Heterocyclic Systems; 11. A Novel Transformation of 4-Oxo-4*H*-1-benzopyran-3-carboxaldehydes to 3-Acetyl-5-(2-hydroxybenzoyl)-2-methylpyridines

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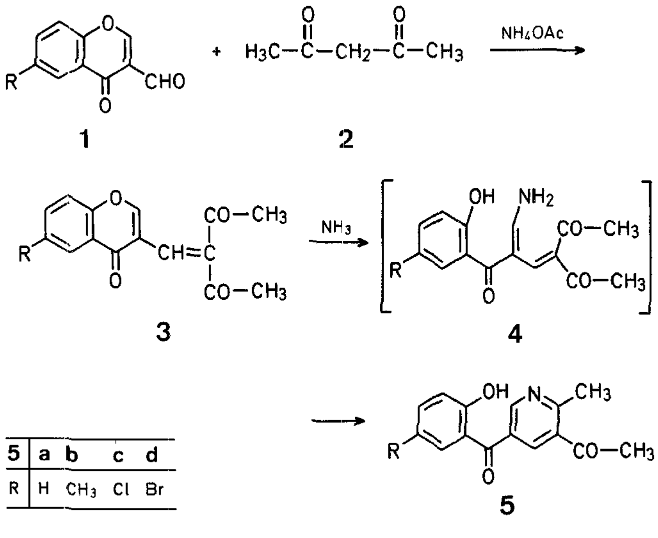
4-Oxo-4*H*-1-benzopyran-3-carboxaldehydes **1** have been utilised to construct various heterocycles[2,3]. We now report a novel one-step transformation of **1** to the titled pyridines **5**.

Refluxing a mixture of **1** (1 equiv.), acetylacetone (**2**; 1 equiv.) and ammonium acetate (4-5 equiv.) in ethanol for 4 h furnished the pyridines **5** (Table) in 20-30% yield. The mechanism for the formation of **5** involves the initial condensation of **1** with acetylacetone (**2**) in presence of the basic catalyst ammonium acetate to afford the 3-methylenepentane-2,4-dione **3**, the pyrone ring of which is cleaved at C-2 by ammonia, the resultant enaminoketone **4** (non-isolable) undergoing cyclisation to **5**. The cleavage at C-2 of the pyrone ring of chromones by amines[4], and particularly that of **3** by a carbanion[5] are well known. Evidence supporting the intermediacy of **3** in the conversion of **1** to **5** is offered by condensation of **3a** with ammonium acetate to form **5a** in 58% yield.



5	a	b	c	d
R	H	CH_3	Cl	Br

3-Acetyl-5-(2-hydroxybenzoyl)-2-methylpyridines (5); General Procedure:

A mixture of 3-formylchromone **1** *(2 mmol), acetylacetone (***2***; 200 mg,* 2 mmol), ammonium acetate (616 mg, 8 mmol), and ethanol (25 ml) is refluxed for 4 h. A portion of the alcohol is evaporated, the reaction mixture is diluted with water (30 ml) and extracted with chloroform (2 × 25 ml). The extract is thoroughly washed with water (3 × 10 ml), dried with anhydrous sodium sulfate, charcoalised, and filtered. The filtrate, on concentration, gives the pyridine **5** which may be further recrystallised from chloroform/light petroleum ether (Table).

3-[(4-Oxo-4*H*-1-benzopyran-3-yl)-methylene]pentan-2,4-dione (3a):

A mixture of **1a** (1.74 g, 10 mmol) and acetylacetone (**2**; 1.0 g, 10 mmol) is refluxed in ethanol (30 ml) containing pyridine (2 drops) for 3 h. On concentrating the reaction mixture, the chromone derivative **3a** is obtained; yield: 2.04 g (80%); m.p. 170 °C (Lit.[5], m.p. 168-170 °C).

Pyridine 5a from 3a:

The chromone **3a** (0.256 g, 1 mmol) and ammonium acetate (0.231 g, 3 mmol) are refluxed together in acetic acid (5 ml) or ethanol (15 ml) for 3 h, then cooled, and diluted with water (30 ml). The deposited solid is filtered, dried, and crystallised with charcoal from chloroform/light petroleum ether to afford **5a**; yield: 0.148 g (58%).

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Table. 3-Acetyl-5-(2-hydroxybenzoyl)-2-methylpyridines **5**

Compound	Yield[a] [%]	M.p.[a] [°C]	Molecular Formula[b]	^1H-N.M.R. ($CDCl_3$/TMS) δ [ppm]
5a	23	135°	$C_{15}H_{13}NO_3$ (255.3)	2.63 (s, 3H); 2.83 (s, 3H); 6.8-7.6 (m, 4H); 8.33 (d, 1H); 8.96 (d, 1H); 11.76 (s, 1H)[c]
5b	22	115°	$C_{16}H_{15}NO_3$ (269.3)	2.27 (s, 3H); 2.65 (s, 3H); 2.83 (s, 3H); 6.9-7.3 (m, 3H); 8.29 (d, 1H); 8.86 (d, 1H); 11.55 (s, 1H)[c]
5c	20	112°	$C_{15}H_{12}ClNO_3$ (289.7)	2.66 (s, 3H); 2.83 (s, 3H); 7.0-7.6 (m, 3H); 8.36 (d, 1H); 8.96 (d, 1H); 11.66 (s, 1H)[c]
5d	29	110°	$C_{15}H_{12}BrNO_3$ (334.2)	2.70 (s, 3H); 2.90 (s, 3H); 7.0-7.8 (m, 3H); 8.40 (d, 1H); 9.00 (d, 1H); 11.70 (s, 1H)[c]

[a] Yield and m.p. of pure, recrystallised (chloroform/light petroleum ether) products are recorded; yield not optimised.
[b] The microanalyses were in satisfactory agreement with the calculated values (C ±0.28, H ±0.24, N ±0.21).
[c] Exchangeable with D_2O.

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