Synthesis of 2*H*-Chromeno[4,3-*b*]pyridine-2,5(1*H*)-diones and Related Heterocycles *via* the Erlenmeyer-Ploechl Reaction

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Received November 17, 2004

1,2-Dihydro-5*H*-[1]benzopyrano[4,3-*b*]pyridine-2,5-diones **4a-j** were synthesized from 4-alkylaminocoumarin-3-carbaldehydes **1** and 5(4*H*)-oxazolinones (azalactones) derived from *N*-acetylglycine (**2a**) and hippuric acid (**2b**). The intermediates **3** (**3j** isolated only) underwent spontaneous recyclization *via* opening of the azalactone and successive formation of the fused 2-pyridones **4**. Attempts to synthesize the selected 2*H*-chromeno[3,4-*f*]-1,7-naphthyridine **6** by Vilsmeier reaction of **4e** failed. Instead, *N*-deacetylation took place, followed by formylation of the amino group to the formamidine **7a**. In addition, pyranopyridine **9a** was obtained by condensation of the 3-formyl-2-pyridone **8** with the azalactone derived from **2a** and acetic anhydride.

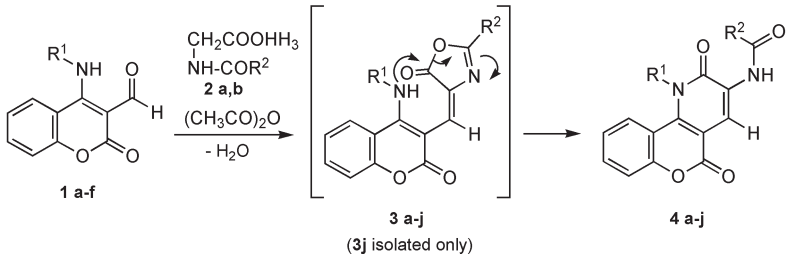
J. Heterocyclic Chem., **42**, 857 (2005).

In continuation of our synthetic studies concerning the reactive behavior of 4-chloro- and 4-aminocoumarin-3-carbaldehydes as useful starting compounds for the preparation of annulated *N*-heterocycles [1-3], we now tried to apply the Erlenmeyer-Ploechl azalactone synthesis [4-6]. This latter reaction has often been used with the aim of synthesizing fused pyran-2-ones by combining condensation with lactonization. For this reason simple one-pot procedures have been developed using 1,3-dicarbonyl compounds, one-carbon synthons (triethyl orthoformate or *N,N*-dimethylformamide-dimethylacetal), *N*-acylglycines and a large excess of acetic anhydride [7-14]. In most cases sodium acetate has been used as a catalyst [4,6]. Another approach for these reactions made use of a two-step synthesis incorporating the one-carbon synthon either in the CH-acidic compound [15,16] or in the azalactone [17-20]. Ring opening reactions of the latter gave rise to derivatives of β-amino-α,β-dehydro-α-amino acids, used as versatile reagents for the synthesis of fused heterocyclic systems [21-23].

Our present study was provoked by the paper of Mulwad and Shirodkar [16] describing the condensation of 3-formyl-4-hydroxycoumarin with hippuric acid or *N*-acetylglycine to form 3-acylamino-2,5-dioxopyrano[3,2-*c*]benzopyrans of type **5** (Scheme 2). In order to apply this method for the synthesis of pyridine ring containing systems, the condensation was first carried out by using 4-alkylaminocoumarin-3-carbaldehydes **1** [2] as starting compounds. As considered, the 2*H*-chromeno[4,3-*b*]pyridine-2,5(1*H*)-diones **4** were readily accessible from **1** and *N*-acetylglycine (**2a**) or hippuric acid (**2b**) (Scheme 1).

