The Vilsmeier Reaction in the Synthesis of 3-Substituted [1]Benzopyrano[4,3-*b*]pyridin-5-ones. An Unusual Pyridine Ring Closure

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Dedicated to Professor Dr. Hans Möhrle, Institute of Pharmaceutical Chemistry, University of Düsseldorf, Federal Republic of Germany, on the occasion of his 65th birthday.

Starting from 4-chlorocoumarin-3-carbaldehyde (**1**) and Wittig phosphoranes **2a-d** the title compounds **6a-c** have been synthesized *via* a four-step sequence. The intermediate 4-alkylamino-3-vinylcoumarins **5a-k** have been prepared by the reaction of 4-chloro-3-vinylcoumarins **3a-d** with primary amines **4a-h**. The coumarin derivatives **5** (except **5k**) underwent an unusual pyridine ring closure under Vilsmeier conditions to form the benzopyrano[4,3-*b*]pyridines **6**. When the aminoaldehydes **7** were treated with the Wittig reagent **2b** the fused *N*-alkyl-2(1*H*)-pyridinones **8** have been obtained as expected.

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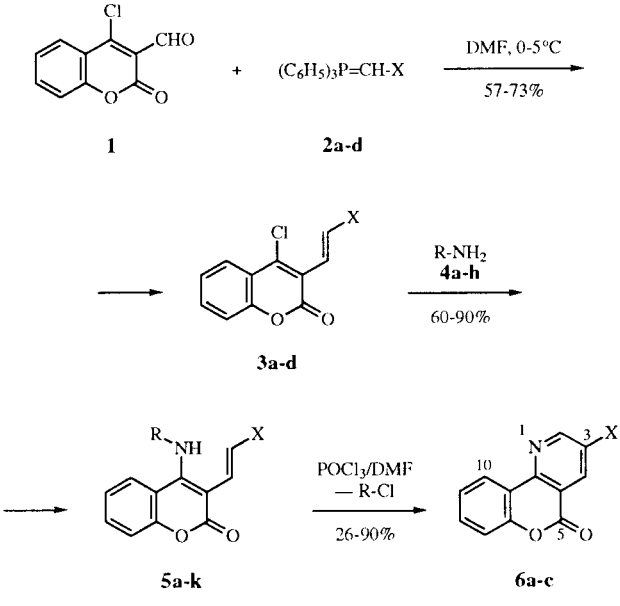
Several approaches [1-14] have been employed until the present for the synthesis of 5*H*-[1]benzopyrano-[4,3-*b*]pyridines by generally starting from salicylaldehyde [1,12], 3-acylchromones [3-7,10], or 4-hydroxycoumarins [1,9,11]. 4-Amino[1]benzopyranes have been obtained as intermediates in most cases [7,9,11,13,14]. These methods are based on a Vilsmeier-Haack [3-7,14], Wittig [3-7], or nucleophilic addition [4,5] reactions in the step prior to the pyridine ring closure. Some representatives of this class are biologically active or possess fluorescent properties [1,3-7,10]. A convenient preparation of [1]benzopyrano[4,3-*b*]pyridines was described in a recent paper [15], starting from 4-aminocoumarins and including, in some cases, a Dimroth-type rearrangement as an intermediate step.

Scheme 1



Scheme 1 (continued)

2, 3, 6	X
a	$COOCH_3$
b	$COOC_2H_5$
c	CN
d	COC_6H_5

4	R
a	CH_3
b	C_2H_5
c	$(CH_2)_3CH_3$
d	$C(CH_3)_3$
e	$CH_2CH=CH_2$
f	$CH_2C_6H_5$
g	$CH_2C_6H_4$-OCH_3-*p*
h	$CH_2C_6H_4$-NO_2-*p*

5	R	X
a	CH_3	$COOC_2H_5$
b	C_2H_5	$COOC_2H_5$
c	$(CH_2)_3CH_3$	$COOC_2H_5$
d	$C(CH_3)_3$	$COOC_2H_5$
e	$CH_2CH=CH_2$	$COOC_2H_5$
f	$CH_2C_6H_5$	$COOC_2H_5$
g	$CH_2C_6H_4$-OCH_3-*p*	$COOC_2H_5$
h	$CH_2C_6H_4$-NO_2-*p*	$COOC_2H_5$
i	$CH_2C_6H_5$	$COOCH_3$
j	$CH_2C_6H_5$	CN
k	$CH_2C_6H_5$	COC_6H_5

In the course of attempts [6] to cyclize some *N*-substituted *trans*-4-amino-3-(2-alkoxycarbonylvinyl)coumarins we found out that, under Vilsmeier conditions, tricyclic aromatic compounds were produced, accompanied by loss of the *N*-substituent and retention of the ester group. We describe now this general method for the synthesis of the hitherto unknown [1]benzopyrano[4,3-*b*]pyridine-5-ones **6a-c** unsubstituted at positions 2 and 4.

