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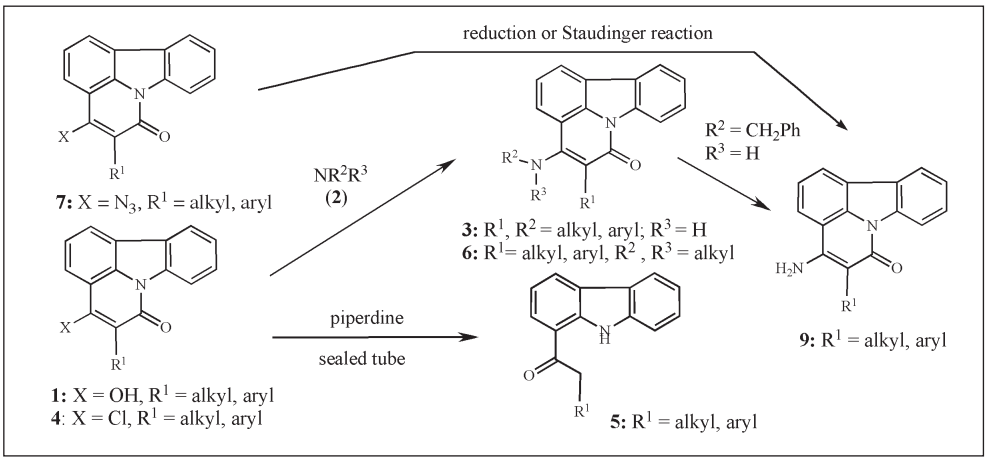

Amination of 4-hydroxypyridocarbazolones **1** with aniline or benzylamine gave in good yields 4-amines **3**. With piperidine in a sealed tube from 4-hydroxy- or 4-chloro-5-alkylpyridocarbazolones **1** or **4** ring opened 1-acylcarbazoles **5** were obtained. Only 4-hydroxy-5-phenyl-pyridocarbazolone **1d** gave 4-amines **6**. Reduction of 4-azidopyridocarbazolones **7** either by catalytic hydrogenation or in a 2-step synthesis *via* phosphazenes **8** gave 4-aminopyridocarbazolones **9**. Amines **9** were also obtained from benzylamines **3** by catalytic debenzylation. A one step amination of 4-hydroxy-5-phenylpyridocarbazolone **1d** *via* debenzylation to **9d** was observed by reaction with benzylammonium chloride. At elevated temperatures the highly fused 6,13b-diazaindeno[1,2,3-*hi*]chrysenone **10** was formed from **1d**.

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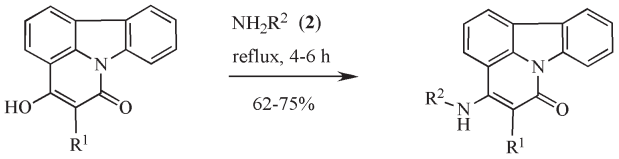
Recently we reported about the synthesis of various 4,5-disubstituted pyrido[3,2,1-*jk*]carbazolones [1], which contain the heterocyclic skeleton of natural products of *Strychnos* alkaloids such as strychninolones and brucinolones [2], picrasidin Q [3] and olivacin alkaloids [4]. It possesses the biologically interesting combination of indole structures and of a 2-pyridone. Moreover, some derivatives have found interest in pharmacological [5] or in dyes chemistry [6]. When we directed our interest to 4-amino-substituted derivatives (*e.g*. structure **3**), a literature survey showed that only a very few syntheses of 4-amino-pyrido[3,2,1-*jk*]carbazole structures are described [7,8], although continuing interest can be observed on theoretical investigations in azafullerenes containing this heterocyclic skeleton [9].

We started our synthetic approach by reaction of 4-hydroxypyridocarbazolones **1** [1] with high boiling amines **2** such as benzylamine or aniline. Whereas benzylamine reacted as assumed to the 4-benzylamino derivatives **3**, in the reaction with aniline acidic catalysis was necessary, which could be achieved by addition of aniline hydrochloride. In this way a series of amino-substituted pyridocarbazolones **3** were obtained in good yields.

The reaction of 4-hydroxypyridocarbazolones **1** with low boiling aliphatic amines such as piperidine or morpholine failed; when more reactive derivatives such as 4-chloro-pyridocarbazolones **4** were used, again no reaction was observed with the exception of the 5-phenyl derivative **4d**. In this case both with piperidine and morpholine the corresponding 4-amino-5-phenyl derivatives **6** were obtained. Experiments to raise the temperature, by performing the reaction in a sealed tube under pressure, brought a surprising result: In no case the desired amines similar to **6** were obtained, however a ring opening took place, which gave

