxylate **13**

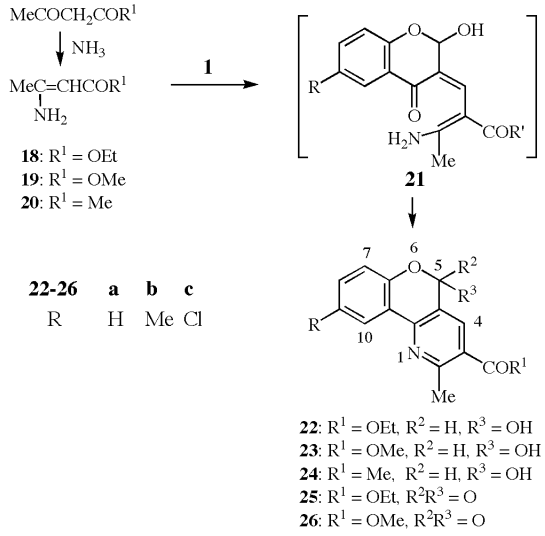
Comp. No (Mol. formula)	Yield (%)	Mp (°C)	Found (Calculated) C	H	N	^{1}H nmr data : δ ppm [a] NH (br s)	OH (br s)	6- or 4-H (d) [b]	4- or 6-H (d) [b]	4´-H	6´-H	5´- and/or 3´-H	OCH_2Me (q)	2-Me (5´-Me) (s)	CH$_2$*Me* (t)
10a ($C_{15}H_{13}NO_5$)	66	154	62.4 (62.7	4.2 4.6	4.7 4.9)	12.58	10.22	8.36	7.90	7.36	7.29	6.91	4.19	—	1.17
10b ($C_{16}H_{15}NO_5$)	72	140	64.1 (63.8	4.8 5.0	4.9 4.6)	12.53	9.98	8.34	7.91	7.16	7.06	6.82	4.18	(2.18)	1.21
10c ($C_{15}H_{12}NClO_5$)	85	178	56.2 (56.0	3.5 3.8	4.5 4.4)	11.59	10.43	8.32	7.93	7.37	7.28	6.93	4.19	—	1.21
11a [c,d] ($C_{13}H_8N_2O_3$)	67	>240	—	—	—	[e]	10.31	8.36	8.02	7.36		6.88	—	—	—
11b ($C_{14}H_{10}N_2O_3$)	76	>240	65.8 (66.1	4.4 4.0	11.3 11.0)	[e]	10.57	8.37	8.06	7.40	7.29	6.94	—	(2.18)	—
11c [c] ($C_{13}H_7N_2ClO_3$)	74	>240	56.5 (56.8	2.9 2.6	10.4 10.2)	[e]	10.04	8.32	8.01	7.17	7.10	6.82	—	—	—
13b ($C_{17}H_{17}NO_4$)	60	91	68.0 (68.2	5.4 5.7	5.0 4.7)	—	11.56	8.83	8.46	7.29	7.25	6.94	4.37	2.89 (2.21)	1.37
13c ($C_{16}H_{14}NClO_4$)	72	98	59.8 (60.1	4.0 4.4	4.6 4.4)	—	11.64	8.86	8.48	7.46		7.03	4.40	2.89	1.39
14a [f] ($C_{14}H_{11}NO_4$)	63	180	65.2 (65.4	4.4 4.3	5.8 5.5)	12.72	10.22	8.32	8.01	7.41	7.33	6.97	—	—	—

[a] Spectra of **10, 11** and **14** were recorded in DMSO-d_6 solution and those of **13** in $CDCl_3$ solution; aromatic protons show normal splitting pattern. [b] $J_{4,6}$ varies from 2.1 to 2.7 Hz. [c] Ir (potassium bromide) for **11a** : 3130 (NH), 3050 (OH), 2200 (CN), 1675 (amide CO); **11c** : 3170 (NH), 3070 (OH), 2230 (CN), 1675 (amide CO), 1630 (ketone CO) cm^{-1}. [d] Lit. [5] mp 266-268 °C (dec.). [e] Not detected. [f] Acetyl protons appear as a singlet at δ 2.56 ppm.

follows the reaction course as depicted in Scheme 1 – path *a* to give the pyridine **9**. In contrast, with ammonia ethyl acetoacetate having a comparatively less active methylene group forms the enamine **18** in preference to the corresponding carbanion. The resultant enamine **18** undergoes Michael addition to the α,β-unsaturated carbonyl functionality of **1** with concomitant opening of the pyran ring [6] and subsequent recyclisation to give the intermediate **21** (R^1 = OEt), the latter ultimately cyclising to **22** (Scheme 2). If ammonia had generated the carbanion from ethyl acetoacetate, **1** would have been converted *via* **6** into the pyridine **13** or **14** (Scheme 1 – path *a*), the latter being indeed obtained by treating the preformed condensate **6** [8,9] with ammonia. Haas *et al*. [7] reported the formation of **13a** (m.p. 66-67°) by refluxing **6a** with liquor ammonia in ethanol. The same procedure gave in our hand **13b** and **13c** respectively from **6b** and **6c** but **14a** from **6a** (Tables 1 and 2).

