Synthesis and Ring Closure Reactions of Pyrido[3,2,1-*jk*]carbazol-6-ones[1]

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4-Hydroxy-5-phenylpyrido[3,2,1-*jk*]carbazol-6-ones (**4**, **5**), which were obtained from carbazoles **1** and malonates **2** or **3**, were converted to reactive intermediates such as 4-chlorides **9** or 4-tosylates **10**, which gave in turn 4-azido-5-phenyl derivatives **11**. 5-Alkyl-4-azides **11** were not obtained in this manner; however a new one-pot azidation reaction was developed starting from 4-hydroxy derivatives **4** which gave azides **11** in good yields. 4-Azido-5-phenyl derivative **11f** cyclized on thermolysis to the indole **12**. The thermal behaviour of the azides **11** was studied by thermoanalytical methods (DSC).

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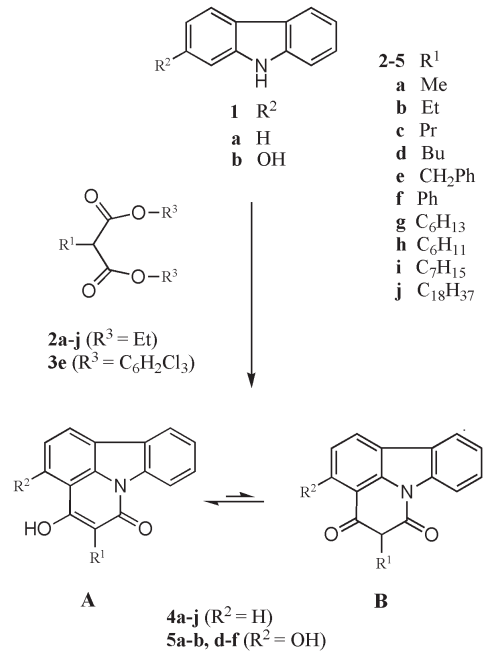
Pyrido[3,2,1-*jk*]carbazol-6-one is part of the heterocyclic skeleton of many natural products (*e.g.*, strychnos alkaloids such as strychninolones and brucinolones [2], picrasidin Q [3] and olivacine alkaloids [4]). It possesses the biologically interesting combination of indole and 2-pyridone structures. Moreover, some derivatives have found interest in pharmacological [5] or in dye chemistry [6]. Our interest is focused to 4-hydroxy-5-substituted pyrido[3,2,1-*jk*]carbazol-6-ones (**4**, **5**) which possess 2 reactive positions: the hydroxy group at C-4, which can be substituted by various nucleophiles, and the CH-acidic proton at C-5, which reacts with a large number of electrophiles. In this contribution we want to report an improved synthesis of 4-hydroxy-5-substituted pyrido-[3,2,1-*jk*]carbazol-6-ones, the acetylation, tosylation and the nucleophilic exchange of the hydroxy groups.

The synthesis of some 4-hydroxy-5-substituted pyrido[3,2,1-*jk*]carbazol-6-ones **4** is described in the literature in a few cases either by thermal condensation of malonates **2** with carbazole **1a** at about 300 °C with moderate yields [7], or by thermal condensation of dichlorophenylmalonates with carbazole **1** at 260 °C with good yields [8]. We adopted the cyclocondensation methods of malonates with 1,3-dinucleophiles earlier described for quinolones and related compounds [9] for the synthesis of 4-hydroxy-5-substituted pyrido[3,2,1-*jk*]carbazol-6-ones **4** and **5**. The first reaction step leads in a condensation reaction at about 200 °C to the monoanilides of the carbazole **1a** with the malonates **2**; the end of this reaction step can be easily observed by the end of ethanol evolution; further thermolysis at higher temperatures (300-350 °C) gives, by elimination of the second equivalent of ethanol, an intermediate α-oxo ketene which attacks in an electrophilic reaction the *ortho*-position of the aromatic ring to cyclize to the pyrido[3,2,1-*jk*]carbazol-6-ones **4**. The yields of this reaction type are within 60-90% except with the octadecyl malonate **2j**; in this case only 24% of **4j** was obtained. It was also possible to carry out this reaction in one step without interruption when a 1:1 mixture of the malonate and the carbazole **1a** was heated for 12 hours in refluxing diphenyl ether solution which limits the thermolysis temperature to 253 °C. The yields are within 60-80% comparable to the stepwise reaction; the workup however is easier and the purity of the products is better.

The more reactive hydroxycarbazoles **1b** reacted already in refluxing malonate **2** (190-280 °C depending on the substituent R^1 of **2**) in a 1:2 mixture in similar yields in 1 hour to the 3,4-dihydroxypyrido[3,2,1-*jk*]carbazol-6-ones **5**. The electron rich hydroxy substituted carbazole part was the favored cyclization partner and no formation of isomers was observed. At these short reaction times and comparable low reaction temperatures we expected a further

Scheme 1

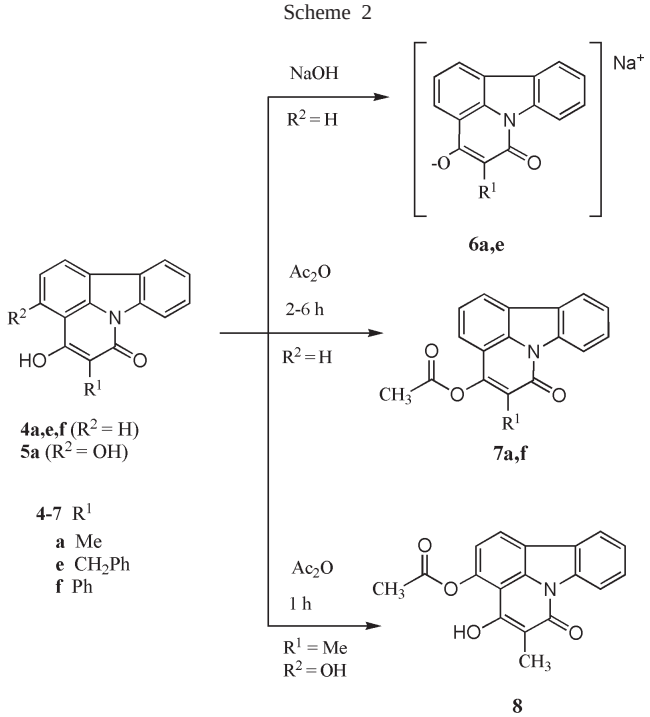


reaction: as shown in similar systems such as 2-naphthols [10,11], the kinetically controlled reaction should lead in a first step *via* the hydroxycarbazole ester to an indolocoumarin, which on thermal rearrangement should give the thermodynamically stable pyrido[3,2,1-*jk*]carbazol-6-ones **5**. However, we could not find in any case coumarin derivatives neither as the major product nor as byproduct. Also attempts with highly reactive malonates such as bis-(2,4,6-trichlorophenyl)benzylmalonate **3e** [12], which cyclized in 15 minutes at 210 °C with 2-hydroxycarbazole (**1b**) afforded pyrido[3,2,1-*jk*]carbazol-6-ones **5**; no trace of a coumarin derivative could be detected.