Scheme 1

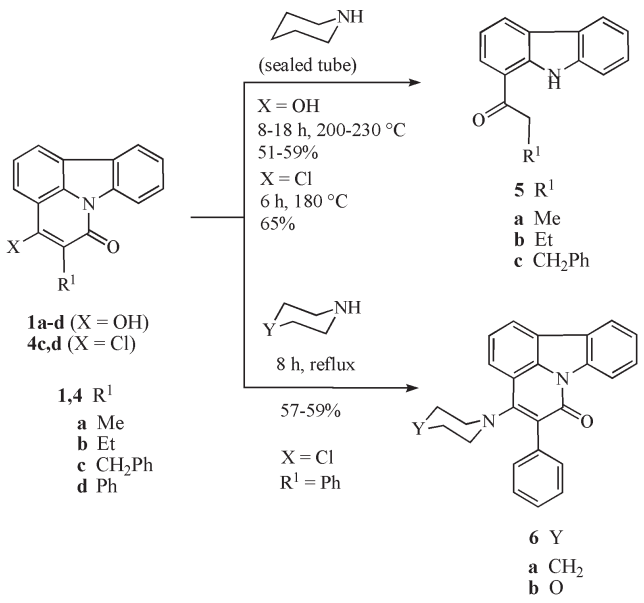


1	R^1
a	Me
b	Et
c	CH_2Ph
d	Ph

2	R^2
a	CH_2Ph
b	Ph

3	R^1	R^2
a	Me	CH_2Ph
b	Me	Ph
c	Et	CH_2Ph
d	Et	Ph
e	CH_2Ph	CH_2Ph
f	CH_2Ph	Ph
g	Ph	CH_2Ph
h	Ph	Ph

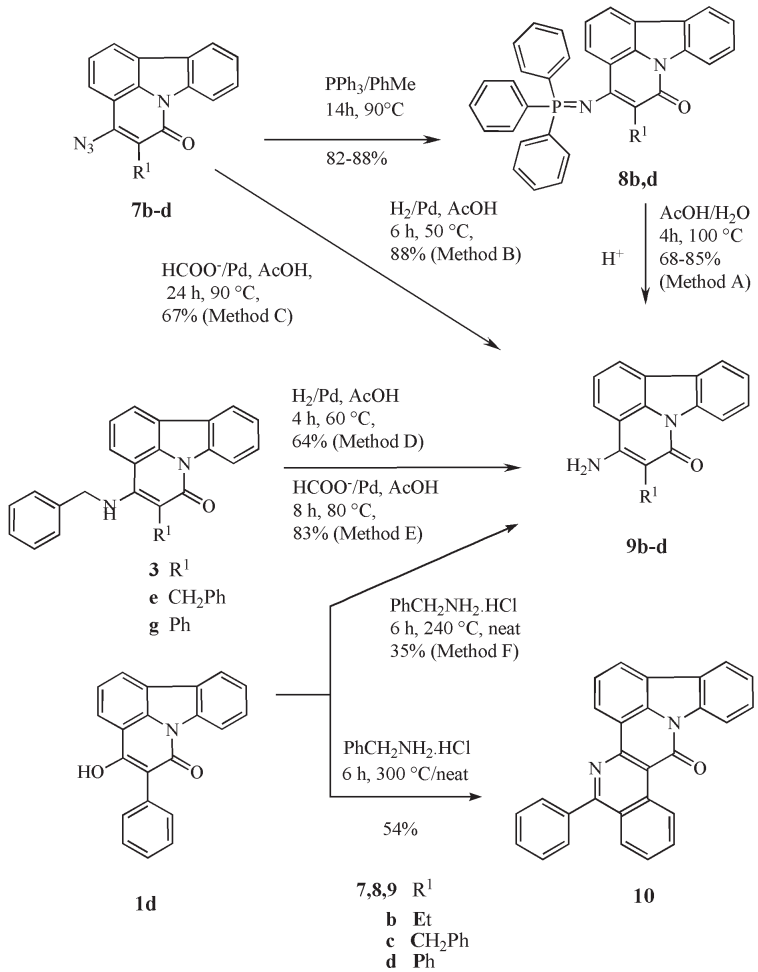
Scheme 2



the 1-acylcarbazoles **5** in good yields. This reactions offers a new, simple and isomer-free approach to versatile substituted 1-acylcarbazoles until now not described in the literature reports, which are mainly restricted to rearrangements starting from 1-acylcarbazoles [10].

The synthetic pathway to N-unsubstituted 4-aminocarbazolones **9** includes a number of possibilities, which were studied to find out suitable candidates. 4-Azidocarbazolones **7** as amine precursors, which were synthesized either directly from 4-hydroxycarbazolones **1** or *via* the 4-chloroderivatives **4** [1], could be reacted *via* a Staudinger reaction *via* the phosphazenes **8** and subsequent hydrolysis with acetic acid (method A) to the desired 4-aminocarbazolones **9**; alternatively, the azides **9** were directly reduced by hydrogenation in one step. The reduction was performed either conventionally with hydrogen under pressure (method B), or we used a method in which hydrogen was produced from resin-bound ammonium formate (method C) similar to a method described recently [11]. In both cases palladium on charcoal was used in glacial acetic acid as the solvent; the yields were slightly better with conventional hydrogenation (88% instead

Scheme 3



of 67%), but reactions were not optimized, and resin-supported hydrogenation is much safer and simpler to handle.

