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**Abstract**

Arylhydrazines 1 react with 2-methylcyclohexanone 2 via Fischer indole synthesis to 4a-methyl-2,3,3,4a-tetrahydro-1H-carbazoles 3, which cyclize with 2-substituted malonates 5 to give 5-aryl- and 5-alkylsubstituted 4-hydroxy-11b-methyl-1,2,3,11b-tetrahydro-6H-pyrido[3,2,1-jk]carbazol-6-ones 6. Pyridocarbazoles 6 can be shown to give a series of reactions, such as electrophilic halogenation to 5-chloro-pyridocarbazole-4,6-dione 9, and nucleophilic halogenation to 4-chloro-pyridocarbazol-6-one 11. 4-Azido-5-phenylpyridocarbazol-6-one 13 cyclizes under thermolysis to the indolo derivative 14. This reaction was studied by differential scanning calorimetry (DSC).

**Introduction**

Tetrahydropyrido[3,2,1-jk]carbazol-6-one (blue structure in A) is part of the heterocyclic skeleton of many natural products (e.g. Strychnos alkaloids A such as strychninolones and derivatives [2, 3a], e.g. Brucine (dimethoxystrychnin) [3b] and Vomicin (12-hydroxy-N-methylpseudostrychnine) [3c]. It possesses the biological interesting combination of the well-known indole structure [4] and the 4-hydroxy-2-pyridone structure.

![A B C D](image)

Especially the pyridone system is noteworthy for several reasons: The basic structure can be found in many natural products, such as the highly toxic Ricinbine (a 4-methoxy-2-oxo-3-pyridinecarbonitrile[3d]), in compounds with antibiotic activity (e.g. Flavipucin [5]), and the yellow fungal pigment Tenellin [6]. A whole class of 4-hydroxy-5,6-dihydro-2-pyridones with antibiotic activity (e.g. Mocimycin [3e]) is produced by Streptomyces species. 4-Hydroxy-2-pyridone itself has been used as
"3-Deaza-uracil" for the preparation of nucleoside analogs [7] and some halogenated derivatives have shown herbicidal activity [8].

Recently we published the syntheses and reactions of a series of pyrido[3,2,1-jk]carbazol-6-ones B with two aromatic benzo rings in the carbazole moiety [9], and of tetrahydropyrido[3,2,1-jk]carbazol-6-ones with one hydrogenated benzo ring of type C [10] (red partial structure), having the pyridone part fused to the aromatic part of the carbazole. Building up the 4-hydroxy-2-pyridone part starting with enamines or azomethines on one side, and reactive malonic acid derivatives on the other side, has attracted our attention for many years [11]. To direct the ring closure reaction to the desired position, in the present work 2,3,4,9-tetrahydrocarbazoles 3 ("indolenines") are tested as substrates for diethyl and trichlorophenyl malonates. The resulting tetrahydro-pyrido[3,2,1-jk]carbazoles of type D (green saturated ring) comprise already four rings as found in Strychnos alkaloids [2] with the two oxygen functions at the correct positions and having the pyridone part fused to the hydrogenated ring.

