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2-Formyl-3-hydroxypyridine and its 6-methyl derivative have been condensed with ethoxycarbonylmethyl-enetriphenylphosphorane and alkyl derivatives to afford 5-azacoumarins substituted in the second case by an alkyl group at 3-position by two different ways according to the used phosphorane.

Introduction.

3-Substituted coumarins form a very important class of compounds. 3-Phenylcoumarins are known as anticoagulant and coronary constricting agents and as fluorescent brightners [1]. 3-Methylcoumarins have anthelmintic, hypnotic and insecticidal properties [2]. One of the most efficient synthesis of this class of compounds was developed by Mali *et al.* [1-3], starting from salicylaldehydes and substituted ethoxycarbonylmethylenetriphenylphosphorane as shown in Scheme I.

Scheme I
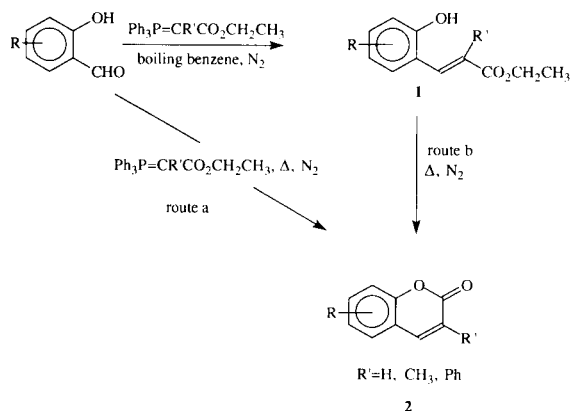
Coumarins **2** were directly obtained by direct heating of the mixture (150° to 250°), for R' = H, CH_3, and Ph (route a), or obtained after isolation of the ethyl (E)-2-hydroxycinnamates when R' = H and CH_3 (route b). By the two methods, coumarins **2** were obtained in 65% to 98% yields.

In the case of 2H-pyrano[3,2-b]pyridin-2-ones, named 5-azacoumarins, only two methods are known for their preparation. Moffet [4] obtained 5-azacoumarin (**3**) in 26% yield and 3-phenyl-5-azacoumarin (**4**) in 12% yield from 2-formyl-3-hydroxypyridine by a Perkin condensation, followed by thermal isomerization and cyclization.
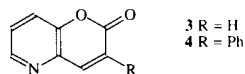

Dejardin and Lapiere [5] prepared 5-azacoumarin (**3**) in 30% yield by a Knoevenagel reaction from a mixture of 2-formyl-3-hydroxypyridine (**5**), malonic acid, and aniline. More recently, Queguiner *et al.* [6] synthesized 6-azacoumarin (**8**) in 45% overall yield (Scheme II).

Scheme II
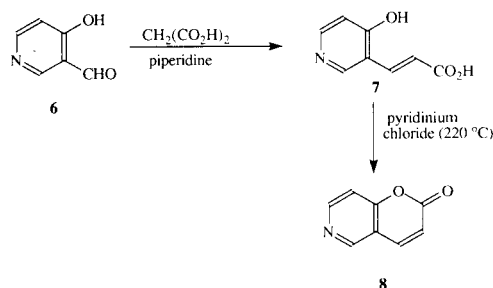
Reaction of the aldehyde **6** under Knoevenagel-Doebner conditions gave the E-isomer of the 3-(4-hydroxypyridin-3-yl)propenoic acid (**7**). Treatment of the latter with pyridinium chloride [7] resulted in isomerization to the Z-configuration and cyclization to the expected 6-azacoumarin (**8**).

We wish now to report our new efficient syntheses of the 5-azacoumarins starting from 2-formyl-3-hydroxypyridine (**5**) or its 6-methyl derivative **9** [8] using the procedure developed by Mali *et al.* [1-3] (Scheme I) with the same phosphoranes.
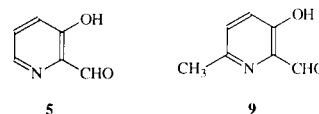
Results and Discussion.