4-Chlorocoumarin-3-carbaldehyde (**1**) reacted with an equimolecular quantity of phosphoranes **2a-d** to give good yields of 3-vinylcoumarins **3a-d**. These were further converted into the dienamines **5a-k** by treatment

Table 1

Reaction Conditions and Physical Data of 4-Alkylamino-3-vinylcoumarins **5a-k**

Compound	Reaction Conditions: Solvent, Time (h)	Temp (°C)	Yield (%)	Mp (°C) (recrystallization solvent)	Mol. Formula (mol. wt.)	Analysis Calcd./Found C	H	N
5a	methanol	20-25	83	216-217	$C_{15}H_{15}NO_4$	65.92	5.53	5.13
	16			ethanol	273.3	65.97	5.53	5.18
5b	ethanol	20-25	87	171-172	$C_{16}H_{17}NO_4$	66.88	5.96	4.88
	16			ethanol	287.3	66.98	6.06	4.86
5c	ethanol	20-25	78	156-158	$C_{18}H_{21}NO_4$	68.55	6.71	4.44
	16			ethanol	315.4	68.59	6.77	4.48
5d	acetonitrile	reflux	90	160-162	$C_{18}H_{21}NO_4$	68.55	6.71	4.44
	7			acetonitrile	315.4	68.78	6.80	4.45
5e	ethanol	20-25	65	147-148	$C_{17}H_{17}NO_4$	68.22	5.72	4.68
	16			ethanol	299.3	68.18	5.73	4.65
5f	ethanol	20-25	71	167-169	$C_{21}H_{19}NO_4$	72.19	5.48	4.01
	16			acetonitrile	349.4	71.92	5.46	4.01
5g	ethanol	20-25	85	144-145	$C_{22}H_{21}NO_5$	69.65	5.58	3.69
	12			ethanol	379.4	69.72	5.71	3.54
5h	ethanol	reflux	78	226-227	$C_{21}H_{18}N_2O_6$	63.96	4.60	7.10
	1			acetone	394.4	63.89	4.58	7.12
5j	ethanol	20-25	61	145-146	$C_{19}H_{14}N_2O_2$	75.48	4.67	9.27
	16			benzene	302.3	75.48	4.68	9.18
5k	ethanol	20-25	89	179-180	$C_{25}H_{19}NO_3$	78.72	5.02	3.67
	16			acetonitrile	381.4	79.03	5.04	3.66