To the best of our knowledge the Erlenmeyer-Ploechl-Reaction has never been formerly used for the synthesis of annulated pyridines of the type **4** described above. It is noteworthy to point out that, with the exception of **3j**, the intermediates **3** could not be isolated and underwent spontaneous recyclization *via* opening of the azalactone ring and formation of the fused 2(1*H*)-pyridone ring. The ^{1}H nmr spectra of compounds **4a-j** showed singlet at δ 8.84-9.04 ppm due to the proton at C-4 and singlet at δ 9.58-

Scheme 1

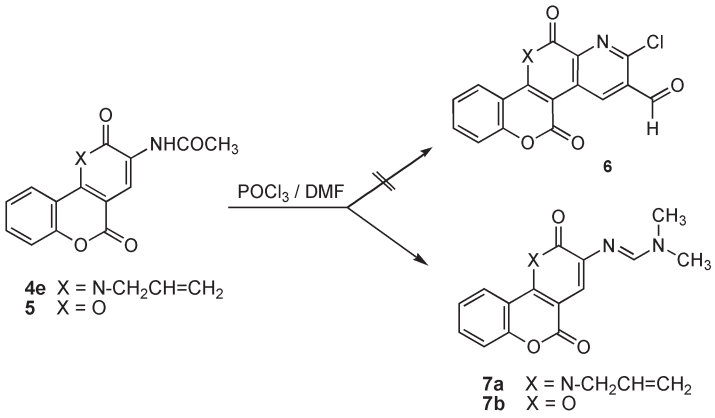


1 - 4	a	b	c	d	e	f	g	h	i	j
R^1	CH_3	C_2H_5	n-C_3H_7	n-C_4H_9	CH_2=$CHCH_2$	$C_6H_5CH_2$	CH_3	C_2H_5	CH_2=$CHCH_2$	$C_6H_5CH_2$
R^2	CH_3	CH_3	CH_3	CH_3	CH_3	CH_3	C_6H_5	C_6H_5	C_6H_5	C_6H_5

9.79 due to the exocyclic *N*-proton. Furthermore, the ^{1}H nmr spectra of compounds **4a-j** showed absence of any signal due to an aldehyde proton. The structure of the novel pyridone derivatives **4a-j** was also supported by the appearance of new amide/lactam carbonyl bands in the range 1619-1675 cm^{-1} in their ir spectra. The molecular masses of all new products were confirmed by means of their ms spectra.

We also succeeded in performing the Erlenmeyer-Ploechl condensation of the 4-hydroxy-3-formyl-2-pyridone **8** [3] with *N*-acetylglycine (**2a**) in the presence of acetic anhydride and thus, the pyranopridine **9a** was prepared in 23% yield of pure product. The ir and ^{1}H nmr spectral properties of **9a** are in good agreement with those of compounds **4a-j** and **5**.

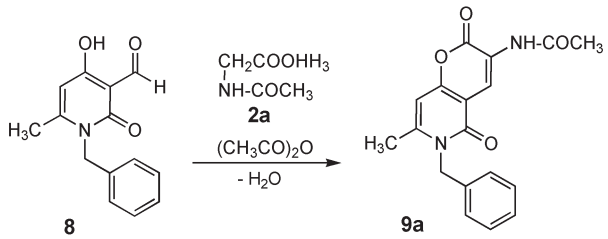
Scheme 2



Initially, we carried out our preliminary trials in the presence of sodium acetate, as recommended in the literature [4-6], but the reaction seemed to proceed more complex, accompanied by partial decomposition, and the isolation of any pure product from the dark-colored reaction mixture was rather difficult.

Our attempts to synthesize 2*H*-chromeno[3,4-*f*]-1,7-naphthyridines of type **6** (X = N; Scheme 2) by a Vilsmeier reaction of **4e**, according to the approach of Meth-Cohn *et al*. [24], failed. Instead, *N*-deacetylation and subsequent formylation of the amino group occurred to give the formamidine **7a**. Similarly, as depicted in Scheme 2, the Vilsmeier formylation of the known compound **5** [13], obtained from 4-hydroxycoumarin-3-carbaldehyde as described in the literature [16], afforded the corresponding oxygen analogue **7b** thus reproducing the same unusual behaviour of **4e**.