While 3-phenyl-5-azacoumarin (**4**) and 6-methyl-3-phenyl-5-azacoumarin (**19**) were directly obtained in good yields (respectively 72% and 67%) by this reaction (route a, Scheme I), 5-azacoumarins and their 3-methyl derivatives were not obtained by direct heating of the reagents (route a, Scheme I).

By the other route (route b, Scheme I), we could isolate the intermediates *trans*-pyridylacrylate esters in good yields (75 to 82%) for phosphoranes with R' = H (**10**) [9]

or R' = CH₃ (**11**) [10] but no reaction took place when R' = Ph (**20**) [11]. We tried to synthesize 5-azacoumarins and 3-methyl-5-azacoumarins by thermal isomerization and cyclization at 200° under a nitrogen atmosphere of the intermediate *trans*-pyridylacrylate esters, but the initial products were decomposed without any isomerization.

So, as Queguiner *et al.* [6] had experienced (Scheme II), we used pyridinium chloride to isomerize and cyclize the above intermediates to 5-azacoumarins and 3-methyl-5-azacoumarins. Under these conditions, we were able to obtain the desired compounds **3, 16-18** in fair to good yields.

12-15   3, 4, 16-19
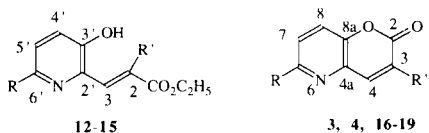
Our syntheses are summarized in Scheme III.

Scheme III
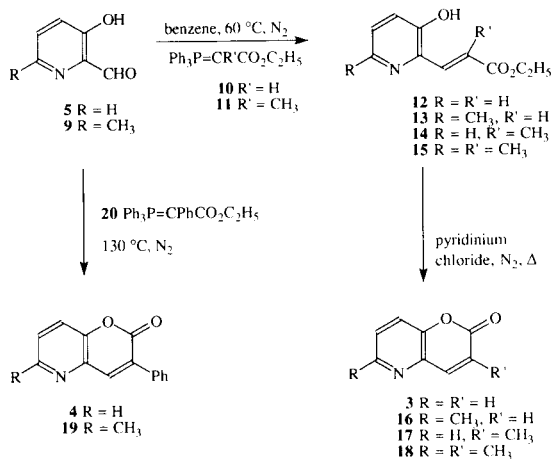
With the exception of compounds **3** and **4**, all the other derivatives were unknown. All the products showed the expected spectral properties in ir, nmr, and mass spectrometry studies; their structures were established as follows. In the ir, 5-azacoumarins presented the characteristic band of the pyridine nucleus at 1590-1430 cm⁻¹. The absorption of the CO group appeared at 1720-1710 cm⁻¹, with a shoulder at 1650-1630 cm⁻¹, attributed to the conjugated double bond. For the uncyclized compounds **12-15**, we noticed the large band at 3300-2500 cm⁻¹ attributed to the OH group. This band disappeared upon cyclization. The absorption at 1710 cm⁻¹ was characteristic of the ester function while the double bond gave a band at 1640 cm⁻¹. In the ¹H nmr study, the *trans* structure of the intermediates was clearly established by the value (15-16 Hz) of the coupling constant between H2–H3 characteristic of the *trans* configuration of the hydrogen atoms for compounds **12** and **13**. In the case of alkyl derivatives **14** and **15**, the