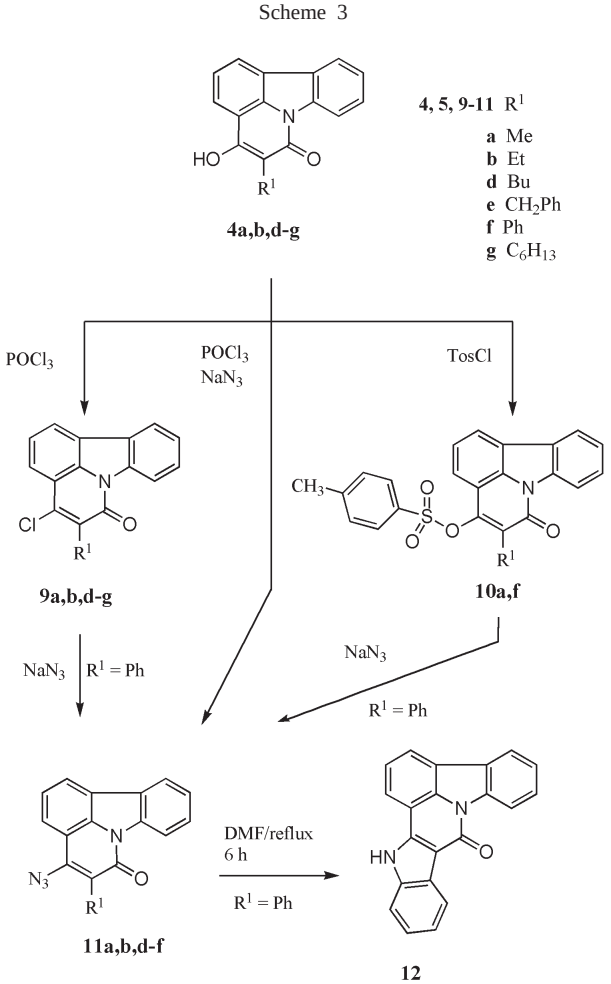
Pyrido[3,2,1-*jk*]carbazolones **4** and **5** can exist in 2 tautomeric structures **A** and **B**. Both spectroscopic data and chemical reactivity confirm that the hydroxy structure **A** is favored: nmr spectra of **4** and **5** do not show an aliphatic proton of **B** at C-5, but the 4-hydroxy signal of **4** at 10.8-11.0 ppm; ir spectra reveal only amide carbonyl signals between 1640 and 1660 cm^{-1}. The dioxo tautomers of type **B** exist only in fixed derivatives such as 5-alkyl-5-arylpyrido[3,2,1-*jk*]carbazol-4,6-diones [13]. The hydroxy form is obviously present when rather stable sodium salts of **4** are formed: already in the synthesis of **4a** and **4e** we found, that during work-up with sodium hydroxide solution an insoluble sodium salt **6a** and **6e** as byproduct was produced, which could be purified and recrystallized. Acetylation of hydroxy derivatives **4a**,**f** with refluxing acetic anhydride formed in 2-6 hours 4-acetyoxypyrido-[3,2,1-*jk*]carbazolones **7**. The acetylation of dihydroxy derivative **5a** afforded in one hour reaction time only the monoacetoxy product **8**. Comparison of nmr signals showed, that the acetylation of **5a** has taken place at the 3- and not at the 4-hydroxy group, probably by kinetically controlled reaction which favors the 3-hydroxy group because of higher reactivity or lack of hydrogen bonds.

Nucleophilic displacement of the 4-hydroxy group of **4** by chlorine was easily achieved by reaction with phosphoryl chloride to give 4-chloropyrido[3,2,1-*jk*]carbazolones **9** in 50-80% yield; 3,4-dihydroxypyrido[3,2,1-*jk*]carbazoles **5** afforded only a mixture of compounds which was not worked up. The nucleophilic exchange of 4-chloro substituents in **9** against the azide group to form 4-azidopyrido[3,2,1-*jk*]carbazolones **11** was only possible with a 5-phenyl substituent in **9f**. With 5-alkyl substituents, only mixtures of the azido product, the chloro product and decomposition products were obtained. For the synthesis of these desired 5-alkyl-4-azidopyrido[3,2,1-*jk*]carbazolones **11**, however, we developed a new one-pot synthesis starting from 4-hydroxypyrido[3,2,1-*jk*]carbazolones **4**, sodium azide and phosphoryl chloride in dimethylformamide. The yield was only 20-50%, but the

Scheme 2



Scheme 3



purity of the products obtained with this method was excellent. Another method for the introduction of azido groups, which was performed successfully in many similar cases (*e.g*., [14]), is the nucleophilic exchange of tosyloxy substituents. In the pyrido[3,2,1-*jk*]carbazolone series, however, again only the reactive 5-phenyl-4-tosyloxy derivative **10f** reacted to the azide **11f**. The example reaction of the 5-methyl derivative **10a** gave again a mixture of compounds containing **11a** that was not further worked up.

Organic azides with reactive *ortho*-groups such as aryl-, heteroaryl- or acyl groups are known to decompose on thermolysis or photolysis followed by a cyclization to heterocycles, either *via* a nitrene or an electrocyclic mechanism [15]. Mainly, this cyclization type leads to five-membered heterocycles. A typical example is the attack of the azide nitrogen to the 2-position of a phenyl ring in *ortho*-position to the azide forming indoles. We have studied a large number of azido heterocycles as candidates for such ring closure or decomposition reactions and we have found that differential scanning calorimetry (DSC) is an excellent tool both for the prediction of the reaction conditions and furthermore for safety hints [11,16]. The DSC diagram of the 4-azido-5-phenyl derivative **11f** showed a single well-shaped signal for the azide decomposition and cyclization, with the typical high reaction enthalpy of -700 J/g [16]. The onset for the cyclization reaction was 165 °C, which allowed us to chose - after consideraton of the typical downshift solvent effects for thermolysis [17] - refluxing dimethylformamide as the solvent for decomposition. In the preparative scale, **11f** gave on cyclization in 60% yield the highly fused indolo[2,3:4,5]pyrido[3,2,1-*jk*]carbazol-9-one **12**, a hitherto unknown heterocyclic system.