Scheme 3



Acknowledgments are due to Dr. U. Girreser (Pharmaceutical Institute, University of Kiel, Germany) for recording the nmr spectra and to the staff of the MS and Microanalytical Laboratory of the Institute of Organic Chemistry, University of Stuttgart, Germany (Head: Dr. J. Opitz).

EXPERIMENTAL

General.

Melting points are uncorrected and were determined with a Büchi 510 melting point apparatus (Switzerland). ^{1}H and ^{13}C nmr spectra (TMS as internal standard) were recorded on a Bruker ARX 300 spectrometer (δ units are given in ppm, J in Hz). The ir spectra were measured as Nujol mull on a Shimadzu FTIR 8100 spectrophotometer (Japan). Reactions and products were monitored by means of thin-layer chromatography using Kieselgel GF$_{254}$ (Merck, Germany) pre-coated aluminium sheets (50 x 100 mm; layer thickness 0.2 mm), eluted by cyclohexane-chloroform-acetic acid 5:5:2 (vol. parts). Yields of recrystalized, tlc pure products are given.

General Procedure for the Preparation of Compounds **4a-j**.

Starting compound **1** (4.8 mmoles) and *N*-acetylglycine **2a** or hippuric acid **2b** (5.8 mmoles) were heated at reflux in acetic anhydride (15 ml; 15.9 mmoles) for a period of time given below for each product. The reaction mixture was allowed to cool for 16 h at 5-8 °C. The separated crystalline product **4a-j** was collected by filtration, washed with cold ethanol and recrystallized from the solvent given below for each product. When preparing **4j** the intermediate **3j** could be isolated as a by-product.

N-(1-Methyl-2,5-dioxo-1,5-dihydro-2*H*-chromeno[4,3-*b*]pyridin-3-yl)acetamide (**4a**).

This compound was obtained after 9 h reflux in 44 % yield as pale yellow crystals, mp > 350° (butanol-DMF 10:1); ir: NH 3335, CO lactone 1717, CO amide 1635, 1622, 1506, 1294, 1261, 1189, 773, 763 cm^{-1}; ^1H nmr (DMSO-d_6): δ 2.20 (s, 3H, CH_3 of acetyl), 3.99 (s, 3H, CH_3N), 7.39-7.55 (m, 2H, 7-$H_{arom.}$, 9-$H_{arom.}$), 7.68 (dd, 1H, 8-$H_{arom.}$, ^3J = 8.3 Hz, ^4J = 1.3 Hz), 8.36 (dd, 1H, 10-$H_{arom.}$, ^3J = 8.4 Hz, ^4J = 1.1 Hz), 8.85 (s, 1H, 4-H), 9.76 (s, 1H, NH); ms: m/z 284 (37; M^+), 243 (14), 242 (100), 214 (6), 200 (7), 186 (2), 171 (2).

Anal. Calcd. for $C_{15}H_{12}N_2O_4$ (284.27): C, 63.38; H, 4.25; N, 9.85. Found: C, 63.32; H, 4.29; N, 9.81.

N-(1-Ethyl-2,5-dioxo-1,5-dihydro-2*H*-chromeno[4,3-*b*]pyridin-3-yl)acetamide (**4b**).

This compound was obtained after 6 h reflux with 56 % yield as yellow needles, mp 283-285° (butanol); ir: NH 3361, CO lactone 1727, 1684w, CO amide 1646, 1630, 1605, 1581, 1234, 1188, 1115, 929, 776, 762 cm^{-1}; ^1H nmr (DMSO-d_6): δ 1.63 (t, 3H, CH_3 of ethyl, ^3J = 6.9 Hz), 2.19 (s, 3H, CH_3 of acetyl), 4.46 (q, 2H, CH_2N, ^3J = 6.9 Hz), 7.45-7.54 (m, 2H, 7-$H_{arom.}$, 9-$H_{arom.}$), 7.69 (dd, 1H, 8-$H_{arom.}$), 8.12 (d, 1H, 10-$H_{arom.}$, ^3J = 8.0 Hz), 8.85 (s, 1H, 4-H), 9.71 (s, 1H, NH); ms: m/z 298 (64; M^+), 257 (16), 256 (100), 228 (56), 200 (12), 172 (3).