A further way to aminocarbazolones **9** was found in the catalytic debenzylation of benzylaminocarbazolones **3e,g**, which was performed again either with hydrogen (method D) or with resin-supported ammonium formate (method E). In this case, the yields were better with formate (80% instead of 64%). Experiments with palladium acetate as catalyst gave 83% yield using the formate reaction (method E). In the quinolone series we have reported some years ago [7,12] about the thermal one-pot amination and debenzylation of 4-hydroxyquinolones with benzylammonium chloride to 4-aminoquinolones. Transformation of this reaction type to hydroxycarbazolones **1** gave good results only with the 5-phenyl derivative **1d**: when it was heated with excess benzylammonium chloride to 240 °C we obtained in 35% yield 4-aminocarbazolone **9d**. Higher reaction temperatures, however, resulted in a ring closure reaction of the benzylamino substituent with the adjacent phenyl group to give the highly fused 6,13b-diazaindeno[1,2,3-*hi*]chrysene derivative **10**, a ring system, which was not described until now.

EXPERIMENTAL

Melting points were determined on a Gallenkamp Melting Point Apparatus, Mod. MFB-595 in open capillary tubes. Infrared spectra were taken on a Galaxy Series FTIR 7000 in potassium bromide pellets. The ^{1}H nmr spectra were recorded on a Bruker AM 360 instrument (360 MHz) or on a Bruker Avance DRX instrument (500 MHz). Chemical shifts are reported in ppm from internal tetramethylsilane standard and are given in δ-units. Elemental analyses were performed on a Fisons elemental analyzer Mod. EA 1108, and are within ±0.4 of the theoretical percentages. Mass spectra were taken on a HP 1100 - LC/MSD mass spectral instrument fitted with a positive and negative ACPI ion source, 50V- 200V. All reactions were monitored by thin layer chromatography, carried out on 0.2 mm silica gel 60 F-254 (Merck) plates using uv light (254 and 366 nm) for detection.

Common reagent-grade chemicals are either commercially available and were used without further purification or prepared by standard literature procedures.

4-Hydroxy-pyrido[3,2,1-*jk*]carbazol-6-ones (**1a-d**).

These compounds were obtained from alkyl- or arylmalonates and carbazole according to the method described in ref [1].

4-Benzylamino-5-methylpyrido[3,2,1-*jk*]carbazol-6-one (**3a**).

A solution of 4-hydroxy-5-methylpyridocarbazolone **1a** (1.50 g, 6 mmol) in excess benzylamine (**2a**) (10 mL) was heated for 6 hours under reflux using an air condenser to remove the reaction water. The excess solvent (about 5 mL) was removed *in vacuo*, then the reaction mixture cooled to room temperature, hexane (10 mL) was added, the resulting precipitate filtered by suction and washed with hexane (10 mL). The yield was 1.26 g (75%) yellow prisms, mp 144 °C (ethanol); ir: 3360 s, 1623 s, 1594 s, 1566 s cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 2.26 (s, Me), 4.63 (s, NH), 4.82 (s, CH_2), 7.34-7.40 (m, 5 PhH), 7.47 and 7.57 (2 t, J = 7.9 Hz, 2-H, 9-H, 10-H), 7.83, 8.04 and 8.08 (3 d, J = 7.6 Hz, 1-H, 3-H, 11-H), 8.76 (d, J = 8.1 Hz, 8-H).

Anal. Calcd. for $C_{23}H_{18}N_2O$: C, 81.63; H, 5.36; N, 8.28. Found: C, 81.72; H, 5.15; N, 8.06.

5-Methyl-4-phenylamino-pyrido[3,2,1-*jk*]carbazol-6-one (**3b**).

A solution of 4-hydroxy-5-methylpyridocarbazolone **1a** (1.50 g, 6 mmol) and aniline hydrochloride (1.50 g, 12 mmol) in excess aniline (**2b**) (20 mL) was heated under reflux using an air condenser to remove the reaction water. The excess solvent (about 15 mL) was removed *in vacuo*, the reaction mixture cooled to room temperature, hexane (20 mL) was added, the resulting precipitate filtered by suction and washed with hexane (10 mL). The residue was digested and washed subsequently with toluene (20 mL) and ethanol (5 mL). The yield was 1.00 g (62%) yellowish prisms, mp 195 °C (ethanol); ir: 3250 s, 1644 s, 1600 s cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 2.26 (s, Me), 6.07 (s, NH), 6.96 (d, J = 7.8 Hz, 2-H and 6-H of phenyl), 7.03 (t, J = 7.3 Hz, 4-H of phenyl), 7.29 (t, J = 7.9 Hz, 3-H and 5-H of phenyl), 7.37, 7.47 and 7.54 (3 t, J = 7.7 Hz, 2-H, 9-H, 10-H), 7.61 and 8.06 (2 d, J = 7.3 Hz, 1-H, 3-H, 11-H), 8.78 (d, J= 7.9 Hz, 8-H).

Anal. Calcd. for $C_{22}H_{16}N_2O$: C, 81.46; H, 4.97; N, 8.64. Found: C, 81.84; H, 4.89; N, 8.56.

4-Benzylamino-5-ethylpyrido[3,2,1-*jk*]carbazol-6-one (**3c**).

This compound was obtained from 5-ethyl-4-hydroxypyridocarbazolone **1b** (1.57 g, 6 mmol) and work up was as described for **3a**. The yield was 1.26 g (68%) yellow prisms, mp 121 °C (ethanol); ir: 3250 s, 1632 s, 1592 s, 1578 s cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 1.18 (t, J = 7.5 Hz, Me), 2.76 (d, J = 7.5 Hz, ethyl-CH_2), 4.47 (s, NH), 4.80 (s, benzyl-CH_2), 7.35-7.37 (m, 5 PhH), 7.42 and 7.55 (2 t, J = 7.8 Hz, 2-H, 9-H, 10-H), 7.84 and 8.03 (2 d, J = 7.9 Hz, 1-H, 3-H, 11-H), 8.76 (d, J = 8.2 Hz, 8-H).