In contrast to the well-shaped DSC diagram of **11f**, the DSC diagrams of **11a-e** showed the typical follow-up series of undefined decomposition maxima together with rather low reaction enthalpies (between -20 and -50 J/g), which made further experiments unnecessary.

EXPERIMENTAL

Melting points were determined on a Gallenkamp Melting Point Apparatus, Mod. MFB-595 in open capillary tubes. Calorimetric data were obtained on a Rheometric Scientific DSC-Plus instrument with the differential scanning calorimetry software Orchestrator V6.2.2. The differential scanning calorimetry plots were recorded between 25 and 400 °C, with a heating rate of 2-10 °C/min, and 1.5-3 mg compound in sealed aluminium crucibles (11 bar). The ^{1}H nmr spectra were recorded on a Bruker AMX 360 instrument (360 MHz) or on a Bruker Avance DRX instrument (500 MHz). The ^{13}C nmr-spectra were recorded on a Bruker AM 360 instrument (90 MHz). Chemical shifts are reported in ppm from internal tetramethylsilane standard and are given in δ-units. The solvent for NMR spectra was deuteriodimethyl sulfoxide unless otherwise stated. Evaluation of the spectra was performed using the software Mestrec 3. Infrared spectra were taken on a Galaxy Series FTIR 7000 in potassium bromide pellets. 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 LC/MSD mass spectral instrument (ESI or APCI: 50-200 eV, nitrogen). 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. Diethyl 2-hexylmalonate (**2g**) was prepared from 1-bromohexane and diethyl malonate as described in ref. [18]. Diethyl 2-cyclohexylmalonate (**2h**) was prepared from 1-bromocyclohexane and diethyl malonate as described in ref. [19]. Diethyl 2-heptylmalonate (**2i)** was prepared from 1-bromoheptane and diethyl malonate as described in ref. [20]. Diethyl 2-octadecylmalonate (**2j**) was prepared from 1-bromooctadecane and diethyl malonate as described in ref. [21]. Bis-(2,4,6-trichlorophenyl) benzylmalonate (**3e**) was prepared from 2,4,6-trichlorophenol and malonic acid as described in ref. [12].

General Procedure for the Preparation of 4-Hydroxypyrido-[3,2,1-*jk*]carbazole-6-ones (**4**).

Method A.

A mixture of the appropriate alkyl- or arylmalonate **2** (0.12 mol) and carbazole **(1a)** (16.7 g, 0.10 mol) was heated to about 250 °C for 2 hours using distillation equipment. During this period the first equivalent of ethanol (about 5 mL) was liberated. Then the temperature was raised to about 330 °C for 30 min. During this period the second equivalent of ethanol (about 4.5 mL) was liberated. After cooling to about 80-100 °C the residue was triturated with methanol; the solid product was collected by suction filtration, washed with cold methanol, dissolved in aqueous sodium hydroxide (0.25 *M*, 1000 mL) and insoluble products were removed by filtration. The filtrate was extracted with toluene (2x 250 mL) and cleared with charcoal (about 7 g). To obtain the product the filtrate was acidified with conc. hydrochloric acid (50 mL); the solid was collected by filtration, washed several times with water, recrystallized from the solvent listed below and dried at 80-100 °C.

Method B.

A solution of the appropriate alkyl- or arylmalonate **2** (0.12 mol) and carbazole (**1a**) (16.7 g, 0.1 mol) in diphenylether was heated under reflux for 12 hours. During this period ethanol (about 9-10 mL) was liberated. Then the excess of diphenyl ether was removed *in vacuo*, the residue was triturated with hexane and the solid collected by suction filtration. The solid product was dissolved in aqueous sodium hydroxide (0.25 *M*, 1000 mL); further workup was accomplished as described in method A.

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

This compound was obtained from diethyl methylmalonate (**2a**) (20.9 g, 0.12 mol) using method B; the yield was 19.66 g (79 %) pale yellow powder, mp 276 °C (ethanol); ir: 3500-2900 m, 1650 s, 1626 s, 1562 s cm^{-1}; ^{1}H nmr: δ 2.20 (s, CH_3), 7.52 and 7.63 (2 t, J = 7.4 Hz, 2-H, 9-H, 10-H), 8.14, 8.29 and 8.36 (3 d, J = 7.6 Hz, 1-H, 3-H, 11-H), 8.61 (d, J = 8.4 Hz, 8-H), 10.91 (s, OH).

Anal. Calcd. for $C_{16}H_{11}NO_2$: C, 77.10; H, 4.45; N, 5.62. Found: C, 77.36; H, 4.39; N, 5.51.

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

This compound was obtained from diethyl ethylmalonate (**2b**) (22.5 g, 0.12 mol) using method A; the yield was 15.2 g (58 %) colorless prisms, mp 257 °C (toluene), lit. mp. 257-258 °C [7]; ir: 3450-3000 m, b, 1640 m, 1620 s, 1595 s, 1575 m cm^{-1}.

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

This compound was obtained from diethyl propylmalonate (**2c**) (24.2 g, 0.12 mol) using method B; the yield was 20.56 g (74%) colorless prisms, mp 247.5 °C (acetic acid); ir: 3350-3100 b, 2960 w, 2840 w, 1640 sh, 1630s, 1595 m, 1575 m cm^{-1}; ^{1}H nmr: δ 0.96 (t, J = 7 Hz, CH_3), 1.54 (q, J = 7 Hz, CH_2), 2.67 (t, J = 7 Hz, Ar-CH_2), 7.48 and 7.58 (2 t, J = 7 Hz, H-2, H-9, H-10), 8.10, 8.24 and 8.31 (3 d, J = 7 Hz, 1-H, 3-H, 11-H), 8.57 (d, J = 7 Hz, 8-H), 10.80 (s, br, OH).

Anal. Calcd. for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45; N, 5.05. Found: C, 77.60; H, 5.38; N, 5.02.

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

This compound was obtained from diethyl butylmalonate (**2d**) (25.9 g, 0.12 mol); using method A, the yield was 22.4 g (77 %); using method B, the yield was 17.5 g (59%); pale yellow powder, mp 242-243 °C (acetic acid); ir: 3350-3040 m, 2960-2840 w, 1640 m, 1630 w, 1620 s, 1595 s, 1575 m cm^{-1}; ^{1}H nmr: δ 0.91 (t, J = 7 Hz, CH_3), 1.33-1.41 (m, CH_2), 1.48-1.52 (m, CH_2), 2.69 (t, J = 7 Hz, Ar-CH_2), 7.46 and 7.57 (2 t, J = 7 Hz, 2-H, 9-H, 10-H), 8.05, 8.27 and 8.33 (3 d, J = 7 Hz, 1-H, 3-H, 11-H), 8.52 (d, J = 7 Hz, 8-H), 10.80 (s, br, OH).