Table 2

IR and NMR Spectral Data of 4-Alkylamino-3-vinylcoumarins **5a-k**

Compound	IR (cm^{-1})	^1H NMR (δ ppm)
5a	3340, 1707, 1668	1.21 (t, J = 7.0, 3H, CH_3), 3.18 (d, J = 5.1 Hz, 3H, NCH_3), 4.20 (q, J = 7.0 Hz, 2H, OCH_2), 6.60 (d, J = 15.3 Hz, 1H, H-2'), 7.20-7.60 (m, 3H arom), 7.83 (d, J = 15.3 Hz, 1H, H-1'), 8.08 (dd, J = 1.9 Hz, J = 6.9 Hz, 1H, H-5), 8.10 (s, br, 1H, NH) [a]
5b	3330, 1712, 1679	1.32 (t, J = 7.0 Hz, 3H, NCH_2CH_3), 1.40 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 3.71 (q, J = 7.0 Hz, 2H, NCH_2), 4.24 (q, J = 7.1 Hz, 2H, OCH_2), 5.30 (s, br, 1H, NH), 6.91 (d, J = 15.5 Hz, 1H, H-2'), 7.30-7.70 (m, 4H arom), 7.80 (d, J = 15.5 Hz, 1H, H-1') [b]
5c	3390, 1693, 1674	0.95 (t, J = 6.6 Hz, 3H, CH_3), 1.32 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 1.30-1.80 (m, 4H, $2CH_2$), 3.65 (t, J = 7.0 Hz, 2H, NCH_2), 4.24 (q, J = 7.1 Hz, 2H, OCH_2), 5.30 (s, br, 1H, NH), 6.92 (d, J = 15.6 Hz, 1H, H-2'), 7.30-7.70 (m, 4H arom), 7.80 (d, J = 15.6 Hz, 1H, H-1') [b]
5d	3297, 1710, 1691, 1676	1.30 (t, J = 7.0 Hz, 3H, CH_3), 1.43 (s, 9H, $3CH_3$), 4.26 (q, J = 7.0 Hz, 2H, OCH_2), 4.63 (s, 1H, NH), 7.19 (d, J = 16.0 Hz, H-2'), 7.20-7.80 (m, 4H arom), 7.87 (d, J = 16.0 Hz, 1H, H-1') [b]
5e	3355, 3330, 1711, 1676	1.33 (t, J = 7.1 Hz, 3H, CH_3), 4.25 (d, J = 7.1 Hz, 2H, NCH_2), 4.25 (q, J = 7.1 Hz, 2H, OCH_2), 5.10-5.80 (s, br, 1H, NH), 5.30-5.55 (m, 2H, $-CH=CH_2$), 5.80-6.10 (m, 1H, $-CH=CH_2$), 6.95 (d, J = 15.6 Hz, 1H, H-2'), 7.30-7.80 (m, 4H arom), 7.77 (d, J = 15.6 Hz, 1H, H-1') [b]
5f	3330, 1715, 1668	1.15 (t, J = 7.0 Hz, 3H, CH_3), 4.10 (q, J = 7.0 Hz, 2H, OCH_2), 4.85 (s, 2H, NCH_2), 6.77 (d, J = 16.0 Hz, 1H, H-2'), 7.44 (s, 5H arom), 7.30-8.00 (m, 3H arom), 7.70 (d, J = 16.0 Hz, 1H, H-1'), 8.44 (s, br, 1H, NH), 8.30-8.60 (m, 1H, H-5) [b]
5g	3375, 1705, 1675	1.29 (t, J = 7.1 Hz, 3H, CH_3), 3.77 (s, 3H, OCH_3), 4.20 (q, J = 7.1 Hz, 2H, OCH_2), 4.70 (d, J = 4.9 Hz, 2H, NCH_2), 5.77 (t, J = 4.9 Hz, 1H, NH), 6.86 (d, J = 8.5 Hz, 2H, H-3", H-5"), 6.92 (d, J = 15.6 Hz, 1H, H-2'), 7.21 (d, J = 8.5 Hz, 2H, H-2", H-6"), 7.25-7.40 (m, 2H arom), 7.50-7.65 (m, 2H arom), 7.82 (d, J = 15.6 Hz, 1H, H-1') [b]
5h	3365, 1695, 1685	1.12 (t, J = 7.1 Hz, 3H, CH_3), 4.03 (q, J = 7.1 Hz, 2H, OCH_2), 4.95 (d, J = 6.4 Hz, 2H, NCH_2), 6.70 (d, J = 15.3 Hz, 1H, H-2'), 7.42-7.58 (m, 3H arom), 7.70-7.80 (m, 3H arom), 8.25-8.50 (m, 3H arom), 8.51 (t, J = 6.4 Hz, 1H, NH) [b]
5j	3362, 2219, 1679	4.77 (d, J = 4.8 Hz, 2H, NCH_2), 5.80 (s, br, 1H, NH), 6.60 (d, J = 16.0 Hz, 1H, H-2'), 7.20-7.60 (s, 4H arom), 7.35 (s, 5H arom), 7.38 (d, J = 16.0 Hz, 1H, H-1') [b]
5k	3330, 1715, 1640	4.70-5.00 (m, 2H, NCH_2), 7.37 (s, 5H arom), 8.50 (s, br, 1H, NH), 7.30-8.60 (m, 11H, 9H arom, H-1', H-2') [b]

[a] Recorded in deuteriodimethyl sulphoxide. [b] Recorded in deuteriochloroform.