Results and Discussion

1. Synthesis of tetrahydrocarbazoles 3 and cyclocondensation with malonates to tetrahydro-pyrido-carbazolones 6

Our approach to the tetrahydro-pyridocarbazole system started with the synthesis of 2,3,4,4a-tetrahydro-1H-carbazoles 3 with suitable substituents at the desired positions. 2-Methylcyclohexanone (2, pink colored) gives, depending on the reaction conditions, via a Fischer indole synthesis a mixture of two isomers, 4a-methyl-2,3,4,4a-tetrahydro-1H-carbazole (3a) and 1-methyl-2,3,4,9-tetrahydro-1H-carbazole (4a) [12]. The isomers were called as the neutral (4) and the basic product (3) [13], a property which makes it easy to separate them [14]. Mechanistic investigations support an intermolecular rearrangement by radical cleavage of the intermediate hydrazones which allow a free rotation of the radical molecules [15]; the structures were assigned in ref. [16]. The ratio of both isomers, 3 and 4, is influenced by the structure of the substituent in position 2 of the cyclohexanone and the kind of the acid catalyst: with soft acids such as acetic acid, product 3 is preferably formed, with hard acids such as sulfuric acid, preferable 4 is formed [17]; however, the yields are low. Our synthetic approach started from commercially available phenylhydrazine hydrochlorides 1a-c and 2-methylcyclohexanone (2), which were brought to reaction directly in glacial acetic acid as solvent without releasing the free phenylhydrazine bases. The work-up includes the extraction of 3 with diethyl ether from the alkaline solution to isolate the crude so-called "basic products" as oils, which crystallized in the case of 3a and 3c on addition of hexane; 3b was obtained as an yellowish oil. Comparison of the $^1$H nmr spectra of 3 with spectra of the isomer 1-methyl-2,3,4,9-tetrahydro-1H-carbazoles 4 [10] show, that the methyl groups in the hydrogenated carbazole rings are located between 1.07-1.08 ppm, whereas the 4a-methyl group in 3 has a signal at 1.30 ppm. In addition, the NH-signal in 9-position, which is visible in all spectra of type 4 at 10.40-10.50 ppm, is missing in structures 3 (Scheme 01).
The thermal cyclocondensation of 4a-methyl-2,3,4,4a-tetrahydro-1H-carbazoles 3a-c with diethyl phenylmalonate and diethyl benzylmalonate (red colored) in diphenylether as the solvent gave via reactive ketene intermediates [11] pyrido-carbazolones, which could be formed in two isomeric structures. The spectral analysis showed that a ring closure directed to the aromatic ring producing 7 can be ruled out, because of the lack of an olefinic proton at position 8 and an fourth aromatic proton from the carbazole part. In this way, tetrahydro-pyridocarbazolones 6a-d were obtained in good yields.

Thermal cyclocondensation of 3a with diethyl butylmalonate 5c gave only very low yields of 6e. However, when the cyclization reaction was performed without solvent at 200 °C with the highly reactive bis-(2,4,6-trichlorophenyl) n-butylmalonate (5d), the so-called "active malonate" [11, 18], the ring closure proceeded in good yields of 70% to 6e.

2. Electrophilic attack directed to 4-hydroxy-11b-methyl-5-phenyl-1,2,3,11b-tetrahydro-6H-pyrido[3,2,1-jk]carbazol-6-one (6a)

The attack with electrophilic reagents on 4-hydroxy-5-phenyl-tetrahydropyridocarbazolone 6a has three possible targets: the positions 1-4 of the benzo ring in carbazole, the phenyl ring in position 5 and position 5 itself in the heterocyclic ring, which can be considered as tautomeric CH-acidic position. Under mild conditions, only position 5 (red marked substituents) is attacked, similar as found in rela-

The electrophilic attack formed in all three examples a 5,5-disubstituted pyridinedione structure deriving from the CH-acidic group of the α,γ-dioxo tautomer of 6a in position 5.

3. Nucleophilic displacement of the 4-hydroxy-group in tetrahydro-pyridocarbazolone 6a

Reaction of boiling phosphoryl chloride with 4-hydroxy-5-phenyl-tetrahydropyridocarbazolones 6a,c gave similar as in quinoline series [20] in very good yields 4-chloro-5-phenyl-tetrahydropyridocarbazolone 11a,b by replacing the 4-hydroxy group in a nucleophilic substitution reaction against the 4-chloro group (Scheme 03, blue marked substituents). The formed 4-chloro derivatives are reactive intermediates and can easily converted to other derivatives, e.g. nitrogen bases or azido groups.
1,2,4-Triazole sodium reacted in dimethylformamide solution with 4-chloro derivative 11a at 60 °C in excellent yields to 5-phenyl-4-triazolyl-tetrahydropyridocarbazolone 12, a structure related to antifungal agents [21]. 4-Chloro derivative 11a and sodium azide gave in boiling ethanol in excellent yields 4-azido-5-phenyl-tetrahydropyridocarbazolone 13. The structure of 13 is supported by the IR signal of the azido group at 2109 cm⁻¹. Both reactions demonstrated the high reactivity of the 4-chloro group against nucleophiles.

4. Thermal cyclization of 4-azido-5-phenyl-tetrahydropyridocarbazolone 13

In the last years we investigated a series of cyclization reactions of azides with reactive ortho-substituents [22, 23]. The thermal cyclization of ortho-phenyl azides in pyridocarbazoles proceeds via nitrene intermediates [24] and is known to produce indolo products [25]. The conditions of the ring closure reaction of the 4-azido derivative 13 was investigated by differential scanning calorimetry (DSC) to obtain the information on the cyclization temperature to indole 14 (red marked) and possible further decomposition. The DSC diagram shows a cyclization range with 139.1 °C onset and 171.8 °C maximum, which allows to use dimethylformamide at reflux temperature as the cyclization solvent (Scheme 04).