Anal. Calcd. for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88; N, 4.81. Found: C, 78.19; H, 5.93; N, 4.71.

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

This compound was obtained from diethyl benzylmalonate (**2e**) (30.0 g, 0.12 mol); using method A, the yield was 25.3 g (78 %); using method B, the yield was 26.9 g (83%) colorless prisms, mp 252 °C; lit. mp 247-248 °C [8]; ir: 3500-2900 m, 1640 s cm^{-1}; ^{1}H nmr: δ 4.05 (s, CH_2), 7.14 (t, J = 7.0 Hz, 4-H of benzyl), 7.24 (t, J = 7.6 Hz, 3-H and 5-H of benzyl), 7.35 (d, J= 7.0 Hz, 2-H and 6-H of benzyl), 7.50, 7.60 and 7.63 (3 t, J = 7.5 Hz, 2-H, 9-H, 10-H), 8.18, 8.28 and 8.38 (3 d, J = 7.7 Hz, 1-H, 3-H,11-H), 8.57 (d, J = 8.3 Hz, 8-H).

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

This compound was obtained from diethyl phenylmalonate (**2f**) (28.3 g, 0.12 mol); using method A, the yield was 28.0 g (90 %); using method B, the yield was 23.3 g (75%) pale yellow prisms, mp 215-216 °C (ethanol), lit. mp 207-210 °C [7,8]; ir: 3220-3000 m, 1650 s, 1625 m, 1610 s, 1594 s, 1575 s cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 7.46-7.61 (m, 2-H, 9-H, 10-H of carbazole, 2 PhH), 8.03, 8.09 and 8.18 (3 d, J = 7.7 Hz, 1-H, 3-H, 11-H), 8.71 (d, J = 8.1 Hz, 8-H), 11.00 (s, OH).

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

This compound was obtained from diethyl hexylmalonate (**2g**) (29.3 g, 0.12 mol) using method A; the yield was 21.0 g (66%), pale yellow prisms, mp 167-171 °C (acetic acid); ir: 3400-3100 b, 2960-2880 w, 1640 m, 1620 s, 1595 s cm^{-1}; ^{1}H nmr: δ 0.85 (t, J = 7 Hz, CH_3) 1.25-1.65 (m, 4 CH_2), 2.60 (t, J = 7 Hz, Ar-CH_2), 7.36-7.70 (m, 2-H, 9-H, 10-H), 8.15-8.35 (m, 1-H, 3-H, 11-H), 8.60 (d, J = 7 Hz, 8-H), 11.00 (s, OH).

Anal. Calcd. for $C_{21}H_{21}NO_2$: C, 78.97; H, 6.63; N, 4.39. Found: C, 79.06; H, 6.21; N, 4.33.

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

This compound was obtained from diethyl cyclohexylmalonate (**2h**) (29.0 g, 0.12 mol) using method A; the yield was 21.5 g (68%) colorless prisms, mp 218.3 °C (acetic acid); ir: 3500-3100 b, 2920 m, 2850 w, 1640 sh, 1620 s, 1600 m cm^{-1}; ^{1}H nmr: δ 1.10-1.90 (m, 5 CH_2), 2.25 (t, J = 7 Hz, CH), 7.40-7.70 (m, 2-H, 9-H, 10-H), 8.20-8.40 (m, 1-H, 3-H, 11-H), 8.61 (d, J = 7 Hz, 8-H).

Anal. Calcd. for $C_{21}H_{19}NO_2$: C, 79.47; H, 6.03; N, 4.41. Found: 79.09; H, 5.68; N, 4.07.

5-Heptyl-4-hydroxypyrido[3,2,1-*jk*]carbazol-6-one (**4i**).

This compound was obtained from diethyl heptylmalonate (**2i**) (31.0 g, 0.12 mol); using method A, the yield was 18.0 g (57 %); using method B, the yield was 21.9 g (66%) pale yellow prisms, mp 167-171 °C; ir: 3400-3100 b, 2920 s, 2850 s, 1645 m, 1620 s, 1595 s, 1580 s cm^{-1}; ^{1}H nmr: δ 0.85 (t, J = 7 Hz, CH_3), 1.20-1.75 (m, 5 CH_2), 2.71 (t, J =7 Hz, Ar-CH_2), 7.42-7.75 (m, 2-H, 9-H, 10-H), 8.10-8.42 (m, 1-H, 3-H, 11-H), 8.62 (dd, J = 2 and 7 Hz, 8-H).

Anal. Calcd. for $C_{22}H_{23}NO_2$: C, 79.25; H, 6.95; N, 4.20. Found: C, 79.61; H, 6.58; N, 4.02.

4-Hydroxy-5-octadecylpyrido[3,2,1-*jk*]carbazol-6-one (**4j**).

This compound was obtained from diethyl octadecylmalonate (**2j**) (49.6 g, 0.12 mol) using method A; the yield was 11.6 g (24%) pale yellow powder, mp 231 °C (acetic acid); ir: 3400-3100 b, 2920 s, 2850 s, 1645 m, 1620 s, 1595 s, 1580 s cm^{-1}.

Anal. Calcd. for $C_{33}H_{45}NO_2$: C, 81.27; H, 9.30; N, 2.87. Found: C, 80.94; H, 9.67; N, 2.88.

General Procedure for the Preparation of 3,4-Dihydroxypyrido-[3,2,1-*jk*]carbazol-6-ones (**5**).

A mixture of 2-hydroxycarbazole (**1b**) (1.82 g, 10 mmol) and the appropriate substituted malonate **2** (20 mmol) was heated for 1 hour under reflux (about 250-300 °C) using distillation equipment. The 2-hydroxycarbazole first dissolved and then a white precipitate separated and 2 equivalents of ethanol (about 9-10 mL) were liberated. The reaction mixture was cooled to room temperature and then quenched with a mixture of diethylether/hexane (1:4). The obtained precipitate was collected by filtration, washed with hexane and recrystallized from the solvent listed below.

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

This compound was obtained from diethyl methylmalonate (**2a**) (3.4 g, 20 mmol); the yield was 2.49 g (94%), colorless needles, mp 274 °C (dimethylformamide); ir: 3380-2700 w, 1655 s, 1620 s, 1600 s, 1580 s cm^{-1}; ^{1}H nmr: δ 2.60 (s, CH_3), 6.98 (d, J = 7 Hz, H-2), 7.42 and 7.47 (2 t, J = 7 Hz, 9-H, 10-H), 8.03 and 8.09 (2 d, J = 7 Hz, 1-H, 11-H), 8.54 (d, J = 8 Hz, 8-H).