with two equivalents of the corresponding primary amine **4a-h**, mainly in ethanol at room temperature. The physical characteristics and spectroscopic data of the new substituted 4-alkylamino-3-vinylcoumarins **5** are listed in Table 1. For vinyl protons, ^{1}H nmr spectroscopy shows an AB or AM system with doublets at δ = 6.60-7.19 and 7.38-7.87, respectively, with J = 15.3-16.0 Hz, typical of a *trans*-configuration of the double bond. The ir spectra of **5a-k** display beside absorption bands for enamino lactone (ν = 1640-1685 cm^{-1}) also bands for a conjugated ester carbonyl (ν = 1690-1715 cm^{-1}) of **5a-i**, a cyano group (ν = 2219 cm^{-1}) of **5j**, and a keto group (ν = 1714 cm^{-1}) of **5k**.

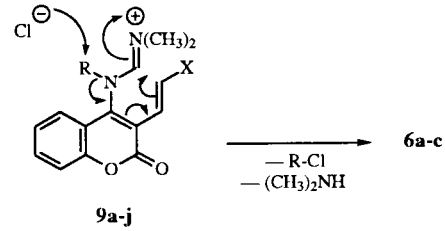
The heterocyclization of **5a-j** occurred smoothly with an excess of the Vilsmeier reagent (mole ratio 1:6) under mild conditions (20-90°) to give the nicotinic acid derivatives **6a-c**, mainly in high yields. We varied the *N*-substituents in order to establish their influence on the reaction rate and yield. The best results were achieved by using the *t*-butyl (**5d**) and *p*-methoxybenzyl (**5g**) derivatives as starting compounds whereas the *n*-butyl compound **5c** gave the lowest yield of the fused pyridine **6b** (*cf.* Table 2). The 3-cyanovinylcoumarin **5j** was successfully transformed into the 3-cyanopyridine derivative **6c** as well. But unfortunately, all attempts to convert the ketone **5k** into the target tricycle failed, resulting in a complex mixture of unidentified products (tlc control).

The structure of **6a-c** was unambiguously deduced from their ir and ^{1}H nmr spectra and elemental analyses. The presence of lactone (ν = 1745-1752 cm^{-1}), ester (**6a,b**: ν = 1714-1728 cm^{-1}) or cyano (**6c**: ν = 2246 cm^{-1}) groups were detected by the ir spectra, and the lack of the *N*-alkyl groups as well as the doublet signals of α- and γ-pyridine protons at δ = 9.10-9.56 and δ = 8.88-9.18, respectively, were observed in the ^{1}H nmr spectra of **6a-c**. In all cases, the signal of H-10 is distinctly shifted downfield to δ = 8.62±0.01. This fact was observed previously [6,15] and could serve as a criterion for the [4,3-*b*]-fusion of the [1]benzopyranopyridine ring system.

Furthermore, we have performed several trials in order to obtain the intermediate compounds **5** in reverse order of the synthetic steps. Aminoaldehydes **7a,b,f** were prepared [6,15] from 4-alkylaminocoumarins and then heated at 80-90° with the Wittig reagent **2b** to give **5a,b,f** (Scheme 2). In all these trials the crude products **5** were contaminated (tlc control) by a fluorescent product which proved to be the corresponding 1-alkyl[1]benzopyrano-[4,3-*b*]pyridine-2,5-dione **8**. The lactamization process went to completion when it was carried out under prolonged reflux in *N,N*-dimethylformamide (DMF) to produce directly **8a,b,f** in good yields. One of them, the benzyl derivative **8f**, has been obtained earlier [6] by heating of **5f** with urea at 180°. The ir and nmr spectral features of **8f** and related compounds are reported in the literature [6,15]. Thus, the route starting from aminoaldehyde **7** is not suitable for the preparation of the 4-alkylaminocoumarins **5**.

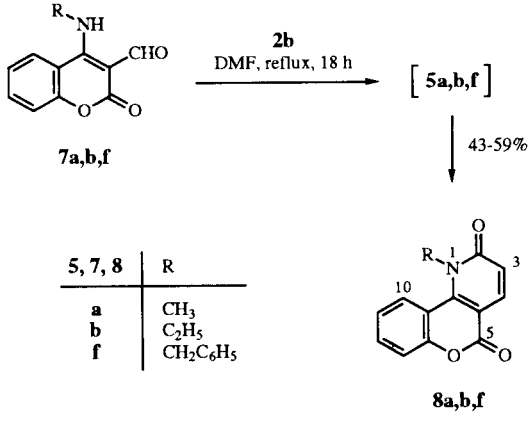
The mechanism of the title heterocyclization probably includes an initial *N*-formylation of the dienamine **5** to give an intermediate dimethyliminium salt **9a-j**. Then, nucleophilic attack of the chloride ion on the *N*-alkyl moiety provokes simultaneous electrocyclic ring closure. As a final step of this sequence, aromatization of the 2,3-dihydropyridine occurs, *via* elimination of dimethylamine, to give the fused pyridines **6a-c**.