Anal. Calcd. for $C_{16}H_{14}N_2O_4$ (298.29): C, 64.42; H, 4.73; N, 9.39. Found: C, 64.52; H, 4.78; N, 9.32.

N-(1-Propyl-2,5-dioxo-1,5-dihydro-2*H*-chromeno[4,3-*b*]pyridin-3-yl)acetamide (**4c**).

This compound was obtained after 7 h reflux in 34 % yield as pale yellow crystals, mp 256-258° (ethanol); ir: NH 3356, CO lactone 1723, CO amide 1640, 1619, 1506, 1229, 1189 cm^{-1}; ^1H nmr (DMSO-d_6): δ 1.02 (t, 3H, CH_3 of propyl, ^3J = 7.1 Hz), 2.00 (m, 2H, CH_2 of propyl), 2.19 (s, 3H, CH_3 of acetyl), 4.37 (m, 2H, CH_2N), 7.47-7.53 (m, 2H, 7-$H_{arom.}$, 9-$H_{arom.}$), 7.65-7.71 (m, 1H, 8-$H_{arom.}$), 8.02 (d, 1H, 10-$H_{arom.}$, ^3J = 8.5 Hz), 8.84 (s, 1H, 4-H), 9.70 (s, 1H, NH); ^{13}C nmr (DMSO-d_6): δ 10.5 (CH_3), 21.0 (CH_2), 23.9 (CH_3), 50.3 (CH_2), 118.0 ($C_{arom.}$), 124.6 ($C_{arom.}$), 125.0 ($C_{arom.}$), 131.6 ($C_{arom.}$), the rest of signals are unobservable because of poor solubility; ms: m/z 312 (66; M^+), 270 (74), 228 (100), 172 (3).

A6nal. Calcd. for $C_{17}H_{16}N_2O_4$ (312.32): C, 65.38; H, 5.16; N, 8.97. Found: C, 65.19; H, 5.19; N, 8.83.

N-(1-Butyl-2,5-dioxo-1,5-dihydro-2*H*-chromeno[4,3-*b*]pyridin-3-yl)acetamide (**4d**).

This compound was obtained after 8 h reflux in 24 % yield as yellow needles, mp 207-209° (butanol); ir: NH 3355, CO lactone 1728, CO amide 1641, CO lactam 1620, 1505, 1415, 1226, 1082, 762 cm^{-1}; ^1H nmr (DMSO-d_6): δ 0.98 (t, 3H, CH_3), 1.47 (m, 2H, CH_2), 1.98 (m, 2H, CH_2), 2.20 (s, 3H, CH_3CO), 4.45 (m, 2H, N-CH_2), 7.45-7.75 (m, 3$H_{arom.}$, 7-H, 8-H, 9-H), 8.08 (d, 1$H_{arom.}$, 10-H), 8.86 (s, 1H, 4-H), 9.72 (s, 1H, NH); ^{13}C nmr (DMSO-d_6): δ 13.4 (DEPT: CH_3), 19.2 (DEPT: CH_2), 23.9 (DEPT: CH_3), 29.6 (DEPT: CH_2), 48.6 (DEPT: N-CH_2), 118.0 (DEPT: $C_{arom.}$-H), 124.5 (DEPT: $C_{arom.}$-H), 125.1 (DEPT: $C_{arom.}$-H), 132.0 (DEPT: $C_{arom.}$-H), 170.0 (C=O lactone), the rest of signals unobservable because of poor solubility; ms: m/z 326 (M^+; 58), 284 (61), 267 (18), 242 (4), 228 (100) , 200 (10).