On subjecting methyl acetoacetate to condensation with **1** in refluxing methanol - liquor ammonia we obtained only **23** (Tables 3 and 4) in contrast to the previously reported [4] exclusive formation of **16**. The fused pyridine **23** arises through condensation of **1** with the enamine **19**, derived *in situ* from methyl acetoacetate and ammonia (Scheme 2). Thus methyl acetoacetate behaves similarly as ethyl acetoacetate towards the aldehyde **1** in the presence of ammonia. In the absence of experimental details [4], it is difficult to pinpoint the reaction conditions under which

Scheme 2



1 with methyl acetoacetate and ammonia gives **16** instead of **23**. The formation of the tricyclic system (**22** and **23**) is independent on the quantity of liquor ammonia used. The presence of hemiacetal functionality in **22** and **23** was confirmed by chromic acid oxidation of these compounds in acetic acid to the coumarinopyridines **25** and **26** (Tables 3 and 4), respectively.

Table 2

^{13}C Nmr Data of the Pyridines **10**, **11**, **13** and **14** [a]

Carbon No./ Type	**10a**	**10b**	**10c**	**11a**	**11b**	**11c**	**13b**	**13c**	**14a**
2	159.1	159.1	159.1	159.0	159.8	159.9	161.2	161.7	160.9
3	119.8	119.8	119.9	103.8	103.3	103.5	128.2	124.0	124.8
4	146.3	146.1	146.5	148.0	148.1	147.9	138.7	138.7	146.1
5	116.0	116.0	115.9	115.7	115.6	115.6	118.6	119.6	116.4
6	143.6	143.6	143.2	146.6	146.6	147.0	151.1	151.1	142.4
1´	125.2	124.0	123.2	124.3	123.9	123.2	125.6	125.8	125.8
2´	155.6	153.6	154.2	155.9	153.7	154.3	162.9	163.6	155.5
3´	116.8	116.7	118.6	116.8	116.7	118.7	118.4	120.4	116.5
4´	133.1	133.7	132.3	133.4	134.0	132.6	137.9	136.8	132.9
5´	119.6	128.3	126.9	119.6	128.3	126.3	131.2	130.5	119.4
6´	130.1	130.0	129.1	130.3	130.2	129.2	132.3	131.6	129.8
Salicyloyl *C*O	191.1	191.2	189.4	190.3	190.3	188.7	198.0	197.3	191.2
2-Me	—	—	—	—	—	—	24.7	24.9	—
3-*C*OR/CN	164.2	164.1	164.1	[b]	116.6	116.6	165.5	165.4	196.2
O*C*H$_2$Me	60.9	60.8	60.9	—	—	—	61.6	61.7	—
OCH$_2$*Me*/CO*Me*	14.4	14.3	14.3	—	—	—	14.1	14.1	30.5
5´-Me	—	20.0	—	—	19.9	—	20.3	—	—

[a] Spectra are recorded in the same solution as stated in the footnote [a] of Table 1. [b] Not detected