The reaction enthalpy with a value of ΔH = -547 J/g is rather large, which must be taken into consideration when larger batches are thermolyzed. At 236.4 °C a melting point is observed, which is identical with the data obtained from the cyclized indolo-pyridocarbazole 14. The structure of 3a-methyl-2,3,3a,14-tetrahydroindolo[2',3':4,5]pyrido[3,2,1-jk]carbazol-9(1H)-one (14) is supported by NMR data, which contain a NH signal at δ 11.97 ppm, and by mass spectral data, which show the molecule peak.

Conclusion

It could be shown, that 4a-methyl-2,3,4,4a-tetrahydro-1H-carbazoles 3 are obtained without by-products of the isomeric 1-methyl-2,3,4,9-tetrahydro-1H-carbazoles 4 in yields of 50-70%. Cyclocondensation of tetrahydrocarbazoles 3 with substituted malonates results in the formation of 4-hydroxy-11b-methyl-1,2,3,11b-tetrahydro-6H-pyrido[3,2,1-jk]carbazol-6-ones 6 without formation of the isomeric pyridocarbazoles 7. Both electrophilic as well as nucleophilic attacks at 6 gave regioselective substitutions in the heterocyclic pyridone ring either in position 5 or position 4, respectively. Thermal
cyclization of 4-azido-5-phenyl-tetrahydropyridocarbazolone 13 was investigated by differential scanning calorimetry (DSC) and produced indolo-pyridocarbazole 14 under suitable conditions obtained from DSC data.

### Methods and Experimental

**General**

Melting points were determined using a Stuart SMP3 Melting Point Apparatus (Bibby Scientific Limited, Stone, Staffordshire, UK) in open capillary tubes. Calorimetric data (DSC data) were obtained on a Perkin Elmer Pyris 1 DSC instrument (Perkin Elmer Corp., Waltham, MA, USA) with the Pyris Software for Windows (Pyris Thermal Analysis System) V3.72. The differential scanning calorimetry plots were recorded between 25-600 °C, with a heating rate of 2-10 °C/min, and 1.5-3.0 mg of compound in sealed aluminum crucibles (11 bar). IR spectra were recorded with a Bruker Alpha-P instrument (Bruker GmbH, Karlsruhe, Germany) with Attenuated Total Reflectance (ATR) measurement, using a reflection method. NMR spectra were recorded on a Bruker Avance III instrument (Bruker GmbH) (300 MHz $^1$H). Chemical shifts are given in ppm (δ) from the internal TMS standard. Elemental analyses were performed at the Microanalytical Laboratory of the University of Vienna, Austria. Mass spectra were obtained from a HP 1100 LC/MSD mass spectral instrument (Agilent Technologies, Santa Clara, CA, USA) with either positive or negative atmospheric pressure chemical ionization (APCI) ion source, 50–200 V, nitrogen, or atmospheric pressure electrospray (AP-ES) method. Analytical HPLC was performed on a Shimadzu LC 20 system equipped with a diode array detector (215 and 254 nm) on a Pathfinder AS reversed phase (4.6150 mm, 5 µm) column, running in acetonitrile/water gradient (30–100% acetonitrile). Dry column flash chromatography [26] was carried out on silica gel 60 H (5–40 µm) (Merck, Darmstadt, Germany). All reactions were monitored by thin layer chromatography on 0.2 mm silica gel F 254 plates (Merck, Darmstadt, Germany) 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.