Anal. Calcd. for $C_{18}H_{18}N_2O_4$ (326.35): C, 66.25; H, 5.56; N, 8.58. Found: C, 66.04; H, 5.61; N, 8.34.

N-(1-Allyl-2,5-dioxo-1,5-dihydro-2*H*-chromeno[4,3-*b*]pyridin-3-yl)acetamide (**4e**).

This compound was obtained after 7 h reflux in 34 % yield as yellow crystals, mp 238-240° (butanol); ir: NH 3325, 3114, CO lactone 1727, CO amide 1641, 1619, 1506, 1237, 1185 cm^{-1}; ^1H nmr (DMSO-d_6):_ δ 2.19 (s, 3H, CH_3), 5.02 (d, 2H, CH_2N, ^3J = 1.5 Hz), 5.19 (d, 1H, H^A from CH_2=CH-CH_2, ^3J = 17.8 Hz, $^2J \approx$ 0 Hz), 5.36 (d, 1H, H^B from CH_2=CH-CH_2, ^3J = 11.8 Hz, $^2J \approx 0$ Hz), 6.30 (qt, 1H, CH_2=C*H*-CH_2), 7.41 (td, 1$H_{arom.}$, 9-H), 7.52 (dd, 1$H_{arom.}$, 7-H), 7.66 (td, 1$H_{arom.}$, 8-H), 8.17 (dd, 1$H_{arom.}$, 10-H), 8.90 (s, 1H, 4-H), 9.79 (s, 1H, NH); ms: m/z 310 (100; M^+), 268 (99), 253 (8), 239 (7), 227 (54), 200 (77).

Anal. Calcd. for $C_{17}H_{14}N_2O_4$ (310.34): C, 65.80; H, 4.55; N, 9.03. Found: C, 65.81; H, 4.63; N, 9.07.

N-(1-Benzyl-2,5-dioxo-1,5-dihydro-2*H*-chromeno[4,3-*b*]-pyridin-3-yl)acetamide (**4f**).

This compound was obtained after 8 h reflux in 30 % yield as yellow crystals, mp 275-277° (butanol); ir: NH 3363, CO lactone 1722, CO amide 1647, CO lactam 1623, 1606, 1507, 1496, 1414 cm^{-1}; ^1H nmr (DMSO-d_6): δ 2.18 (s, 3H, CH_3), 5.68 (s, 2H, N-CH_2), 7.14-7.62 (m, 8$H_{arom.}$, phenyl and 7-H, 8-H, 9-H), 7.79 (q, 1$H_{arom.}$, 10-H, ^3J = 8.4 Hz, ^4J = 1.0 Hz), 8.93 (s, 1H, 4-H), 9.72 (s, 1H, NH); ^{13}C nmr (75.5 MHz; DMSO-d_6): δ 23.9 (DEPT: CH_3), 52.7 (DEPT: CH_2), 105.4, 113.4, 117.9 (DEPT: $C_{arom.}$-H), 118.0, 118.4 (DEPT: $C_{arom.}$-H), 124.1 (DEPT: $C_{arom.}$-H), 124.9 (DEPT: $C_{arom.}$-H), 125.5 (DEPT: 2$C_{arom.}$-H), 127.2 (DEPT: $C_{arom.}$-H), 128.7 (DEPT: 2$C_{arom.}$-H), 128.8, 131.7 (DEPT: $C_{arom.}$-H), 141.6 (C-2), 151.6 (C-3), 158.7 (C=O amide), 159.1 (C=O amide), 170.1 (C=O lactone); ms: m/z 360 (M^+, 29), 318 (17), 227 (1), 200 (4), 91 (100; $C_6H_5CH_2^+$).

Anal. Calcd. for $C_{21}H_{16}N_2O_4$ (360.36): C, 69.99; H, 4.48; N, 7.77. Found: C, 69.73; H, 4.58; N, 7.70.