Table 3

1-Benzopyrano[4,3-*b*]pyridines **22-26**

Comp. No. (Mol. formula)	Yield (%)	M.p (ºC) (M.p[6])	Found (Calculated) C	H	N	^{1}H nmr data : δ ppm [a] 4-H (s)	10-H	OH (d) [b]	8-H	9- and/or 7-H	5-H (d) [b]	OC*H*$_2$Me (q)	2-Me (CO$_2$Me or COMe) (s)	CH$_2$*Me* (t)
22a [c]	52	190	67.1	5.0	5.2	8.19	8.21	7.67	7.41	7.08	6.49	4.28	2.76	1.29
($C_{16}H_{15}NO_4$)			(67.4	5.3	4.9)									
22b [d]	48	210	68.2	5.3	4.8	8.13	8.01	7.58	7.23	6.93	6.45	4.29	2.77	1.30
($C_{17}H_{17}NO_4$)			(68.2	5.7	4.6)									
22c	57	220	60.4	4.1	4.6	8.23	8.18	7.79	7.49	7.14	6.58	4.34	2.80	1.35
($C_{16}H_{14}NClO_4$)			(60.1	4.4	4.4)									
23a	43	210	66.7	4.5	5.4	8.20	8.25	7.69	7.47	7.13	6.53	—	2.81	—
($C_{15}H_{13}NO_4$)		(237)	(66.4	4.8	5.2)								(3.87)	
23b [d]	46	182	67.1	5.0	5.2	8.12	7.99	7.61	7.20	6.93	6.42	—	2.75	—
($C_{16}H_{15}NO_4$)			(67.4	5.2	4.9)								(3.81)	
23c	47	214	60.2	4.2	4.2	8.13	8.09	7.78	7.41	7.06	6.48	—	2.74	—
($C_{15}H_{12}NClO_4$)		(202)	(58.9	4.0	4.6)								(3.82)	
24a	22	170	70.9	4.8	5.7	8.22	8.20	7.40	7.14-7.03		6.48	—	2.68	—
($C_{15}H_{13}NO_3$)			(70.6	5.1	5.5)								(2.57)	
24b [d]	25	175	71.7	5.2	5.0	7.95	8.10	4.75	7.22	6.98	6.47	—	2.83	—
($C_{16}H_{15}NO_3$)			(71.4	5.6	5.2)								(2.61)	
24c [c]	18	222	62.0	4.5	5.1	8.22	8.12	7.76	7.41	7.08	6.48	—	2.67	—
($C_{15}H_{12}NClO_3$)		(202)	(62.2	4.2	4.8)								(2.56)	
25a [c]	53	168	67.4	4.3	5.1	9.02	8.55	—	7.59	7.36	—	4.43	2.99	1.44
($C_{16}H_{13}NO_4$)			(67.8	4.6	5.0)									
25b [d]	47	192	68.4	5.0	4.3	9.03	8.34	—	7.38	7.23	—	4.43	3.00	1.43
($C_{17}H_{15}NO_4$)			(68.7	5.1	4.7)									
25c	61	168	60.1	3.4	4.2	9.08	8.59	—	7.56	7.34	—	4.45	3.04	1.45
($C_{16}H_{12}NClO_4$)			(60.5	3.8	4.4)									
26a	42	210	67.3	3.7	5.4	9.10	8.63	—	7.63	7.41	—	—	3.04	—
($C_{15}H_{11}NO_4$)			(66.9	4.1	5.2)								(3.97)	
26c	65	197	59.7	3.5	4.9	8.97	8.42	—	7.49	7.24	—	—	3.02	—
($C_{15}H_{10}NClO_4$)			(59.3	3.3	4.6)								(3.96)	

[a] Spectra of **24b, 25** and **26** were recorded in $CDCl_3$ and those of others in DMSO-d_6; aromatic protons show normal splitting. [b] J ~ 6.0 Hz. [c] Ir (potassium bromide) for **22a** : 3130 (OH), 1710 (ester CO) cm^{-1}; **24c** : 3130 (OH), 1675 (CO) cm^{-1}; **25a** : 1735 (lactone CO), 1715 (ester CO) cm^{-1}; **25b**: 1740 (lactone CO), 1720 (ester CO) cm^{-1}. [d] 9-Me protons of **22b, 23b, 24b** and **25b** appear as singlets at δ 2.31, 2.29, 2.39 and 2.46 ppm, respectively.

Table 4

^{13}C Nmr Data of the 1-Benzopyrano[4,3-*b*]pyridines **22-24** in DMSO-d_6 and of **25** and **26** in $CDCl_3$