allylic coupling between CH₃ and H4 (1.1-1.3 Hz) was observed instead of the above ethylenic coupling. The cyclized compounds **3** and **16** exhibited for the ethylenic hydrogens a coupling constant of 10 Hz for the unsubstituted compounds characteristic of a *cis* double bond, which disappeared for the 3-alkyl derivative. We noticed in this case an allylic coupling value of 1.5 Hz between H4 and the CH₃ group borne at the 3 position. In all cases the hydrogens of the heterocyclic moiety formed an AMX system for which the most deshielded signal was attributed to the H6 hydrogen as the X part between 7.6-7.7 ppm. The AM part appeared at 7.4-7.6 ppm and was attributed to the H7, H8 hydrogens with regard to the coupling constants (J$_{H6-H7}$ = 4.6 Hz, J$_{H6-H8}$ = 1.3 Hz, J$_{H7-H8}$ = 8.4 Hz). For the 6-substituted compounds, we noticed the disappearance of the H6 signal and the emergence of a doublet for H7 and H8 (J$_{H7-H8}$ = 8.5 Hz). For the uncyclized compounds, the H6 signal was more deshielded (δ H6 = 8-9 ppm) and H6, H5, and H4 formed an ABX system. For the ¹³C nmr spectrum, the assignments were made by analogy with similar compounds and with the aid of the increment values of the substituents borne by the heterocyclic moiety and do not require special comments.

Conclusion.

In conclusion, this work presents a new efficient synthesis of 5-azacoumarins in good yields and some alkyl derivatives according to two methods, by condensation of 2-formyl-3-hydroxypyridine and its 3-methyl derivative with ethoxycarbonylmethylenetriphenylphosphorane and derivatives.

EXPERIMENTAL

Procedure A.

Ethoxycarbonylalkylmethylenetriphenylphosphorane (10 mmoles, alkyl = H or CH₃), *o*-hydroxyformylpyridine (10 mmoles), and 50 ml of dried benzene were placed in a three-necked flask under a nitrogen atmosphere. The mixture was heated at 60° and magnetically stirred for 3 hours. The solution was totally evaporated under reduced pressure and the resulting yellow solid was dissolved in a minimal amount of dried hot chloroform. After 2 hours at –20°, the expected *trans*-pyridyl-

acrylate ester was filtered with a glass-funnel and recrystallized from dried chloroform.

Procedure B.

Ethoxycarbonylalkylmethylenetriphenylphosphorane (10 mmoles, alkyl = H or CH$_3$), o-hydroxyformylpyridine (10 mmoles), and 50 ml of dried benzene were placed in a three-necked flask under a nitrogen atmosphere. The mixture was heated at 60° and magnetically stirred for 3 hours. The solution was totally evaporated under reduced pressure and the resulting yellow solid was poured with stirring into 100 ml of a 15 x 10^{-2} M aqueous potassium carbonate solution. The solution was filtered with a glass-funnel in order to eliminate solid triphenylphosphine oxide and extracted with 20 ml of chloroform. The aqueous solution was then adjusted to pH = 7 with 1 N hydrochloric acid solution and extracted with 3 50 ml portions of chloroform. The combined organic layers were dried over magnesium sulfate and totally evaporated under reduced pressure to afford pure expected trans-pyridylacrylate ester.

Procedure C.

The above trans-pyridylacrylate esters (procedures A and B, 1 g) were mixed with 15 g (0.13 mole) of dried pyridinium chloride under a nitrogen atmosphere. The mixture was magnetically stirred and heated at 220° during 20 minutes and the hot solution was poured onto 100 g of ice with vigorous stirring. The aqueous solution was extracted with 3 30 ml portions of chloroform and the combined organic layers were dried over magnesium sulfate. After total evaporation, the solid 5-azacoumarins were recrystallized.

Procedure D.

o-Hydroxyformylpyridine (10 mmoles) and 4.24 g (10 mmoles) of ethoxycarbonylbenzylidenetriphenylphosphorane (20) [11] was heated at 130° and magnetically stirred under a nitrogen atmosphere for 3 hours. The resulting dark mixture was then passed through a column of basic alumina (Brockmann I) with dried toluene as the eluant. After total evaporation of the solvent under reduced pressure, the solid was recrystallized to afford pure 3-phenyl-5-azacoumarins.

Ethyl (E)-3-(3-Hydroxypyridin-2-yl)propenoate (12).