Mechanism



9a-j

Scheme 2



To confirm this mechanism we succeeded in isolating benzyl chloride (from **5f**) and *p*-nitrobenzyl chloride (from **5h**) as by-products which were identified by comparing their physical constants and ir spectra with those of authentic samples. Thus, *N*-alkyl groups which provide stable carbenium ions, such as *tert*-butyl, allyl, benzyl, or *p*-methoxybenzyl, favor the reaction (*cf.* Table 2). On the other hand, compounds with primary alkyl substituents (*e.g.* in **5a-c**) react bimolecularly in nucleophilic substitution reactions and consequently gave lower yields of the benzopyranopyridines **6**.

It cannot be excluded absolutely that in contrast to the above mechanism the reaction is initiated by a C-formylation of the dienamine structure. For example, the synthesis of substituted 3-ethoxycarbonylquinolines probably involves such an attack of the electrophilic Vilsmeier reagent at ethyl anilinobutenoates [16].

EXPERIMENTAL

Melting points were determined in open capillary tubes with a Büchi 535 melting point apparatus (Switzerland) and are uncorrected. The structure of all compounds are consistent with spectroscopic data (ir, ^{1}H nmr, and ms) and satisfactory elemental analyses were obtained where stated. The ir spectra were recorded as potassium bromide pellets or in nujol on a C. Zeiss UR-20 spectrometer (Jena, Germany), ν in cm^{-1}, and the mass spectra on a JEOL JMS D300 instrument (Japan). The ^{1}H nmr spectra were obtained on a Bruker WP 100 spectrometer (Germany). Chemical shifts were expressed in δ (ppm) downfield from tetramethylsilane as an internal reference. Microanalyses were carried out in the Microanalytical laboratory of the Institute of Organic Chemistry, University of Stuttgart. Merck Kieselgel 60 F_{254} on aluminium sheets was used for tlc monitoring, elution by toluene-chloroform-acetone (2:1, volume parts) for compounds **5-8**, detection by uv (254 and 366 nm). Yields of isolated, tlc homogenous products are given.

The Wittig phosphoranes **2c** [17] and **2d** [18] as well as the 4-aminocoumarin **5i** [6] were prepared as previously reported.

Improved Procedure for the Preparation of 4-Chlorocoumarin-3-carbaldehyde (**1**) (*cf.* lit [19,20]).

To a stirred mixture of 4-hydroxycoumarin (9.72 g, 60 mmoles) in anhydrous *N,N*-dimethylformamide (46.2 ml, 0.6 mole) was added dropwise phosphorus oxychloride (27.6 g, 0.18 mole) at -10 to -5° over a period of 1 hour and stirring was continued for another hour. The resulting mixture was then heated and stirred at 60° for 1 hour accompanied by changing of the suspension to a solution. It was then poured onto crushed ice (200-300 g) with thorough stirring. After storing the mixture overnight at 0° the pale yellow solid which separated was collected by filtration and washed successively with 5% sodium bicarbonate and water, and then was air-dried. Recrystallization from 2-propanol is possible but not recommended, yield 10.61 g (85%), pale yellow powder with mp 120-122° (lit mp 120-122° [19], 125-127° [20]).

Substituted 4-Chloro-3-vinylcoumarins **3a-d**. General Procedure.

Similarly to the procedure for **3a** [6], the phosphorane **2b-d** (3.5 mmoles) was added with stirring to an ice-cooled mixture of the coumarin **1** (3.0 mmoles) in anhydrous dimethylformamide (3.0 ml) for a period of 15 minutes and stirring was continued until room temperature was reached. The mixture was allowed to stand overnight, then diluted with an equal volume of 2-propanol (except **3b**), the crystals which separated were filtered, and washed with 2-propanol.