Anal. Calcd. for $C_{24}H_{20}N_2O$: C, 81.79; H, 5.72; N, 7.95. Found: C, 81.44; H, 5.80; N, 8.01.

5-Ethyl-4-phenylaminopyrido[3,2,1-*jk*]carbazol-6-one (**3d**).

This compound was obtained from 5-ethyl-4-hydroxypyridocarbazolone **1b** (1.57 g, 6 mmol) and work up was as described for **3b**. The yield was 1.25 g (71%) yellow prisms, mp 174 °C; ir: 3250 s, 1651 s, 1599 s, 1561 s cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 1.24 (t, J = 7.5 Hz, Me), 2.87 (q, J = 7.5 Hz, CH_2), 6.01 (s, NH), 6.98 (d, J = 7.7 Hz, 2-H and 6-H of phenyl), 7.03 (t, J = 7.4 Hz, 4-H of phenyl), 7.27 (t, J = 7.9 Hz, 3-H and 5-H of phenyl), 7.30, 7.46 and 7.47 (3 t, J = 7.7 Hz, 2-H, 9-H, 10-H), 7.58 and 8.03 (2 d, J = 7.5 Hz, 1-H, 3-H, 11-H), 8.78 (d, J = 8.1 Hz, 8-H).

Anal. Calcd. for $C_{23}H_{18}N_2O$: C, 81.63; H, 5.36: N, 8.28. Found: C, 81.30; H, 5.34: N, 8.20.

5-Benzyl-4-benzylaminopyrido[3,2,1-*jk*]carbazol-6-one (**3e**).

This compound was obtained from 5-benzyl-4-hydroxypyridocarbazolone **1c** (1.50 g, 4.6 mmol) and worked up as described for **3a**. The yield was 1.00 g (75%) yellow prisms, mp 178 °C (ethanol); ir: 3250 s, 1627 s, 1595 s, 1556 s cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 4.16 (s, benzyl-CH_2), 4.63 (s, NH), 4.73 (s, CH_2 of benzylamine), 7.19-7.27 (m, 5 PhH), 7.25-7.36 (m, 5 PhH), 7.46 and 7.59 (2 t, J = 7.8 Hz, 2-H, 9-H, 10-H), 7.93, 8.07 and 8.13 (3 d, J = 7.7 Hz, 1-H, 3-H, 11-H), 8.8 (d, J = 8.1 Hz, 8-H).

Anal. Calcd. for $C_{29}H_{22}N_2O$: C, 84.03; H, 5.35; N, 6.76. Found: C, 83.93; H, 5.38; N, 6.64.

5-Benzyl-4-phenylaminopyrido[3,2,1-*jk*]carbazol-6-one (**3f**).

This compound was obtained from 5-benzyl-4-hydroxypyridocarbazolone **1c** (1.50 g, 4.6 mmol) and work up was as described for **3b**. The yield was 1.50 g (75%) yellow prisms, mp 176 °C (hexane); ir: 3250 s, 1644 s, 1626 s, 1598 s cm^{-1}; ^1H nmr ($CDCl_3$): δ 4.26 (s, CH_2), 6.09 (s, NH), 6.92 (d, J = 7.7 Hz, 2-H and 6-H of phenylamine), 7.04 (t, J = 7.4 Hz, 4-H of phenylamine), 7.27 (t, J = 7.9 Hz, 3-H and 5-H of phenylamine), 7.30 (t, J = 7.7 Hz, 2-H), 7.30-7.36 (m, 5 PhH), 7.46 and 7.47 (2 t, J = 7.3 Hz, 9-H, 10-H), 7.58 and 8.06 (2 t, J = 7.3 Hz, 1-H, 3-H, 11-H), 8.80 (d, J= 8.1 Hz, 8-H).

Anal. Calcd. for $C_{28}H_{20}N_2O$: C, 83.98; H, 5.03; N, 6.99. Found: C, 83.65; H, 5.07; N, 6.80.

4-Benzylamino-5-phenylpyrido[3,2,1-*jk*]carbazol-6-one (**3g**).

A solution of 4-hydroxy-5-phenylpyridocarbazolone **1d** (1.50 g, 4.8 mmol) in excess benzylamine (**2a**) (10 mL) was heated for 4 hours under reflux using an air condenser to remove the reaction water. The excess solvent (about 5 mL) was removed *in vacuo*, then the reaction mixture was cooled to room temperature, hexane (10 mL) and diethylether (5 mL) was added and the mixture stirred for 1 hour; the resulting precipitate was filtered by suction and washed with hexane (10 mL). The yield was 1.26 g (63%) yellow prisms, mp 173 °C (ethanol); ir: 3329 s, 1627 s, 1606 s, 1522 s cm^{-1}; ^1H nmr ($CDCl_3$): δ 4.41 (s, CH_2), 4.77 (s, NH), 7.22-7.37 (m, 5 PhH of benzyl), 7.48 and 7.55 (2 t, J = 7.8 Hz, 2-H, 9-H, 10-H), 7.83, 8.06 and 8.15 (3 d, J = 7.6 Hz, 1-H, 3-H, 11-H), 8.71 (d, J = 8.1 Hz, 8-H).