N-(1-Methyl-2,5-dioxo-1,5-dihydro-2*H*-chromeno[4,3-*b*]-pyridin-3-yl)benzamide (**4g**).

This compound was obtained in 46 % yield as colorless crystals, mp 259-261° (butanol); ir: NH 3383, CO lactone 1724, CO amide 1675, CO lactam 1629, 1601, 963, 758 cm^{-1}; ^1H nmr (DMSO-d_6): δ 4.04 (s, 3H, N-CH_3), 7.42-7.74 (m, 6$H_{arom.}$, phenyl and 8-H), 7.96 (m, 2$H_{arom.}$, 7-H and 9-H), 8.40 (dd, 1H, 10-H, $^3J \approx$ 7.5 Hz), 8.90 (s, 1H, 4-H), 9.58 (s, 1H, NH); ms: m/z 347 (35), 346 (35; M^+), 106 (7), 105 (100; $C_6H_5CO^+$), 77 (30).

Anal. Calcd. for $C_{20}H_{14}N_2O_4$ (346.34): C, 69.36; H, 4.07; N, 8.09. Found: C, 69.11; H, 4.07; N, 8.10.

N-(1-Ethyl-2,5-dioxo-1,5-dihydro-2*H*-chromeno[4,3-*b*]pyridin-3-yl)benzamide (**4h**).

This compound was obtained after 7 h at 100° in 31 % yield as colorless needles, mp 228-230° (ethanol); ir: NH 3375, CO lactone 1723, CO amide 1646, CO lactam 1628, 1506 cm^{-1}; ^1H nmr (DMSO-d_6): δ 1.66 (t, 3H, CH_3), 4.52 (q, 2H, N-CH_2), 7.5-7.8 (m, 6$H_{arom.}$, phenyl protons and 8-H), 7.97 (m, 2$H_{arom.}$, 7-H and 9-H), 8.16 (d, 1$H_{arom.}$, 10-H), 8.94 (s, 1H, 4-H), 9.58 (s, 1H, NH); ^{13}C nmr (75.5 MHz; DMSO-d_6): δ 13.7 (CH_3), 45.0 (CH_2), 127.3 ($C_{arom.}$), 128.8 ($C_{arom.}$), the rest of signals unobservable because of poor solubility; ms: m/z 360 (44; M^+), 256 (1), 228 (2), 200 (1), 105 (100; $C_6H_5CO^+$), 77 (22).

Anal. Calcd. for $C_{21}H_{16}N_2O_4$ (360.36): C, 69.99; H, 4.48; N, 7.77. Found: C, 69.83; H, 4.49; N, 7.68.

N-(1-Allyl-2,5-dioxo-1,5-dihydro-2*H*-chromeno[4,3-*b*]pyridin-3-yl)benzamide (**4i**).

This compound was obtained after 10 h reflux in 33 % yield as colorless crystals (butanol), mp 234-236°; ir: NH 3379, CO lactone 1722, 1717, CO amide 1646, CO lactam 1625, 1599, 1515, 1489, 1454, 1445, 1442, 1379 cm^{-1}; ^1H nmr (DMSO-d_6): δ 5.06 (m, 2H, allyl-CH_2N), 5.23 (d, 1H, H^A from CH_2=CH-CH$_2$, ^3J = 17.5 Hz, $^2J \approx 0$ Hz), 5.38 (d, 1H, H^B from CH_2=CH-CH$_2$, ^3J = 10.8 Hz, $^2J \approx 0$ Hz), 6.22-6.40 (m, 1H, CH$_2$=C*H*-CH$_2$), 7.43 (m, 1H$_{arom.}$, 8-H), 7.51-7.74 (m, 5H$_{arom.}$, phenyl), 7.97 (dm, 2H$_{arom.}$, 7-H and 9-H, ^3J = 6.8 Hz, ^4J = 1.2 Hz), 8.21 (dd, 1H$_{arom.}$, 10-H, ^3J = 8.4 Hz, ^4J = 1.2 Hz), 8.97 (s, 1H, 4-H), 9.60 (s, 1H, NH); ms: m/z 373 (9), 372 (38; M^+), 267 (1), 200 (1), 105 (100; $C_6H_5CO^+$), 77 (24).