Anal. Calcd. for $C_{16}H_{11}NO_3$: C, 72.45; H, 4.18; N, 5.28. Found: C, 72.83; H, 4.26; N, 5.33.

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

This compound was obtained from diethyl ethylmalonate (**2b**) (3.9 g, 20 mmol); the yield was 2.34 g (84%) colorless prisms, mp 290 °C (dimethylformamide/water); ir: 3400-2700 m, 1655 s, 1610 s, 1595 s cm^{-1}; ^{1}H nmr: δ 1.15 (t, J = 7 Hz, CH_3), 2.60 (q, J = 7 Hz, CH_2), 6.95 (d, J = 7 Hz, 2-H), 7.30-7.69 (m, 9-H, 10-H), 7.95 and 8.05 (2 d, J = 8 Hz, 1-H, 11-H), 8.55 (d, J = 8 Hz, 8-H).

Anal. Calcd. for $C_{17}H_{13}NO_3$: C, 73.11; H; 4.69; N, 5.01. Found: C, 73.01; H, 4.72; N, 4.97.

5-Butyl-3,4-dihydroxy-pyrido[3,2,1-*jk*]carbazol-6-one (**5d**).

This compound was obtained from diethyl butylmalonate (**2d**) (4.4 g, 20 mmol); the yield was 2.52 g (82%), colorless needles, mp 310 °C (dimethylformamide); ir: 3375 m, 3240-2800 m, 1655 s, 1625 sh, 1610 s, 1595 s cm^{-1}; ^{1}H nmr (CF_3COOH): δ 1.05 (t, J = 7 Hz, CH_3), 1.40-1.80 (m, 2 CH_2), 2.70-3.10 (m, Ar-CH_2), 7.10 (d, J = 8 Hz, 2-H), 7.30-7.60 (m, 9-H, 10-H), 7.80 and 8.00 (2 d, J = 8 Hz, 1-H and 11-H), 8.25 (d, J = 8 Hz, 8-H).

Anal. Calcd. for $C_{19}H_{17}NO_3$: C, 74.25; H, 5.58; N, 4.56. Found: C, 74.30; H, 5.67; N, 4.58.

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

Method A: This compound was obtained from diethyl benzylmalonate (**2e**) (5.0 g, 20 mmol) using the general method for **5** in 1.8 g (53%) yield.

Method B: A mixture of 2-hydroxycarbazole (**1b**) (0.37 g, 2 mmol) and bis-(2,4,6-trichlorophenyl) benzylmalonate (**3e**) (1.1 g, 2 mmol) was heated for 15 min in an oil bath adjusted at 210 °C. Then the reaction mixture was cooled to room temperature and treated several times with a mixture of diethylether/hexane (1:4) until a solid was formed. The precipitate was collected by filration and recrystallized from dimethylformamide/methanol. The yield was 0.58 g (85%) as colorless plates, mp 280 °C (dimethylformamide/methanol); ir: 3380-2600 m, 1655 m, 1625 sh, 1615 s, 1600 s cm^{-1}; ^{1}H nmr: δ 4.15 (s, CH_2), 7.05 (d, J = 8 Hz, 2-H), 7.30-7.60 (m, 9-H, 10-H, 5 PhH of benzyl), 7.80 and 8.00 (2 d, J = 8 Hz, 1-H, 11-H), 8.12 (d, J = 7 Hz, 8-H).

Anal. Calcd. for $C_{22}H_{15}NO_3$: C, 77.41; H, 4.43; N, 4.10. Found: C, 76.93; H, 4.67; N, 4.31.

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

This compound was obtained from diethyl phenylmalonate (**2f**) (4.8 g, 20 mmol) using Method A; the yield was 2.4 g (86%), colorless prisms, mp 312 °C (DMF); ir: 3380-2700 m, 1655 m, 1620 sh, 1610 sh, 1600 s, 1570 s cm^{-1}; ^{1}H nmr: δ 7.38-7.44 (m, 2-H, 9-H), 7.45-7.50 (m, 5 PhH), 7.55 (t, J = 8 Hz, 10-H), 7. 62 and 8.41 (2 d, J = 8 Hz, 1-H, 11-H), 8.58 (d, J = 8 Hz, 8-H), 8.99 (s, OH).

Anal. Calcd. for $C_{21}H_{13}NO_3$: C, 77.06; H, 4.00; N, 4.28. Found: C, 76.91; H, 4.16; N, 4.43.

Sodium 5-Methyl-6-oxo-6*H*-pyrido[3,2,1-*jk*]carbazol-4-olate (**6a**).

A mixture of carbazole (**1a**) (8.35 g, 50 mmol) and diethyl methylmalonate (**2a)** (8.70 g, 50 mmol) was heated to 270 °C for 2 hours; the liberated ethanol was removed *via* an air condenser. The reaction mixture was cooled to 100 °C, then methanol was added and the solid material was crushed, collected by suction filtration, and dissolved in 1 *M* sodium hydroxide solution (200 mL). The alkaline solution was filtered by suction and the insoluble residue was isolated, washed with a small amount of cold water and dried. The yield was 9.83 g (79%), yellowish powder, mp > 350 °C (sublimation) (dimethylformamide); ir: 3500-2900 m, 1612 s, 1571 s cm-1; 1H nmr: δ 1.90 (s, CH_3), 7.35 and 7.48 (2 t, J = 7.4 Hz, 2-H, 9-H, 10-H), 7.85, 8.08 and 8.12 (3 d, J = 7.6 Hz, 1-H, 3-H, 11-H), 8.61 (d, J = 8.4 Hz, 8-H); MS: m/z (%) = 250 (M + 1 of **4a**, 100%).

Anal. Calcd. for $C_{16}H_{10}NNaO_2$: C, 70.85; H, 3.72; N, 5.16. Found: C, 70.61; H, 3.63; N, 4.76.

Sodium 5-Benzyl-6-oxo-6*H*-pyrido[3,2,1-*jk*]carbazol-4-olate (**6e**).

A mixture of carbazole (**1a**) (1.67 g, 10 mmol) and diethyl benzylmalonate (**2a)** (1.74 g, 10 mmol) was reacted and worked up according to the procedure described for **4e** (Method A). The residue, which was insoluble in 0.25 *M* sodium hydroxide solution, was isolated by filtration, washed with cold water and dried. The yield was 0.57 g (16%) colorless prisms, mp 245 °C from toluene/ethanol; ir: 3500-2900 m, 1711 s, 1684 s, 1599 s cm^{-1}; ^{1}H nmr: δ 4.05 (s, CH_2), 7.14 (t, J = 7.0 Hz, 4-H of benzyl), 7.24 (t, J = 7.6 Hz, 3-H and 5-H of benzyl), 7.35 (d, J = 7.0 Hz, 3-H and 6-H of benzyl), 7.48, 7.59 and 7.63 (3 t, J = 7.5 Hz, 2-H, 9-H, 10-H), 8.18, 8.26 and 8.36 (3 d, J = 7.7 Hz, 1-H, 3-H, 11-H), 8.55 (d, J = 8.3 Hz, 8-H).