Anal. Calcd. for $C_{28}H_{20}N_2O$: C, 83.98; H, 5.03; N, 6.99. Found: C, 83.70; H, 4.90; N, 6.91.

5-Phenyl-4-phenylaminopyrido[3,2,1-*jk*]carbazol-6-one (**3h**).

A solution of 4-hydroxy-5-phenylpyridocarbazolone **1d** (1.50 g, 4.8 mmol) and aniline hydrochloride (0.50 g, 4 mmol) in excess aniline (**2b**) (20 mL) was heated for 4 hours under reflux using an air condenser to remove the reaction water. The excess solvent (about 15 mL) was removed *in vacuo*, then the reaction mixture was cooled to room temperature, hexane (20 mL) was added and the mixture stirred for 1 hour; the resulting precipitate was filtered by suction and washed with ethanol (10 mL). The yield was 1.35 g (70%) yellow prisms, mp 203 °C (ethanol): ir: 3255 s, 1644 s, 1626 s, 1598 s cm^{-1}; ^1H nmr ($CDCl_3$): δ 6.06 (s, NH), 7.05 (d, J = 7.8 Hz, 2-H and 6-H of phenylamine), 7.10 (t, J = 7.4 Hz, 4-H of phenylamine); 7.28 (t, J = 7.9 Hz, 3-H and 5-H of phenylamine), 7.30 (t, J = 7.7 Hz, 2-H), 7.42-7.45 (m, 5 PhH), 7.47 and 7.50 (2 t, J = 7.5 Hz, 9-H, 10-H), 7.56 and 8.06 (2 d, J = 7.5 Hz, 1-H, 3-H, 11-H), 8.73 (d, J = 8.1 Hz, 8-H).

Anal. Calcd. for $C_{27}H_{18}N_2O$: C, 83.92; H, 4.69; N, 7.25. Found: C, 84.31; H, 4.50; N, 6.88.

4-Chloropyrido[3,2,1-*jk*]carbazol-6-ones (**4a-d**).

These compounds were obtained from 4-hydroxypyridocarbazolones **1a-d** and phosphoryl chloride according to the method described in ref [1].

1-(9*H*-Carbazol-1-yl)-propan-1-one (**5a**).

A solution of 4-hydroxy-5-methylpyridocarbazolone **1a** (2.03 g, 8 mmol) in excess piperidine (10 mL) was heated at 230 °C for 8 hours in a sealed tube (8 bar). After cooling, the reaction mixture was treated with a mixture of diethylether (20 mL) and hexane (40 mL). The residue was triturated with hot ethanol and after cooling to room temperature filtered, washed with cold ethanol (10 mL) and dried. The yield was 0.9 g (51%) yellow prisms, mp 130 °C (methanol); ir: 3400-2800 s, 1655 s, 1624 s, 1598 s, 1575 s cm^{-1}; ^1H nmr ($CDCl_3$): δ 1.34 (t, J = 7.3 Hz, Me), 3.20 (q, J = 7.3 Hz, CH_2), 7.32-7.36 (m, 9-H, 10-H), 7.47-7.55 (m, 2-H, 11-H), 8.03 (d, J = 7.8 Hz, 3-H), 8.12 (d, J = 7.8 Hz, 1-H), 8.32 (d, J = 7.5 Hz, 8-H), 10.65 (s, NH).

Anal. Calcd. for $C_{15}H_{13}NO$: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.58; H, 5.88; N, 6.25.

1-(9*H*-Carbazol-1-yl)-butan-1-one (**5b**).

This compound was obtained from 5-ethyl-4-hydroxypyridocarbazolone **1b** (4.00 g, 15 mmol) at 220 °C after 18 hours according to the procedure and work-up described for **5a**. The yield was 2.1 g (59%) yellow prisms, mp 110 °C (methanol); ir: 3400-2800 s, 1655 s, 1624 s, 1598 s, 1575 s cm^{-1}; ^1H nmr ($CDCl_3$): δ 1.11 (t, J = 7.3 Hz, Me), 1.89 (q, J = 7.3 Hz, CH_2), 3.15 (t, J = 7.3 Hz, CO-CH_2), 7.26-7.32 (m, 9-H, 10-H), 7.48-7.55 (m, 2-H, 11-H), 8.03 (d, J = 7.8 Hz, 3-H), 8.12 (d, J = 7.8 Hz, 1-H), 8.31 (d, J = 7.5 Hz, 8-H); 10.65 (s, NH).

Anal. Calcd. for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90. Found: C, 80.67; H, 6.29; N, 5.83.

1-(9*H*-Carbazol-1-yl)-3-phenylpropan-1-one (**5c**).

Method A: This compound was obtained from 5-benzyl-4-hydroxypyridocarbazolone **1c** (2.50 g, 8 mmol) at 200 °C after 18 hours according to the procedure and work-up described for **5a**. The yield was 1.41 g (59%) yellow prisms, mp 136 °C (methanol).