Anal. Calcd. for $C_{22}H_{16}N_2O_4$ (372.37): C, 70.96; H, 4.33; N, 7.52. Found: C, 70.85; H, 4.36; N, 7.46.

N-(1-Benzyl-2,5-dioxo-1,5-dihydro-2*H*-chromeno[4,3-*b*]pyridin-3-yl)benzamide (**4j**) and 4-{[4-(Benzylamino)-2-oxo-2*H*-chromen-3-yl]methylene}-2-phenyl-1,3-oxazol-5(4*H*)-one (**3j**).

The crude product **4j** was collected by filtration and washed with ethyl acetate. On concentrating and cooling the azalactone **3j** crystallized from the red-colored filtrate as by-product. The main product **4j** was obtained after 7 h reflux in 29 % yield as colorless crystals (butanol), mp 248-250°; ir: NH 3368, CO lactone 1721, CO amide 1652, CO lactam 1646, 1605, 1484 cm^{-1}; ^1H nmr (DMSO-d_6): δ 5.72 (s, 2H, phenyl-CH$_2$), 7.20 (m, 1H$_{arom.}$, 8-H), 7.28-7.68 (m, 10H$_{arom.}$, phenyl), 7.83 (dd, 1H, 10-H $_{arom.}$, ^3J = 8.3 Hz, $^4J \approx 1$ Hz), 7.98 (dm, 2H$_{arom.}$, 7-H and 9-H, $^3J \approx 6.9$ Hz), 9.04 (s, 1H, 4-H), 9.75 (s, 1H, NH); ms: m/z 423 (12), 422 (44; M^+), 361 (3), 362 (9), 318 (7), 317 (9), 291 (3), 228 (2), 106 (5), 105 (67; $C_6H_5CO^+$), 91 (100; $C_6H_5CH_2^+$), 77 (18).

Anal. Calcd. for $C_{26}H_{18}N_2O_4$ (422.44): C, 73.92; H, 4.29; N, 6.63. Found: C, 73.62; H, 4.44; N, 6.53.

Compound **3j** was obtained in 2 % yield as red crystals from ethyl acetate; mp 206° (decomposes to give **4j**); ir (chloroform): CO 1799, 1767, 1703, 1631, 1470, 1418, 1331, 1172, 702 cm^{-1}; ms: m/z (%) 423 (17), 422 (55; M^+), 360 (2), 318 (3), 317 (8), 106 (7), 105 (97; $C_6H_5CO^+$), 91 (100; $C_6H_5CH_2^+$), 77 (28). Attempts to record nmr spectra failed because of its rapid decomposition in solution.

Anal. Calcd. for $C_{26}H_{18}N_2O_4$ (422.44): C, 73.92; H, 4.29; N, 6.63. Found: C, 73.52; H, 4.35; N, 6.54.

N'-(1-Allyl-2,5-dioxo-1,5-dihydro-2*H*-chromeno[4,3-*b*]pyridin-3-yl)-*N,N*-dimethylformamidine (**7a**).