Anal. Calcd. for $C_{22}H_{14}NNaO_2$: C, 76.07; H, 4.06; N, 4.03. Found: C, 75.74; N, 3.85; N, 3.67.

5-Methyl-6-oxo-6*H*-pyrido[3,2,1-*jk*]carbazol-4-yl Acetate (**7a**).

A mixture of the 4-hydroxy-pyridocarbazolone **4a** (1.30 g, 5 mmol), acetic anhydride (3.00 g, 29 mmol) and glacial acetic acid (20 mL) was heated under reflux for 2 hours. Then the reaction mixture was cooled to room temperature, poured into ice/water (100 mL). The solid was collected by suction filtration and washed with water. The yield was 1.20 g (68 %), yellow prisms, mp 190 °C (from ethyl acetate/ethanol); ir: 1770 s, 1664 s, 1636 sh, 1602 m cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 2.23 (s, acetyl-CH_3), 2.52 (s, CH_3), 7.45-7.60 (m, 2-H, 9-H, 10-H, 3-H), 8.04 and 8.08 (2 d, J = 7.6 Hz, 1-H, 11-H), 8.72 (d, J = 8.1 Hz, 8-H).

Anal. Calcd. for $C_{18}H_{13}NO_3$: C, 74.22 H; 4.50; N, 4.81. Found: C, 74.20 ; H, 4.48; N, 5.01

6-Oxo-5-phenyl-6*H*-pyrido[3,2,1-*jk*]carbazol-4-yl Acetate (**7f**).

A mixture of the 4-hydroxy-pyridocarbazolone **4f** (1.50 g, 4.6 mmol), acetic anhydride (3.00 g, 29 mmol) and glacial acetic acid (20 mL) was heated under reflux for 6 hours followed by work-up as described for **6a**. The yield was 1.20 g (68 %), yellow prisms, mp 207 °C (from ethyl acetate/ethanol); ir: 1773 s, 1666 s, 1639 s, 1608 s, 1574 s cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 2.17 (s, CH_3), 7.43-7.46 (m, 5 PhH), 7.46 and 7.55 (2 t, J = 7.6 Hz, 2-H, 9-H, 10-H), 7.64, 8.06 and 8.15 (2 d, J = 7.5 Hz, 1-H, 3-H, 11-H), 8.71 (d, J= 8.1 Hz, 8-H).

Anal. Calcd. for $C_{23}H_{15}NO_3$: C, 78.18; H, 4.28; N, 3.96. Found: C, 77.79; H, 4.16; N, 3.89.

4-Hydroxy-5-methyl-6-oxo-6*H*-pyrido[3,2,1-*jk*]carbazol-3-yl Acetate (**8**).

A solution of 3,4-dihydroxy-pyridocarbazolone **5a** (0.53 g, 2 mmol) in acetic anhydride (0.5 mL, 5 mmol) and acetic acid (4.5 mL) was heated under reflux for 1 hour, cooled to room temperature and taken to dryness under reduced pressure. The yield was 0.68 g (90%) colorless prisms, mp 292 °C (glacial acetic acid); ir: 3340-3100 m, 1765 m, 1730 w, 1700 s, 1640 s, 1615 m, 1590 m cm^{-1}; ^{1}H nmr (CF_3COOH): δ 1.80 (s, acetyl-CH_3), 2.60 (s, CH_3), 6.70-7.60 (m, 2-H, 9-H, 10-H), 8.00-8.20 (m, 1-H, 11-H, 8-H).

Anal. Calcd. for $C_{18}H_{13}NO_4$: C, 70.35; H, 4.26; N, 4.56. Found: C, 69.96; H, 4.61; N, 4.19.

4-Chloro-5-methylpyrido[3,2,1-*jk*]carbazol-6-one (**9a**).

A mixture of 4-hydroxypyridocarbazolone **4a** (2.49 g, 10 mmol) and phosphorylchloride (3.1 g, 20 mmol) was heated for 1 hour to 100 °C. The reaction mixture was cooled to room temper-

ature and then poured into ice/water (100 mL). The mixture was brought to pH 4-6 with 0.25 *M* sodium hydroxide solution; the solid, collected by suction filtration, was washed with water and dried. The yield was 2.00 g (75%), ash-grey powder, mp 162 °C from ethanol; ir: 3500-2900 m, 1664 s, 1602 s cm^{-1}; ^1H nmr ($CDCl_3$): δ 2.48 (s, CH_3), 7.47, 7.52 and 7.58 (3 t, J = 7.5 Hz, 2-H, 9-H, 10-H), 7.85, 8.00 and 8.04 (3 d, J = 7.4 Hz, 1-H, 3-H, 11-H), 8.66 (d, J = 7.8 Hz, 8-H).

Anal. Calcd. for $C_{16}H_{10}ClNO$: C, 71.78; H, 3.77; N, 5.23. Found: C, 71.88; H, 3.66; 5.08.

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

This compound was obtained from 4-hydroxypyridocarbazolone **4b** (2.73 g, 10 mmol) according to the procedure described for **9a**; the yield was 2.30 g (82%) yellowish prisms, mp 130 °C from ethanol; ir: 3500-2900, 1657 s, 1603 s cm^{-1}; ^1H nmr ($CDCl_3$): δ 1.30 (t, J = 7.5 Hz, CH_3), 3.04 (q, J = 7.3 Hz, CH_2), 7.51, 7.58 and 7.62 (3 t, J = 7.6 Hz, 2-H, 9-H, 10-H), 7.96, 8.08 and 8.14 (2 d, J = 7.8 Hz, 1-H, 3-H, 11-H), 8.74 (d, J = 7.8 Hz, 8-H).

Anal. Calcd. for $C_{17}H_{12}ClNO$: C, 72.47; H, 4.29; N, 4.97. Found: C, 72.30; H, 4.22; N, 4.87.

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

This compound was obtained from 4-hydroxypyridocarbazolone **4d** (2.91 g, 10 mmol) according to the procedure described for **9a**; the yield was 1.57 g (51%) yellowish powder, mp 194 °C; ir: 3400-2500, 1660 s, 1605 s cm^{-1}.

Anal. Calcd. for $C_{19}H_{16}ClNO$: C, 73.66; H, 5.21; N, 4.52. Found: C, 73.29; H, 5.13; N, 4.78.