This compound was prepared by procedure A, starting from 2-formyl-3-hydroxypyridine (5) (1.23 g, 10 mmoles) and ethoxycarbonylmethylenetriphenylphosphorane (10) [9] (3.48 g, 10 mmoles), white crystals, 82% yield, mp 173°; ir (potassium bromide): ν cm^{-1} 3200-2500 (bonded OH), 1710 (C=O ester), 1640 (conjugated C=C); ^{1}H nmr (hexadeuteriodimethyl sulfoxide): δ ppm 1.26 (t, 3H, J = 7.2 Hz), 4.19 (q, 2H, J = 7.2 Hz), 6.82 (d, 1H, H2, J$_{H2-H3}$ = 15.5 Hz), 7.28 (m, 2H, H4', H5'), 7.92 (d, 1H, H3, J$_{H2-H3}$ = 15.5 Hz), 8.12 (dd, 1H, H6'), 10.62 (bs, 1H, OH); ^{13}C nmr (hexadeuteriodimethyl sulfoxide): δ ppm 14.1 (CH$_3$), 59.9 (CH$_2$), 119.8 (C2), 123.6 and 125.9 (C4' and C5'), 138.4 (C6'), 139.4 (C2'), 140.8 (C3), 153.2 (C3'), 166.2 (C1); ms: m/z (relative abundance) 193 (10.7, M$^+$), 120 (100).

Anal. Calcd. for C$_{10}$H$_{11}$NO$_3$: C, 62.17; H, 5.74; N, 7.25. Found: C, 62.18; H, 5.64; N, 7.01.

Ethyl (E)-3-(3-Hydroxy-6-methylpyridin-2-yl)propenoate (13).

This compound was prepared by procedure A, starting from 2-formyl-3-hydroxy-6-methylpyridine (9) (1.37 g, 10 mmoles) and ethoxycarbonylmethylenetriphenylphosphorane (10) [9] (3.48 g,

10 mmoles), yellow crystals, 80% yield, mp 202°; ir (potassium bromide): ν cm^{-1} 3200-2600 (bonded OH), 1710 (CO ester), 1640 (conjugated C=C); ^{1}H nmr (hexadeuteriodimethyl sulfoxide): δ ppm 1.27 (t, 3H, J = 7.1 Hz), 2.39 (s, 3H, CH$_3$-6'), 4.17 (q, 2H, J = 7.1 Hz), 6.81 (d, 1H, H2, J$_{H2-H3}$ = 15.8 Hz), 7.13 (d, 1H, H4' or H5', J$_{H4'-H5'}$ = 8.3 Hz), 7.21 (d, 1H, H4' or H5', J$_{H4'-H5'}$ = 8.3 Hz), 7.90 (d, 1H, H3, J$_{H2-H3}$ = 15.8 Hz), 10.33 (bs, 1H, OH); ^{13}C nmr (hexadeuteriodimethyl sulfoxide): δ ppm 14.1 (CH$_3$ ester), 23.1 (CH$_3$-6'), 59.9 (CH$_2$), 119.4 (C2), 124.3 and 125.6 (C4' and C5'), 138.0 (C2'), 138.4 (C3), 148.5 (C6'), 151.1 (C3'), 166.3 (C1); ms: m/z (relative abundance) 207 (16.1, M$^+$), 134 (100).

Anal. Calcd. for C$_{11}$H$_{13}$NO$_3$: C, 63.76; H, 6.32; N, 6.76. Found: C, 63.57; H, 6.33; N, 6.64.

Ethyl (E)-2-Methyl-3-(3-hydroxypyridin-2-yl)propenoate (14).