Carbon No./Type	**22a**	**22b**	**22c**	**23a**	**23b**	**23c**	**24a**	**24c**	**25a**	**25b**	**26c**
2	159.5	159.5	159.7	159.0	159.5	159.7	157.8	158.0	160.4	160.7	159.6
3	124.5	[nd]	124.8	124.1	123.6	124.5	131.4	132.0	125.9	125.6	126.1
4	136.5	136.4	136.7	135.9	136.5	136.7	135.7	135.8	140.7	140.8	140.8
4a	124.0	123.9	124.5	123.5	124.6	124.4	124.1	124.3	114.9	114.8	141.9
5	91.8	91.7	92.0	91.7	91.8	92.1	91.7	92.1	166.8	166.7	167.0
6a	153.8	151.7	152.4	153.5	151.8	152.5	153.6	152.3	153.4	152.8	151.7
7	118.1	117.9	120.2	117.5	117.9	120.1	117.9	120.0	117.2	117.0	118.7
8	132.4	133.1	131.8	131.8	133.0	131.8	132.0	131.5	132.9	134.0	132.9
9	122.7	131.0	126.1	121.5	130.9	126.1	121.9	126.0	124.9	134.7	130.7
10	124.7	124.6	123.7	124.3	124.6	123.7	124.4	123.5	125.4	125.0	124.7
10a	120.7	120.4	122.1	120.3	120.3	122.1	120.7	122.2	118.8	118.2	119.8
10b	148.0	148.2	146.6	147.8	148.3	146.7	147.1	145.7	152.7	151.4	151.6
2-Me	24.3	24.9	24.9	24.2	24.8	24.7	24.7	24.6	25.7	25.8	25.7
3-*C*OR	165.8	165.8	165.6	165.9	166.2	166.0	199.9	199.8	165.0	165.1	165.2
OCH_2Me	61.3	61.3	61.3	—	—	—	—	—	61.7	61.7	—
OCH_2*M*e	14.3	14.3	14.2	—	—	—	—	—	14.2	14.2	—
OMe/Me	—	—	—	51.8	52.4	52.5	29.4	29.4	—	—	52.7
9-Me	—	20.6	—	—	20.5	—	—	—	—	20.9	—

[nd] not detected.

The mechanism as proposed for the formation of **22** and **23** (Scheme 2) envisages the pyranopyridine **24** to arise from the treatment of **1** with the preformed enamine **20**. This contention was proved to be correct when **24** (Tables 3 and 4) was indeed formed by treating **1** with a solution of **20** obtained by prior refluxing an ethanolic solution of acetylacetone with liquor ammonia for 2 hours. In their ^{1}H nmr spectra in perdeuteriodimethyl sulfoxide, 5-hydroxy protons of **22-24** appear as doublets at a very low field region (δ 7.40-7.79) due to some kind of their association with the highly polar solvent whereas that of **24b** in deuteriochloroform appears as a broadened singlet at δ 3.84 ppm (Table 3).

EXPERIMENTAL

Yields and uncorrected melting points of the crystallised products are reported and no attempts were made to optimise the yield. Nmr and ir spectra were recorded on Bruker AM 300L and Perkin-Elmer 782 spectrometers, respectively. Light petroleum refers to the fraction, bp 40-60°.

General Procedure for the Treatment of the Aldehyde **1** with Acetylacetone, Diethyl Malonate and Ethyl Cyanoacetate.

The aldehyde **1** (3 mmoles) and the appropriate active methylene compound **2** (6 mmoles) were dissolved in a mixture of ethanol (25 ml) and liquor ammonia (10 ml) and the reaction mixture gently refluxed for 2 hours. An aliquot (10 ml) of liquor ammonia was added. More alcohol was added, if necessary, to make the reaction mixture homogeneous. After heating the reaction mixture under reflux for further 2 hours, most of the solvent was distilled out and the residue cooled. The deposited solid was collected by filtration and dried. By this procedure **1a** gave **9a** with acetylacetone, the pyridines **10** and **11** (Tables 1 and 2) respectively with diethyl malonate and ethyl cyanoacetate. The pyridine **9a** was crystallised from chloroform-light petroleum, and **10** and **11** from ethanol.

3-Acetyl-5-(2-hydroxybenzoyl)-2-methylpyridine (**9a**).

This compound was obtained from **1a** and acetylacetone in 64% yield as light yellow crystals, mp and mixed [3] mp 135°; ^{13}C nmr : δ 199.2, 198.2, 163.2, 161.4, 131.0, 125.0, 123.3 (s), 150.7, 137.0, 136.9, 132.6, 119.2, 118.9 (d), 29.2, 24.6 (q).

Treatment of the Acrylic Ester **6** with Ammonia.

A solution of the ester **6** (0.5 mmoles) in ethanol (20 ml) and liquor ammonia (10 ml) was heated under reflux for 3 hours. The reaction mixture was then concentrated, diluted with water and extracted with chloroform. The organic extract was dried over anhydrous sodium sulphate, concentrated and cooled. The precipitated solid was isolated by filtration and crystallised from chloroform-light petroleum to give the product as shining yellow crystals. This procedure gave 3-acetyl-5-(2-hydroxybenzoyl)pyridin-2-one (**14a**) from **6a** but ethyl 2-methyl-5-(2-hydroxy-5-methylbenzoyl)- and 2-methyl-5-(5-chloro-2-hydroxybenzoyl)-pyridine-3-carboxylate **13b** and **13c** from **6b** and **6c**, respectively. The characterisation data of the above products are given Tables 1 and 2.

Ethyl 5-hydroxy-2-methyl-5*H*[1]benzopyrano[4,3-*b*]pyridine-3-carboxylate (**22**).