To *N,N*-dimethyformamide (4.6 ml; 41 mmoles), chilled to –5 – 0° (ice - calcium chloride), phosphoryl chloride (0.48 g; 5.2 mmoles) was added dropwise under stirring. After stirring for 30 min. compound **4e** (0.9 g; 2.9 mmoles) was added and the mixture was stirred for further 10 min. Then the mixture was heated at 60° under stirring for 1 h, poured into 50 ml cold water and neutralized with sodium carbonate to pH ≈ 9. The separated precipitate was collected by filtration, washed with water and recrystallized from methanol. Yield 62 % of colorless crystals, mp 190-191°; ir: CO lactone 1714, CO lactam 1665, C=N/C=C 1637, 1571, 1355, 1267, 1100, 1007, 763 cm^{-1}; ^1H nmr (DMSO-d_6): δ 2.96 (s, 3H, N-CH$_3$), 3.05 (s, 3H, N-CH$_3$), 4.96 (br. s, 2H, N-CH$_2$), 5.16 (d, 1H, H^A of CH_2=CH- allyl, ^3J = 17.1 Hz), 5.34 (d, 1H, H^B of CH$_2$=C allyl, ^3J = 10.6 Hz), 6.27 (m, 1H, CH$_2$=C*H*-allyl), 7.39 (m, 2H$_{arom.}$, 7-H and 9-H), 7.47 (d, 1H$_{arom.}$, 10-H, ^3J = 7.5 Hz), 7.61 (m, 1H$_{arom.}$, 8-H), 8.16 (d, 1H, N=C*H*-NMe$_2$, J = 8.3 Hz), 8.36 (s, 1H, 4-H); ms: m/z 324 (19), 323 (97; M^+), 295 (4), 283 (17), 282 (100), 267 (21), 255 (17), 239 (13), 212 (7).

Anal. Calcd. for $C_{18}H_{17}N_3O_3$ (323.35): C, 66.86; H, 5.30; N, 13.00. Found: C, 66.87; H, 5.20; N, 12.92.

N'-(2,5-Dioxo-2*H*,5*H*-pyrano[3,2-*c*]chromen-3-yl)-*N,N*-dimethylformamidine (**7b**).

This compound was obtained as described above for **7a** starting from compound **5** (prepared analogous to [16]) after 1.5 h heating at 60° in 55 % yield as colorless crystals, mp 197-199° (methanol); ir: CO lactone 1733, CO lactone 1700, C=N 1640, 1299, 1101, 1057, 766, 532, 510 cm^{-1}; ^1H nmr (DMSO-d_6): δ 3.28 (s, 3H, N-CH$_3$), 3.36 (s, 3H, N-CH$_3$), 7.49-7.60 (m, 2H$_{arom.}$, 7-H and 9-H), 7.81 (m, 1H$_{arom.}$, 8-H), 8.02 (d, 1H$_{arom.}$, 10-H, ^3J = 9.6 Hz, ^4J = 1.5 Hz), 8.11 (s, 1H, N=C*H*-NMe$_2$), 8.68 (s, 1H, 4-H).

Anal. Calcd. for $C_{15}H_{12}N_2O_4$ (284.27): C, 63.38; H, 4.25; N, 9.85. Found: C, 63.44; H, 4.19; N, 9.80.

N-(6-Benzyl-7-methyl-2,5-dioxo-5,6-dihydro-2*H*-pyrano[3,2-*c*]pyridin-3-yl)acetamide (**9a**).

This compound was obtained from 1-benzyl-4-hydroxy-6-methyl-2(1*H*)-pyridone-3-carbaldehyde **8** (prepared as described in [3]) according to the general procedure for compounds **4a-i** after 2 h reflux with 23% yield as colorless crystals, mp 252-254° (ethanol); ir (potassium bromide): NH amide 3331, CO lactone 1716, CO amide 1680, CO lactam 1661, 1584, 1574, 1524, 1421, 1245 cm^{-1}; ^1H nmr (deuteriochloroform): δ 2.23 (s, 3H, COCH$_3$), 2.38 (s, 3H, 7-CH$_3$), 5.38 (s, 2H, N-CH$_2$), 6.15 (s, 1H, 8-H), 7.1-7.4 (m, 5H$_{arom.}$, phenyl), 7.89 (s, 1H, 4-H), 8.93 (s, 1H, NH); ms (positive APCI): m/z 325 (98; M+1), 279 (9), 213 (13), 202 (10), 201 (100).

Anal. Calcd. for $C_{18}H_{16}N_2O_4$ (324.34): C, 66.66; H, 4.97; N, 8.64. Found: C, 66.54; H, 4.90; N, 8.69.

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