This compound was prepared by procedure B, starting from 2-formyl-3-hydroxy-6-methylpyridine (5) (1.37 g, 10 mmoles) and (α-ethoxycarbonylethylidene)triphenylphosphorane (11) [10] (3.62 g, 10 mmoles), viscous yellow oil, 78% yield; ir (chloroform, 45 mg/ml): ν cm^{-1} 3300 (bonded OH), 1710 (C=O ester), 1640 (conjugated C=C); ^{1}H nmr (deuteriochloroform): δ ppm 1.30 (t, 3H, J = 7.2 Hz), 2.15 (d, 3H, J = 1.1 Hz, allylic coupling constant), 4.23 (q, 2H, CH$_3$-2, J = 7.2 Hz), 7.18 (m, 2H, H4' and H5'), 7.84 (bs, 1H, H3), 8.14 (dd, 1H, H6'), 9.40 (bs, 1H, OH); ^{13}C nmr (deuteriochloroform): δ ppm 14.0 and 14.2 (CH$_3$-2 and CH$_3$ ester), 61.0 (CH$_2$), 123.8 and 124.2 (C4' and C5'), 132.0 (C3), 132.8 (C2), 139.5 (C6'), 142.9 (C2'), 152.8 (C3'), 168.6 (C1); ms: m/z (relative abundance) 207 (19.9, M$^+$), 133 (100).

Anal. Calcd. for C$_{11}$H$_{13}$NO$_3$: C, 63.76; H, 6.32; N, 6.76. Found: C, 63.73; H, 6.02; N, 6.72.

Ethyl (E)-2-Methyl-3-(3-hydroxy-6-methylpyridin-2-yl)propenoate (15).

This compound was prepared by procedure B, starting from 2-formyl-3-hydroxy-6-methylpyridine (9) (1.37 g, 10 mmoles) and (α-ethoxycarbonylethylidene)triphenylphosphorane (11) [10] (3.62 g, 10 mmoles), white solid from hexane, 75% yield; ir (potassium bromide): ν cm^{-1} 3200-2500 (bonded OH), 1710 (C=O ester), 1640 (conjugated C=C); ^{1}H nmr (deuteriochloroform): δ ppm 1.27 (t, 3H, J = 7.1 Hz), 2.12 (d, 3H, CH$_3$-2, J = 1.3 Hz, allylic coupling constant), 2.46 (s, 3H, CH$_3$-6'), 4.19 (q, 2H, J = 7.1 Hz), 6.95 (d, 1H, H4' or H5', J$_{H4'-H5'}$ = 8.3 Hz), 7.04 (d, 1H, H4' or H5', J$_{H4'-H5'}$ = 8.3 Hz), 7.74 (bs, 1H, H3), 8.65 (bs, 1H, OH); ^{13}C nmr (deuteriochloroform): δ ppm 14.2 and 14.4 (CH$_3$-2 and CH$_3$ ester), 22.9 (CH$_3$-6'), 61.1 (CH$_2$), 124.0 and 124.7 (C4' and C5'), 132.5 (C3), 132.7 (C2), 141.8 (C2'), 148.8 (C6'), 150.1 (C3'), 168.8 (C1); ms: m/z (relative abundance) 221 (31.1, M$^+$), 148 (100).

Anal. Calcd. for C$_{12}$H$_{15}$NO$_3$: C, 65.14; H, 6.83; N, 6.33. Found: C, 64.81; H, 6.78; N, 6.10.

2H-Pyrano[3,2-b]pyridin-2-one (3).

This compound was obtained as a white solid (absolute ethanol) in a 66% yield by the procedure C starting from compound 12 (1 g, 5.2 mmoles), mp 108° (lit [4,5] 108°); ir (potassium bromide): ν cm^{-1} 1730 (C=O pyrone), 1180 (C–O α-pyrone); ^{1}H nmr (deuteriochloroform): δ ppm 6.62 (d, 1H, H3, J$_{H3-H4}$ = 10 Hz), 7.41 (dd, 1H, H7, J$_{H6-H7}$ = 4.4 Hz, J$_{H7-H8}$ = 8.4 Hz), 7.59 (dd, 1H, H8, J$_{H6-H8}$ = 1.3 Hz, J$_{H7-H8}$ = 8.4 Hz), 7.89 (d, 1H, H4, J$_{H3-H4}$ = 10 Hz), 8.56 (dd, 1H, H6, J$_{H6-H7}$ = 4.4 Hz, J$_{H6-H8}$ = 1.3 Hz); ^{13}C nmr (deuteriochloroform): δ ppm 120.5 (C3), 124.2 and 125.7 (C7 and C8), 137.5 (C4a), 144.8 (C4), 146.7 (C6), 150.8 (C8a), 159.3 (C2); ms: m/z (relative abundance) 147 (100, M$^+$).