Method B: A solution of 5-benzyl-4-chloropyridocarbazolone **4c** (2.74 g, 8 mmol) in excess piperidine (10 mL) was heated at 180 °C for 6 hours in a sealed tube (5 bar) and worked-up as described for method A. The yield was 1.55 g (65 %), yellow prisms, mp 136 °C (methanol); ir: 3400-2800 s, 1667 s, 1622 s, 1586 s, 1575 s cm^{-1}; ^1H nmr ($CDCl_3$): δ 3.2 (t, J = 7.9 Hz, CH_2) 3.52 (t, J = 8.0 Hz, CH_2), 7.24-7.34 (m, 9-H, 10-H), 7.24-7.34 (m, 5 PhH), 7.47-7.56 (m, 2-H, 11-H), 8.01 (d, J = 7.2 Hz, 3-H), 8.13 (d, J = 7.8 Hz, 1-H), 8.32 (d, J = 7.5 Hz, 8-H), 10.65 (s, NH); ms: *m/z* (%) 300 (15, M+1), 299 (M, 100), 295 (33), 167 (7), 132 (18), 104 (58).

Anal. Calcd. for $C_{21}H_{17}NO$: C, 84.25; H, 5.72; N, 4.68. Found: C, 84.64; H, 5.85; N, 4.66.

5-Phenyl-4-piperidin-1-ylpyrido[3,2,1-*jk*]carbazol-6-one (**6a**).

A solution of 4-chloro-5-phenylpyridocarbazol-one **4d** (3.30 g, 10 mmol) in excess piperidine (10 mL) was heated under reflux for 8 hours. The excess solvent was removed *in vacuo*, the mixture cooled to room temperature, treated with a mixture of hexane (10 mL) and diethylether (5 mL) and stirred for 1 hour. The resulting precipitate was filtered by suction, washed with hexane (10 mL) and dried. The yield was 2.25 g (59%) yellow prisms, mp 184 °C (ethanol); ir: 2800 - 3000 s, 1653 s, 1600 s, 1544 s cm^{-1}; ^1H nmr ($CDCl_3$): δ 1.67 (t, J = 5.7 Hz, 3 CH_2 of piperidine), 2.93 (m, 2 N-CH_2 of piperidine), 7.37-7.48 (m, 5 PhH), 7.48 and 7.56 (2 t, J = 7.6 Hz, 2-H, 9-H, 10-H), 7.93, 8.08 and 8.12 (3 d, J = 7.6 Hz, 1-H, 3-H, 11-H), 8.71 (d, J = 8.1 Hz, 8-H).

Anal. Calcd. for $C_{26}H_{22}N_2O$: C, 82.51; H, 5.86; N, 7.40. Found: C, 82.28; H, 5.74; N, 7.34.

4-Morpholin-4-yl-5-phenylpyrido[3,2,1-*jk*]carbazol-6-one (**6b**).

This compound was obtained from 4-chloro-5-phenylpyrido-

carbazolone (**4d**) (3.30 g, 10 mmol) in excess morpholine (10 mL) using the procedure and work-up described for **6a**. The yield was 2.16 g (57%) yellow prisms, mp 190 °C (ethanol); ir: 2800 - 3000 s, 1644 s, 1600 s, 1541s cm^{-1}; ^1H nmr ($CDCl_3$): δ 2.99 (m, 2 CH_2 of morpholine), 3.80 (t, J = 4.4 Hz, 2 CH_2 of morpholine), 7.38-7.49 (m, 5 PhH), 7.51 and 7.57 (2 t, J = 7.8 Hz, 2-H, 9-H, 10-H), 7.90, 8.08 and 8.14 (3 d, J = 7.9 Hz, 1-H, 3-H, 11-H), 8.71 (d, J = 7.7 Hz, 8-H).

Anal. Calcd. for $C_{25}H_{20}N_2O_2$: C, 78.93; H, 5.30; N, 7.36. Found: C, 78.65; H, 5.22; N, 7.28.

4-Azido-pyrido[3,2,1-*jk*]carbazol-6-ones (**7b-d**).

These compounds were obtained from appropriate substituted 4-hydroxypyridocarbazolones **1** or 4-chloro-pyridocarbazolones **4** and sodium azide according to the methods described in ref [1].

5-Ethyl-4-triphenylphosphoranylideneaminopyrido[3,2,1-*jk*]carbazol-6-one (**8b**).

To a solution of triphenylphosphane (1.57 g, 6 mmol) in dry toluene (15 mL) was added 4-azido-5-ethylpyridocarbazolone **7b** (1.44 g, 5 mmol); then the reaction mixture was heated for 14 hours to 90 °C under stirring. The reaction mixture was cooled to 50 °C, then toluene (10 mL) and cyclohexane (20 mL) was added, the precipitate filtered by suction and washed with cyclohexane. The yield was 2.30 g (88%), yellowish prisms, mp 192 °C (dioxane/toluene); ir: 3051 - 2928 s, 1645 s, 1626 s, 1598 s cm^{-1}; ^1H nmr ($CDCl_3$): δ 0.97 (t, J = 7.4 Hz, Me), 2.77 (q, J = 7.4 Hz, CH_2), 7.14 and 7.41 (2 t, J = 7.7 Hz, 2-H, 9-H), 7.69-7.74 (m, 10-H, 5 PhH), 7.45-7.59 (m, 11-H, 10 PhH), 7.93 (d, J = 7.4 Hz, 1-H), 8.02 (d, J = 7.6 Hz, 3-H), 8.79 (d, J = 8.1 Hz, 8-H).