5-Benzyl-4-chloropyrido[3,2,1-*jk*]carbazol-6-one (**9e**).

This compound was obtained from 4-hydroxypyridocarbazolone **4e** (3.25 g, 10 mmol) according to the procedure described for **9a**; the yield was 2.00 g (58%) colorless prisms, mp 242 °C from ethanol; ir: 3500-2900 m, 1661 s, 1604 s cm^{-1}; ^1H nmr ($CDCl_3$): δ 4.37 (s, CH_2), 7.21 (t, J = 7.0 Hz, 4-H of benzyl), 7.23 (t, J = 7.6 Hz, 3-H and 5-H of benzyl), 7.32 (d, J = 7.0 Hz, 2-H and 6-H of benzyl), 7.50, 7.55 and 7.58 (3 t, J = 7.5 Hz, 2-H, 9-H, 10-H), 7.97, 8.05 and 8.13 (3 d, J = 7.6 Hz, 1-H, 3-H, 11-H), 8.73 (d, J = 8.3 Hz, 8-H).

Anal. Calcd. for $C_{22}H_{14}ClNO$: C, 76.86; H, 4.10; N, 4.07. Found: C, 77.11; H, 4.28; N, 3.81.

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

This compound was obtained from 4-hydroxypyridocarbazolone **4f** (3.11 g, 10 mmol) according to the procedure described for **9a**; the yield was 2.20 g (67%) yellowish prisms, mp 247 °C (ligroin or acetic acid); ir: 2300 – 3400, 1669 s, 1604 s, 1554 s, 1439 s, 1337 s, 849 s, 756 s cm^{1}; ^1H nmr ($CDCl_3$): δ 7.66-7.47 (m, 2-H, 9-H, 10-H, 5 PhH), 8.06, 8.11 and 8.22 (3 d, J = 7.8 Hz, 1-H, 3-H, 11-H), 8.72 (d, J = 8.0 Hz, 8-H).

Anal. Calcd. for $C_{21}H_{12}ClNO$: C, 76.48; H, 3.67; N, 4.25. Found: C, 76.29; H, 4.06; N, 4.07.

4-Chloro-5-hexylpyrido[3,2,1-*jk*]carbazol-6-one (**9g**).

This compound was obtained from 4-hydroxypyridocarbazolone **4g** (3.19 g, 10 mmol) according to the procedure described for **9a**; the yield was 2.66 g (79%) yellowish prisms, mp 104-107 °C (toluene); ir: 3550-2950, 1660 s, 1600 s cm^{-1}.

Anal. Calcd. for $C_{21}H_{20}ClNO$: C, 74.66; H, 5.97; N, 4.15. Found: C, 74.27; H, 5.59; N, 4.25.

5-Methyl-6-oxo-6*H*-pyrido[3,2,1-*jk*]carbazol-4-yl Toluene-4-sulfonate (**10a**).

A mixture of 4-hydroxypyridocarbazolone **4a** (2.50 g, 10 mmol), *p*-toluenesulfonyl chloride (7.60 g, 20 mmol) and triethylamine (2.00 g, 20 mmol) in dry acetonitrile (50 mL) was stirred and heated under reflux for 18 hours. The reaction mixture was cooled to room temperature and poured into ice/water (100 mL). The obtained precipitate was collected by filtration, washed with water and dried. The yield was 3.19 g (79%) colorless prisms, mp 240 °C from ethanol; ir: 2918 m, 1667 s, 1636 w, 1605m, 1600 sh, 1580 w cm^{-1}; ^1H nmr ($CDCl_3$): δ 2.04 (s, CH_3 of CH_3), 2.52 (s, p-tosyl-CH_3), 7.43-7.52 (m, 9-H, 10-H and 2 ArH of p-tosyl), 7.60 (t, J= 7.8 Hz, 2-H), 7.70 (d, J = 7.9 Hz, 1 ArH of p-tosyl), 7.92 (m, 11-H, 1 ArH of p-tosyl), 8.08 and 8.12 (2 d, J = 7.6 Hz, 1-H, 3-H), 8.72 (d, J = 8.2 Hz, 8-H).

Anal. Calcd. for $C_{23}H_{17}NO_4S$: C, 68.47; H, 4.25; N, 3.47. Found: C, 68.36; H, 4.17; N, 3.48.

6-Oxo-5-phenyl-6*H*-pyrido[3,2,1-*jk*]carbazol-4-yl Toluene-4-sulfonate (**10f**).

This compound was obtained from 4-hydroxypyridocarbazolone **4f** (3.10 g, 10 mmol) according to the method described for **10a**. The yield was 3.20 g (69%) colorless prisms, mp 198 °C from ethanol; ir: 1669 s, 1603 s, 1569 s cm^{-1}; ^1H nmr ($CDCl_3$): δ 2.42 (s, CH_3), 7.08 (d, J = 8.1 Hz, 2 ArH of p-tosyl), 7.29-7.33 (m, 2 ArH of p-tosyl, 5 PhH), 7.53, 7.59 and 7.67 (3 t, J = 7.7 Hz, 2-H, 9-H, 10-H), 8.10, 8.18 and 8.21 (3 d, J = 7.8 Hz, 1-H, 3-H 11-H), 8.71 (d, J = 8.1 Hz, 8-H).

Anal. Calcd. for $C_{28}H_{19}NO_4S$: C, 72.24; H, 4.11; N, 3.01. Found: C, 71.87; H, 4.05; N, 3.00.

4-Azido-5-methylpyrido[3,2,1-*jk*]carbazol-6-one (**11a**).

A mixture of 4-hydroxypyridocarbazolone **4a** (3.0 g, 12 mmol) and sodium azide (1.50 g , 23 mmol) in dimethylformamide (15 mL) was heated to 100 °C. At this temperature, phosphorylchloride (3.1 ml, 20 mmol) was added dropwise. The reaction mixture was held at 100 °C for 1 hour, then cooled to room temperature and poured into ice/water (100 mL). The precipitate was collected by suction filtration and dried. The yield was 1.50 g (55%) yellowish prisms, mp/dec 126 °C (methanol); calorimetric data for the thermolysis: decomposition at 119.6 °C onset, 130.5 °C maximum; mp at 146.8 °C onset, 152.8 °C maximum, ΔH = 2.4 J/g; decomposition at 154.7 °C onset, 162.2°C maximum, ΔH = -48 J/g; ir: 3500-2900 m, 2116 m, 1663 s, 1646 s, 1622 s, 1592 s cm^{-1}; ^1H nmr ($CDCl_3$): δ 2.50 (s, CH_3), 7.46, 7.48 and 7.62 (3 t, J = 7.6 Hz, 2-H, 9-H, 10-H), 7.95, 8.08 and 8.13 (3 d, J = 7.7 Hz, 1-H, 3-H, 11-H), 8.73 (d, J = 8.1 Hz, 8-H).