6-Methyl-2H-pyrano[3,2-b]pyridin-2-one (16).

This compound was obtained as a brown solid (absolute ethanol) in a 62% yield by procedure C starting from compound **13** (1 g, 4.8 mmoles), mp 158°; ir (potassium bromide): ν cm^{-1} 1720 (C=O pyrone), 1630 (conjugated C=C), 1180 (C-O α-pyrone); ^{1}H nmr (deuteriochloroform): δ ppm 2.63 (s, 3H, CH$_3$-6), 6.63 (d, 1H, H3, J$_{H3-H4}$ = 9.8 Hz), 7.32 (d, 1H, H7, J$_{H7-H8}$ = 8.5 Hz), 7.54 (d, 1H, H8, J$_{H7-H8}$ = 8.5 Hz), 7.87 (d, 1H, H4, J$_{H3-H4}$ = 9.8 Hz); ^{13}C nmr (deuteriochloroform): δ ppm 24.0 (CH$_3$-6), 120.2 (C3), 124.6 and 125.9 (C7 and C8), 136.4 (C4a), 144.8 (C4), 149.2 (C8a), 155.7 (C6), 159.9 (C2); ms: m/z (relative abundance) 161 (100, M$^+$).

Anal. Calcd. for C$_9$H$_7$NO$_2$: C, 67.08; H, 4.38; N, 8.69. Found: C, 66.98; H, 4.37; N, 8.60.

3-Methyl-2H-pyrano[3,2-b]pyridin-2-one (17).

This compound was obtained as a solid (absolute ethanol) in a 55% yield by procedure C starting from compound **14** (1 g, 4.8 mmoles), mp 167°; ir (potassium bromide): ν cm^{-1} 1720 (C=O pyrone), 1630 (conjugated C=C), 1180 (C-O α-pyrone); ^{1}H nmr (deuteriochloroform): δ ppm 2.28 (d, 3H, CH$_3$-3, J = 1.4 Hz allylic coupling constant), 7.40 (dd, 1H, H7, J$_{H6-H7}$ = 4.6 Hz, J$_{H7-H8}$ = 8.4 Hz), 7.62 (dd, 1H, H8, J$_{H7-H8}$ = 8.5 Hz, J$_{H6-H8}$ = 1.3 Hz), 7.74 (bs, 1H, H4), 8.55 (dd, 1H, H6, J$_{H6-H7}$ = 4.6 Hz, J$_{H6-H8}$ = 1.3 Hz); ^{13}C nmr (deuteriochloroform): δ ppm 17.5 (CH$_3$-3), 123.7 and 124.6 (C7 and C8), 130.3 (C3), 138.3 (C4a), 140.6 (C4), 146.5 (C6), 149.8 (C8a), 160.9 (C2); ms: m/z (relative abundance) 161 (100, M$^+$).

Anal. Calcd. for C$_9$H$_7$NO$_2$: C, 67.08; H, 4.38; N, 8.69. Found: C, 67.25; H, 4.38; N, 8.63.

3,6-Dimethyl-2H-pyrano[3,2-b]pyridin-2-one (18).