Anal. Calcd. for $C_{35}H_{27}N_2OP$: C, 80.44; H, 5.21; N, 5.36. Found: C, 80.44; H, 5.28; N, 5.28.

5-Phenyl-4-triphenylphosphoranylideneamino-pyrido[3,2,1-*jk*]carbazol-6-one (**8d**).

This compound was obtained from triphenylphosphane (3.14 g, 12 mmol) and 4-azido-5-phenylpyridocarbazolone **7d** (3.36 g, 10 mmol) using the procedure and work-up described for **8b**; the yield was 4.70 g (82 %), yellow prisms, mp 223 °C (dioxane/toluene); ir: 3057 s, 2360 s, 1626 s, 1599 s cm^{-1}; ^1H nmr (DMSO-d_6): δ 7.11-7.54 (m, 20 PhH, 2-H, 9-H, 10-H, 1-H), 8.01 (d, J = 7.5 Hz, 11- H), 8.04 (d, J = 7.7 Hz, 3-H), 8.75 (d, J = 8.2 Hz, 8-H).

Anal. Calcd. for $C_{39}H_{27}N_2OP$: C, 82.09; H, 4.77; N, 4.91. Found: C, 81.96; H, 4.66; N, 4.84.

4-Amino-5-ethylpyrido[3,2,1-*jk*]carbazol-6-one (**9b**).

Method A: A solution of 5-ethyl-4-triphenylphosphoranylideneaminopyridocarbazolone **8b** (1.50 g, 2.9 mmol) in acetic acid (75%, 40 mL) was heated to 100 °C for 4 hours. Then the reaction mixture was poured into ice/water (200 mL), the precipitate filtered by suction and washed with water (100 mL). The yield was 0.36 g (68%) colorless powder, mp 243 °C (ethyl acetate/ethanol).

Method B: A mixture of 4-azido-5-ethylpyridocarbazolone **7b** (0.30 g, 1 mmol) and palladium/charcoal (10%, 0.30 g) in glacial acetic acid (100 mL) was hydrogenated under pressure (3 bar) at 50 °C for 6 hours and then filtered at 90 °C. The filtrate was taken to dryness *in vacuo*, and the residue dissolved in ethanol (50 mL), precipitated with water (50 mL), filtered by suction and crystallized from ethanol. The yield was 0.23 g (88%), yellowish prisms, mp 243 °C (toluene/dioxane).

Method C: a) Amberlite-supported formate was prepared using a modified method described in ref. [11] by treatment of Amberlit IRA 400 (Cl^- form) with formic acid: Amberlite IRA 400 (10 g) was suspended in water (3x 50 mL) and filtered by suction. Then the resin was washed with dichloromethane (3x 100 mL), then stirred for 2x10 min in a mixture of formic acid (2x10 mL) and dichloromethane (2x25 mL), filtered by suction and washed with dichloromethane (2x50 mL). The resin was obtained solvent-free by suction filtration and the solid dried at 60 °C for 12 hours.

b) To a solution of 4-azido-5-ethylpyridocarbazolone **7b** (0.50 g, 1.7 mmol) in glacial acetic acid (200 mL) Amberlite-supported formate (3.2 g) was added as hydrogen generator and palladium/charcoal (10%, 0.50 g) as catalyst. The mixture was heated to 90 °C under stirring for 24 hours, the solvent removed *in vacuo*, the black residue heated in boiling ethanol (100 mL) and filtered while hot. The filtrate was taken to dryness *in vacuo* and the residue crystallized from ethanol. The yield was 0.30 g (67%) colorless powder, mp 243 °C (ethanol); ir: 3349 s, 1649 s, 1640 s, 1619 s, 1594 s, 1577 s cm^{-1}; ^1H nmr (DMSO-d_6): δ 1.09 (t, J = 7.3 Hz, Me), 2.67 (q, J = 7.3 Hz, CH_2), 6.84 (s, NH_2), 7.44 (t, J = 7.5 Hz, 2-H), 7.52-7.57 (m, 9-H, 10-H), 8.23 (d, J = 7.8 Hz, 1- H, 11-H), 8.29 (d, J = 7.5 Hz, 3-H), 8.58 (d, J = 8.0 Hz, 8-H).

Anal. Calcd. for $C_{17}H_{14}N_2O$: C, 77.84; H, 5.38; N, 10.68. Found: C, 77.90; H, 5.31; N, 10.32.

4-Amino-5-benzylpyrido[3,2,1-*jk*]carbazol-6-one (**9c**).

Method D: A mixture of 5-benzyl-4-benzylaminopyridocarbazolone **3e** (0.50 g, 1.2 mmol), palladium/charcoal (10%, 0.20 g) and glacial acetic acid (150 mL) was hydrogenated under pressure (3 bar) at 60 °C for 4 hours. The reaction mixture was then filtered at 90 °C and the filtrate taken to dryness *in vacuo* The residue was dissolved in dimethylformamide (50 mL), filtered at 150 °C, cooled to room temperature, filtered by suction and washed with water. The yield was 0.25 g (64%) yellow prisms, mp 234 °C (ethanol/ethyl acetate).