4-Chloro-3-(2-ethoxycarbonylvinyl)coumarin (**3b**).

The product was obtained in 73% yield (from ethanol), needles, mp 125-126°; ms: (m/z) 278 (M$^+$).

Anal. Calcd. for $C_{14}H_{11}ClO_4$ (278.7): C, 60.34; H, 3.98; Cl, 12.72. Found: C, 60.27; H, 3.97; Cl, 12.73.

4-Chloro-3-(2-cyanovinyl)coumarin (**3c**).

The product was obtained in 58% yield (from ethanol), needles, mp 155-156°; ms: (m/z) 231 (M$^+$).

Anal. Calcd. for $C_{12}H_6ClNO_2$ (231.6): C, 62.22; H, 2.61; N, 6.05; Cl, 15.31. Found: C, 62.43; H, 2.65; N, 5.86; Cl, 15.27.

4-Chloro-3-(2-benzoylvinyl)coumarin (**3d**).

The product was obtained in 65% yield (from ethanol), yellow crystals, mp 139-142°; ms: (m/z) 310 (M$^+$).

Anal. Calcd. for $C_{18}H_{11}ClO_3$ (310.7): C, 69.58; H, 3.57; Cl, 11.41. Found: C, 69.47; H, 3.58; Cl, 11.00.

Substituted 4-Alkylamino-3-vinylcoumarins **5a-k**. General Procedure.

A solution of the amine **4a-h** (2.1 mmoles) in the corresponding reaction solvent (5.0 ml) was added dropwise at 0-5° to a stirred mixture of **3a-d** (1.0 mmole) in the same solvent (5.0 ml) over a period of 30 minutes. The reaction was then carried out under the conditions given in Table 1. On cooling, the crystalline product which separated was collected by filtration, washed successively with the reaction solvent and water, and, if necessary, recrystallized. After concentrating the filtrates under reduced pressure additional product was obtained; for more details, see Table 1 and 2.

3-Substituted 5-Oxo-[1]benzopyrano[4,3-*b*]pyridines **6a-c**. General Procedure.

Table 3

Preparation of 3-Substituted 5-Oxo[1]benzopyrano[4,3-*b*]pyridines **6a-c**

Starting Compound	Reaction Conditions		Workup	Product	Yield (%)
	Temp (°C)	Time (h)			
5a	90	4	A	**6b**	40
5b	90	4	B	**6b**	62
5c	90	3	B	**6b**	26
5d	70	2	C	**6b**	86
5e	70	3	A	**6b**	71
5f	70	3	A	**6b**	80
5g	20-25	3	A	**6b**	90
5h	20-25	4	A	**6b**	90
5i	20-25	4	A	**6a**	85
5j	40	3	A	**6c**	74

Phosphorus oxychloride (12.0 mmoles) was added dropwise to a stirred mixture of anhydrous dimethylformamide (4.5 ml) at -10 to -5° over a period of 1 hour. Stirring was continued for another hour and then **5a-j** (2.0 mmoles) was added. The reaction was carried out under conditions given in Table 3. The resulting mixture was worked up in one of the following ways: (A) On storing the mixture overnight at 0°, the colorless crystalline product which separated was collected by filtration, washed thoroughly with ethanol, and recrystallized. (B) After cooling, the mixture was poured onto ice-water (50 g) and the crystalline precipitate thus obtained was filtered, washed with water, and recrystallized. (C) After cooling, the mixture was diluted with ethanol and the separated solid was filtered, washed successively with ethanol and water, and recrystallized; for more details see Table 3.

Methyl 5-Oxo[1]benzopyrano[4,3-*b*]pyridine-3-carboxylate (**6a**). (See Table 2).

This compound had mp 193-194° (methanol); ir (nujol): 1728 (ester C=O), 1752 cm^{-1} (lactone C=O); ^1H nmr (deuteriochloroform): δ 4.03 (s, 3H, OCH_3), 7.40-7.70 (m, 3H, H-7, H-8, H-9), 8.63 (dd, 1H, J = 1.9 Hz, J = 8.1 Hz, H-10), 9.18 (d, 1H, J = 2.2 Hz, H-4), 9.56 (d, 1H, J = 2.2 Hz, H-2).

Anal. Calcd. for $C_{14}H_9NO_4$ (255.2): C, 65.88; H, 3.55; N, 5.49. Found: C, 65.94; H, 3.57; N, 5.44.