Anal. Calcd. for $C_{16}H_{10}N_4O$: C, 70.07; H, 3.67; N, 20.43. Found: C, 70.68; H, 3.93; N, 19.69.

No correct analysis was obtained because of the ease of decomposition of the azido compound.

4-Azido-5-ethylpyrido[3,2,1-*jk*]carbazol-6-one (**11b**).

This compound was obtained from 4-hydroxypyridocarbazolone **4b** (2.63 g, 10 mmol) according to the method described for **11a**; the yield was 1.80 g (52%), yellowish prisms, mp/dec 125 °C (methanol); calorimetric data for the thermolysis: mp at 125.4 °C onset, 128.3 °C maximum, ΔH = 20.5 J/g; decomposition at 148.5 °C onset, 150.6 °C maximum, ΔH = - 24 mcal/mg; ir: 3500-2900 m, 2115 m, 1657 s, 1602 s cm^{-1}; ^1H nmr ($CDCl_3$): δ 1.31 (t, J = 7.2 Hz, CH_3), 3.03 (q, J = 7.4 Hz, CH_2), 7.46, 7.61 and 7.47 (3 t,

J = 7.6 Hz, 2-H, 9-H, 10-H), 7.92, 8.04 and 8.09 (3 d, J = 7.6 Hz, 1-H, 3-H, 11-H), 8.71 (d, J = 7.9 Hz, 8-H).

Anal. Calcd. for $C_{17}H_{12}N_4O$: C, 70.82; H, 4.20; N, 19.43. Found: C, 71.35; H, 4.15; N, 18.55.

No correct analysis was obtained because of the ease of decomposition of the azido compound.

4-Azido-5-butylpyrido[3,2,1-*jk*]carbazol-6-one (**11d**).

This compound was obtained from 4-hydroxypyridocarbazolone **4d** (2.89 g, 10 mmol) according to the method described for **11a**; the yield was 0.66 g (21%), brownish prisms, mp/dec 84 °C (methanol); ir: 3600-2800 m, 2110 m, 1660 s, 1605 s cm^{-1}.

Anal. Calcd. for $C_{19}H_{16}N_4O$: C, 72.14; H, 5.10; N, 17.71. Found: C, 72.41; H, 5.48; N, 17.33.

4-Azido-5-benzylpyrido[3,2,1-*jk*]carbazol-6-one (**11e**).

This compound was obtained from 4-hydroxypyridocarbazolone **4e** (3.23 g, 10 mmol) according to the method described for **11a**; the yield was 1.70 g (49%) yellowish prisms, mp/dec 135 °C (methanol); calorimetric data for the thermolysis: decomposition at 134.4 °C onset, 137.2 °C maximum, ΔH = - 44 J/g; ir: 3500-2900 m, 2143 m, 1657 s, 1606 s, 1573 s cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 4.17 (s, CH_2), 7.14 (t, J = 7.0 Hz, 4-H of benzyl), 7.22 (t, J = 7.6 Hz, 3-H and 5-H of benzyl), 7.38 (d, J = 7.0 Hz, 3-H and 6-H of benzyl), 7.50, 7.60 and 7.63 (3 t, J = 7.5 Hz, 2-H, 9-H, 10-H), 8.18, 8.28 and 8.38 (d, J = 7.6 Hz, 1-H, 3-H, 11-H), 8.57 (d, J = 8.3 Hz, 8-H).

Anal. Calcd. for $C_{22}H_{14}N_4O$: C, 75.42; H, 4.03; N, 15.99. Found: C, 75.79; H, 4.41; N, 15.60.

4-Azido-5-phenylpyrido[3,2,1-*jk*]carbazol-6-one (**11f**).

Method A: A mixture of pyridocarbazolyl toluene-4-sulfonate **9f** (4.65 g, 10 mmol) and sodium azide (1.50 g, 23 mmol) in dimethylformamide (30 mL) was heated to 80 °C for 30 min with intensive stirring. Then the mixture was cooled to room temperature and poured into ice/water (500 mL); the obtained precipitate was collected by suction filtration and washed with water. The yield was 2.30 g (68%) yellowish powder, mp/dec 170 °C (methanol).

Method B: A mixture of 4-chloropyridocarbazolone **10f** (3.29 g, 10 mmol) and sodium azide (1.50 g, 23 mmol) in dimethylformamide (50 mL) was heated to 80 °C for 2 hours with intensive stirring. Workup was performed as described in method A. The yield was 2.78 g (83%) brownish powder, mp/dec 162-168 °C (methanol); calorimetric data for the thermolysis: decomposition at 166.7 °C onset, 173.7 °C maximum, ΔH = - 723 J/g; ir: 2109 s, 1664 s, 1604 s, 1569 s cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 7.29-7.50 (m, 5 PhH), 7.52, 7.55 and 7.59 (3 t, J = 7.7 Hz, 2-H, 9-H, 10-H), 7.98, 8.09 and 8.19 (3 d, J = 7.4 Hz, 1-H, 3-H, 11-H), 8.70 (d, J = 7.9 Hz, 8-H).

Anal. Calcd. for $C_{21}H_{12}N_4O$: C, 74.99; H, 3.60; N, 16.66. Found: C, 75.36; H, 3.89; N, 16.27.

14*H*-Indolo[2,3:4,5]pyrido[3,2,1-*jk*]carbazol-9-one (**12**).

A solution of 4-azido-5-phenylpyridocarbazolone **11f** (1.7 g, 5 mmol) in dimethylformamide (15 mL) was heated under reflux for 6 hours. The mixture was cooled to room temperature and then poured onto ice/water (100 mL); the resulting precipitate was collected by suction filtration and washed with water. The yield was 0.90 g (58 %), yellowish prisms, mp > 300 °C (dimethylformamide/methanol); ir: 3287 s, 3055 w, 1654 m, 1640s, 1597 w, 1582 w cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 7.35 (t, J = 7.3 Hz, 2-H), 7.42 (t, J = 7.8 Hz, 5-H), 7.53 (t, J = 7.6 Hz, 6-H), 7.65 - 7.75 (m, 11-H, 12-H, 13-H), 8.30 - 8.40 (m, 1-H, 3-H, 4-H, 10-H), 8.77 (d, J = 8.1 Hz, 7-H), 13.06 (s, 1 H, NH); MS: m/z (%) = 309 (M+1, 100).

Anal. Calcd. for $C_{21}H_{12}N_2O$: C, 81.80; H, 3.92; N, 9.09. Found: C, 81.60; H, 3.62; N, 8.71.

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