Method E: To a solution of 5-benzyl-4-benzylaminopyridocarbazolone **3e** (0.50 g, 1.2 mmol) in glacial acetic acid (10 mL), Amberlite-supported formate [11] (1.5 g) was added as hydrogen generator and palladium/charcoal (10%, 0.50 g) as catalyst. The mixture was heated to reflux under stirring for 8 hours, the solvent removed *in vacuo*, the black residue heated in boiling dimethylformamide (100 mL) and filtered while hot. The filtrate was treated with water the formed precipitate filtered by suction and washed with water (50 mL). The yield was 0.26 g (80%), yellow prisms, mp 234 °C (ethanol/ethyl acetate). Under the same conditions with 1.0 g palladium acetate as catalyst, the yield was 0.27 g (83%); ir: 3500 - 2900 s, 1649 s, 1616 s, 1590 s, 1574 s cm^{-1}; ^1H nmr (DMSO-d_6): δ 4.01 (s, CH_2). 6.97 (s, NH_2), 7.14 (t, J = 7.3 Hz, 1 ArH), 7.37 (m, 2 ArH), 7.24 (m, 2 ArH), 7.44 (t, J = 7.7 Hz, 1 ArH), 7.58 (m, 2 ArH), 8.25 (m, 1-H, 11-H), 8.32 (d, J = 7.5 Hz, 3-H), 8.57 (d, J = 8.1 Hz, 8-H).

Anal. Calcd. for $C_{22}H_{16}N_2O$: C, 81.46; H, 4.97; N, 8.64. Found: C, 81.85; H, 4.99; N, 8.58.

4-Amino-5-phenylpyrido[3,2,1-*jk*]carbazol-6-one (**9d**).

Method A: This compound was obtained from 5-phenyl-4-triphenylphosphoranylideneamino-pyrido[3,2,1-*jk*]carbazol-6-one (**8d**) (1.00 g, 1.8 mmol) in acetic acid (75%, 35 mL) according to the procedure and work-up described for **9b** (method A); the yield was 0.45 g (85 %), yellow prisms, mp 230 °C (ethanol/ethyl acetate).

Method F: An intimate mixture of 4-hydroxy-5-phenylpyridocarbazolone **1d** (1.55 g, 5 mmol) and benzylammonium chloride (3.0 g, 21 mmol) was heated to 240 °C for 6 hours without solvent. After cooling to room temperature, water (20 mL) was added to the mixture and the solid was crushed, filtered by suction and washed with water. The solid was stirred in 0.25 *M* sodium hydroxide solution (100 mL) for 30 min at room temperature, then filtered by suction, washed and dried. The residue was purified by dry column flash chromatography (silica gel 60 H; elution with hexane and ethyl acetate). The yield was 0.54 g (35%) yellow prisms, mp 230 °C (ethyl acetate); ir: 3315 s, 1645 s, 1619 s, 1591 s cm^{-1}; ^1H nmr ($CDCl_3$): δ 6.56 (s, NH_2), 7.38-7.44 (m, 5 PhH), 7.47, 7.53 and 7.58 (3 t, J = 7.0 Hz, 2-H, 9-H, 10-H), 8.27 and 8.34 (3 d, J = 7.7 Hz, 1-H, 3-H, 11-H), 8.37 (d, J = 7.5 Hz, 8-H); ms: *m/z* (%) 311 (3, M+1), 310 (6, M), 309 (3, M–1), 167 (18, carbazol), 120 (100), 118 (48), 77 (100).

Anal. Calcd. for $C_{21}H_{14}N_2O$: C, 81.27; H, 4.55; N, 9.03. Found: C, 80.88; H, 4.60; N 8.75.

5-Phenyl-6,13b-diaza-indeno[1,2,3-*hi*]chrysen-14-one (**10**).

An intimate mixture of 4-hydroxy-5-phenylpyridocarbazolone **1d** (1.55 g, 5 mmol) and benzylammonium chloride (3.0 g, 21 mmol) was heated to 300 °C for 6 hours without solvent. After cooling to room temperature, water (20 mL) was added to the mixture and the solid was crushed, filtered by suction and washed with water. The solid was stirred in 0.25 *M* sodium hydroxide solution (100 mL) for 30 min at room temperature, then filtered by suction, washed and dried. The yield was 1.07 g (54%) yellow prisms, mp 275 °C (dimethylformamide/methanol); ms: m/z (%) = 396 (m, 100); ir: 3000 s, 1668 s, 1603 s, 1564 s cm^{-1}; ^1H nmr ($CDCl_3$): δ 7.51 and 7.61 (2 t, J = 7.4 Hz, 2-H, 3-H), 7.71-7.63 (m, 5 PhH), 7.90, 7.91 and 7.98 (3 t, J = 7.5 Hz, 8-H, 11-H, 12-H), 8.11, 8.17, 8.29, 8.80, 8.95 and 10.33 (6 d, J = 7.6-8.5 Hz, 1-H, 4-H, 7-H, 9-H, 10-H, 13-H).

Anal. Calcd. for $C_{28}H_{16}N_2O$: C, 84.83; H, 4.07; N, 7.07. Found: C, 84.96; H, 3.96; N, 6.93.

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