This compound was obtained as a solid (hexane-absolute ethanol 50/50) in a 55% yield by procedure C starting from compound **15** (1 g, 4.5 mmoles), mp 171°; ir (potassium bromide): ν cm^{-1} 1720 (C=O pyrone), 1640 (conjugated C=C), 1180 (C-O α-pyrone); ^{1}H nmr (deuteriochloroform): δ ppm 2.26 (d, 3H, CH$_3$-3, J = 1.5 Hz, allylic coupling constant), 2.61 (s, 3H, CH$_3$-6), 7.25 (d, 1H, H7, J$_{H7-H8}$ = 8.5 Hz), 7.50 (d, 1H, H8, J$_{H7-H8}$ = 8.5 Hz), 7.69 (bs, 1H, H4); ^{13}C nmr (deuteriochloroform): δ ppm 17.6 (CH$_3$-3), 24.0 (CH$_3$-6), 124.0 and 124.7 (C7 and C8), 129.9 (C3), 137.2 (C4a), 140.6 (C4), 148.2 (C8a), 155.4 (C6), 161.2 (C2); ms: m/z (relative abundance) 175 (100, M$^+$).

Anal. Calcd. for C$_{10}$H$_9$NO$_2$: C, 68.56; H, 5.18; N, 7.99. Found: C, 68.43; H, 5.22; N, 7.86.

3-Phenyl-2H-pyrano[3,2-b]pyridin-2-one (4).

This compound was prepared by procedure D, starting from 2-formyl-3-hydroxypyridine (**5**) (1.23 g, 10 mmoles): purple needles (absolute ethanol), 72% yield; mp 154-155° (lit [4] 156-157.5°); ir (potassium bromide): ν cm^{-1} 1730 (C=O pyrone), 1650 (conjugated C=C), 1210 (C-O α-pyrone); ^{1}H nmr (deuteriochloroform): δ ppm 7.45 (dd, 1H, H7, J$_{H6-H7}$ = 4.6 Hz, J$_{H7-H8}$ = 8.3 Hz), 7.45 and 7.75 (m, 5H, phenyl), 7.66 (dd, 1H, H8, J$_{H7-H8}$ = 8.3 Hz, J$_{H6-H8}$ = 1.3 Hz), 8.05 (s, 1H, H4), 8.59 (dd, 1H, H6, J$_{H6-H7}$ = 4.6 Hz, J$_{H6-H8}$ = 1.3 Hz); ^{13}C nmr (deuteriochloroform): δ ppm 123.7 and 125.3 (C7 and C8), 128.6 (p and m), 129.5 (o), 132.1 (C3), 134.0 (i), 138.3 (C4a), 140.7 (C4), 146.9 (C6), 150.2 (C8a), 159.3 (C2); ms: m/z (relative abundance) 223 (100, M$^+$).

6-Methyl-3-phenyl-2H-pyrano[3,2-b]pyridin-2-one (19).

This compound was prepared by procedure D, starting from 2-formyl-6-methyl-3-hydroxypyridine (**9**) (1.37 g, 10 mmoles), 67% yield (absolute ethanol), mp 133-134°; ir (potassium bromide): ν cm^{-1} 1730 (C=O pyrone), 1650 (conjugated C=C), 1180 (C-O α-pyrone); ^{1}H nmr: δ ppm 2.63 (s, 3H, CH$_3$-6), 7.30 (d, 1H, H7, J$_{H7-H8}$ = 8.5 Hz), 7.46 and 7.75 (m, 5H, phenyl), 7.54 (d, 1H, H8, J$_{H7-H8}$ = 8.5 Hz), 8.01 (s, 1H, H4); ^{13}C nmr (deuteriochloroform): δ ppm 24.1 (CH$_3$-6), 124.0 and 125.4 (C7 and C8), 128.6 (p and m), 129.3 (o), 131.6 (C3), 134.2 (i), 137.2 (C4a), 140.7 (C4), 148.6 (C8a), 155.8 (C6), 159.6 (C2); ms: m/z (relative abundance) 237 (100, M$^+$).

Anal. Calcd. for C$_{15}$H$_{11}$NO$_2$: C, 75.94; H, 4.67; N, 5.90. Found: C, 75.50; H, 5.12; N, 5.70.

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