Ethyl 5-Oxo[1]benzopyrano[4,3-*b*]pyridine-3-carboxylate (**6b**). (See Table 2).

This compound had mp 143-144° (ethanol); ms: (m/z) 269 (M^+); ir (potassium bromide): 1714 (ester C=O), 1746 cm^{-1} (lactone C=O); ^1H nmr (deuteriochloroform): δ 1.47 (t, 3H, J = 7.1 Hz, CH_3), 4.49 (q, 2H, J = 7.1 Hz, OCH_2), 7.30-7.70 (m, 3H, H-7, H-8, H-9), 8.62 (dd, 1H, J = 1.9 Hz, J = 8.0 Hz, H-10), 9.17 (d, 1H, J = 2.2 Hz, H-4), 9.55 (d, 1H, J = 2.2 Hz, H-2).

Anal. Calcd. for $C_{15}H_{11}NO_4$ (269.3): C, 66.91; H, 4.12; N, 5.20. Found: C, 67.10; H, 4.15; N, 5.11.

5-Oxo[1]benzopyrano[4,3-*b*]pyridine-3-carbonitrile (**6c**).

This compound had mp 246-247° (acetone); ms: (m/z) 222 (M^+); ir (nujol): 1745 cm^{-1} (lactone C=O), 2246 (CN); ^1H nmr (deuteriochloroform): δ 7.30-7.80 (m, 3H, H-7, H-8, H-9), 8.61 (dd, 1H, J = 2.0 Hz, J = 7.8 Hz, H-10), 8.88 (d, 1H, J = 2.1 Hz, H-4), 9.20 (d, 1H, J = 2.1 Hz, H-2).

Anal. Calcd. for $C_{13}H_6N_2O_2$ (222.2): C, 70.27; H, 2.72; N, 12.61. Found: C, 70.11; H, 2.66; N, 12.33.

General Procedure for the Preparation of 1*H*,5*H*-[1]Benzopyrano[4,3-*b*]pyridine-2,5-diones **8**.

A mixture of the coumarin **7** (4.0 mmoles) and the phosphorane **2b** (4.0 mmoles) in *N,N*-dimethylformamide (5 ml) was refluxed for 18 hours. On cooling, the crystalline product **8** which separated was collected by filtration, washed with ether, and recrystallized.

1-Methyl-1*H*,5*H*-[1]benzopyrano[4,3-*b*]pyridine-2,5-dione (**8a**).

This compound had mp 210-212° (ethanol); ir (nujol): 1675 (lactam C=O), 1728 cm^{-1} (lactone C=O); ^1H nmr (deuteriochloroform): δ 4.02 (s, 3H, NCH_3), 7.71 (d, 1H, J = 9.6 Hz, H-3), 7.20-7.70 (m, 3H arom), 8.15 (d, 1H, J = 9.6 Hz, H-4), 8.19 (dd, 1H, partially overlapped, H-10).

Anal. Calcd. for $C_{13}H_9NO_3$ (227.2): C, 68.72; H, 3.99; N, 6.16. Found: C, 68.73; H, 3.95; N, 6.14.

1-Ethyl-1*H*,5*H*-[1]benzopyrano[4,3-*b*]pyridine-2,5-dione (**8b**).

This compound had mp 192-193° (ethanol); ms: (m/z) 241 (M^+); ir (nujol): 1667 (lactam C=O), 1718 cm^{-1} (lactone C=O); ^1H nmr (deuteriochloroform): δ 1.74 (t, 3H, J = 6.9 Hz, CH_3), 4.50 (q, 2H, J = 6.9 Hz, OCH_2), 6.69 (d, 1H, J = 9.6 Hz, H-3), 7.30-7.70 (m, 3H arom), 8.16 (d, 1H, J = 9.6 Hz, H-4), 8.14 (dd, 1H, partially overlapped, H-10).

Anal. Calcd. for $C_{14}H_{11}NO_3$ (241.2): C, 69.70; H, 4.59; N, 5.80. Found: C, 69.56; H, 4.60; N, 5.67.

1-Benzyl-1*H*,5*H*-[1]benzopyrano[4,3-*b*]pyridine-2,5-dione (**8f**).

Compound **8f** was prepared from **7f** and **2b**, yield 59%, mp 203-204° (ethanol); lit [6] mp 199°.

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