The aldehyde **1a** (348 mg, 2 mmoles) and ethyl acetoacetate (520 mg, 4 mmoles) were refluxed together in ethanol (25 ml) containing liquor ammonia (10 ml) for 4 hours. The reaction mixture was concentrated, diluted with water, cooled and the deposited solid isolated by filtration and crystallised from dimethylformamide - water to give the title pyranopyridine **22a**. The mother liquor after isolation of **22a** from the reaction mixture was extracted with chloroform. This extract after usual work-up did not produce any solid compound. 9-Methyl and 9-chloro substituted analogues of **22a** were similarly prepared from **6b** and **6c**, respectively (Tables 3 and 4).

The Pyranopyridine **22a** from **1a** and Ethyl β-aminocrotonate (**18**).

A solution of **1a** (348 mg, 2 mmoles) and **18** (323 mg, 2.5 mmoles) in ethanol (25 ml) was heated under reflux for 3 hours. Usual work-up of the reaction mixture gave **22a** (342 mg, 60%) identical (mp, mixed mp and superimposable ir) with that previously obtained by treating **1a** with ethyl acetoacetate and ammonia.

Methyl 5-Hydroxy-2-methyl-5*H*-[1]benzopyrano[4,3-*b*]pyridine-3-carboxylate (**23**).

The substrate **1** dissolved in methanol was treated with methyl acetoacetate similarly as previously described for the treatment of **1** with ethyl acetoacetate in the presence of ammonia to afford the ester **23**, the characterisation data of the product crystallised from dimethylformamide-water being presented in Tables 3 and 4.

3-Acetyl-5-hydroxy-2-methyl-5*H*-[1]benzopyrano[4,3-*b*]pyridine (**24**).

A solution of acetylacetone (~ 1.0 g, 10 mmoles) and liquor ammonia (15 ml) in ethanol (25 ml) was refluxed for 2 hours. Then **1a** (522 mg, 3 mmoles) dissolved in ethanol (25 ml) was added to the above solution. The reaction mixture was heated under reflux for 3 hours, concentrated by distilling out most of the alcohol, diluted with water and cooled. The deposited solid was isolated by filtration and crystallised from dimethylformamide - water to afford the title pyridine **24a**, its two other analogues **24b** and **24c** (Tables 3 and 4) being similarly prepared from **1b** and **1c**, respectively.

General Procedure for Oxidation of the Pyridines **22** and **23**.

Chromium trioxide (~ 30 mg) was added to **22** or **23** (70-100 mg) dissolved in minimum amount of glacial acetic acid. The reaction mixture was kept at room temperature for 6-8 hours and then diluted with water. The deposited solid was collected by filtration, washed with water, dried and crystallised from chloroform. By this procedure the pyridines **22** and **23** were oxidised respectively to ethyl and methyl 2-methyl-5-oxo-5*H*[1]benzopyrano[4,3-*b*]pyridine-3-carboxylate **25** and **26** (Tables 3 and 4).

Acknowledgement.

Financial assistance from CSIR, New Delhi [Scheme No. 01(1622)/EMR-II] is duly acknowledged.

REFERENCES AND NOTES

[1] Part 41 : C. K. Ghosh, S. Bhattacharyya and A. Patra, *J. Chem. Soc., Perkin Trans. 1*, 3005 (1999).

[2] For reviews see C. K. Ghosh, *J. Heterocyclic Chem*., **20**, 1437 (1983); G. Sabitha, *Aldrichimica Acta*, **29**, 15 (1996).

[3] C. K. Ghosh and S. Khan, *Synthesis*, 903 (1981).

[4] M. Satyanarayana Reddy, G. L. David Krupadanam and G. Srimannarayana, *Indian J. Chem.*, **29B**, 978 (1990).

[5] A. Nohara, T. Ishiguro and Y. Sanno, *Tetrahedron Lett*., 1183 (1974).

[6] D. Heber, *Synthesis*, 691 (1978); *Pharm. Z.*, **123**, 1650 (1978).

[7] G. Haas, J. L. Stanton, A. von Sprecher and P. Wenk, *J. Heterocyclic Chem*., **18**, 607 (1981).

[8] W. D. Jones and W. L. Albrecht, *J. Org. Chem.*, **41**, 706 (1976).

[9] C. K. Ghosh, C. Bandyopadhyay, S. Biswas and A. K. Chakravarty, *Indian J. Chem*., **29B**, 814 (1990); C. K. Ghosh, S. Sahana and C. Bandyopadhyay, *Indian J. Chem*., **32B**, 624 (1993).