**4a-Methyl-2,3,3,4a-tetrahydro-1H-carbazole (3a):** A suspension of phenylhydrazinium chloride (1a) (30.8 g, 0.21 mol) in glacial acetic acid (170 mL) was warmed to 50 °C. To this suspension, a solution of 2-methylcyclohexanone 2 (22.7 g, 0.20 mol) in glacial acetic acid (35 mL) was added dropwise rapidly under stirring. After addition, the mixture was heated under reflux for further 2 hours and then cooled to room temperature. The solvent was removed under reduced pressure, the residual brown oil diluted with water (10 mL) and then 2 M aq. sodium hydroxide solution (130 mL) was added to the residue until an alkaline pH was reached. The product was extracted with diethyl ether (100 mL), the organic phase dried with sodium sulfate, filtered and the solvent removed at the rotary evaporator. The residue was distilled under reduced pressure to get a light yellow oil at 144–155 °C / 13 mm Hg.; lit. bp 158 °C/20 mm Hg [27]. On addition of a few drops of hexane, transparent crystals were formed within a few minutes. The yield was 27.7 g (71%); colorless prisms, mp 68 °C (hexane) lit. mp 69 °C [27]. IR: 3043 w, 2968 w, 2942 m, 2852 w, 1609 w, 1574 s cm$^{-1}$. $^1$H NMR (CDCl$_3$): δ 1.19 (dt, 1 H, J = 7.0 + 2.0 Hz, 3-CH$_2$(ax)), 1.33 (s, 3 H, Me), 1.44 (dt, J = 7.0+ 2.0 Hz, 1 H, 3-CH$_2$(eq)), 1.72-1.84 (m, 2 H, 2-H), 2.19-2.30 (m, 2 H, 4-CH$_2$), 2.55-2.66 (dt, J = 7.0 + 2.0 Hz, 1 H, 1-CH$_2$(ax)), 2.85-2.91 (m, 1 H, 1-CH$_2$(eq)), 7.21 (dt, J = 7.0+1.5 Hz, 1 H, ArH), 7.30-7.36 (m, 2 H, ArH), 7.61 (d, J = 7.0 Hz, 1 H, 5-H). Anal. calcd for C$_{13}$H$_{15}$N (185.27): C, 84.28; H, 8.16; N, 7.56. Found: C, 83.81; H, 8.36; N, 7.66.

**6-Methoxy-4a-methyl-2,3,3,4a-tetrahydro-1H-carbazole (3b):** This compound was obtained from 4-methoxyphenylhydrazinium chloride (1b) (17.7 g, 0.10 mol) and 2-methylcyclohexanone (2) (11.2 g, 0.10
mol) using the procedure and work-up described for 3a. The yield was 9.89 g (46%), yellowish oil, bp 190 °C/14 mm Hg; lit. bp 122 °C/2 mm Hg [28].

6-Chloro-4a-methyl-2,3,4,4a-tetrahydro-1H-carbazole (3c): This compound was obtained from 4-chlorophenylhydrazinium chloride (1c) (7.16 g, 40 mmol) and 2-methylcyclohexanone (2) (4.49 g, 40 mmol) using the procedure and work-up described for 3a to obtain after distillation a yellowish oil, bp 170 °C/14 mm Hg. The oily liquid crystallized on addition of hexane. The solid was filtered by suction, washed with cold hexane and dried at room temperature under reduced pressure. The yield was 3.05 g (47%), colorless crystals, mp 66 °C (toluene). IR: 2930 m, 2720 m, 1610 m, 1600 m cm⁻¹.

4-Hydroxy-11b-methyl-5-phenyl-1,2,3,11b-tetrahydro-6H-pyrido[3,2,1-jk]carbazol-6-one (6a): A mixture of tetrahydrocarbazole 3a (1.85 g, 10 mmol) and diethyl phenylmalonate (5a) (2.37g, 10 mmol) in diphenyl ether (10 mL) was heated in a 2-necked flask equipped with a distillation bridge and a 20 cm Vigreux column to 230-240 °C internal temperature and kept for 3 hours at this temperature. Then the temperature was raised to 250 °C and the distillation was continued until no more ethanol was liberated (about 1 hour). The reaction mixture was cooled to room temperature, treated with hexane (50 mL) and stirred for 24 hours. The resulting solid product was filtered by suction, dissolved in hot toluene (200 mL), heated with char-coal, filtered and the solvent reduced to 50 mL i. vac.. The residue was filtered, washed with cold methanol (20 mL) and dried under reduced pressure at 40 °C. The yield was 1.61 g (49%), gray-white powder, mp 213 °C (toluene). IR: 3044 w, 2921 w, 2962 m, 2881 w, 1682 s, 1608 m, 1556 s cm⁻¹.

10-Chloro-4-hydroxy-11b-methyl-5-phenyl-1,2,3,11b-tetrahydro-6H-pyrido[3,2,1-jk]carbazol-6-one (6c): This compound was obtained from 6-chloro-tetrahydrocarbazole 3b (2.15 g, 10 mmol) and diethyl phenylmalonate (5a) (2.37g, 10 mmol) using the procedure and work-up described for 6a. The yield was 1.97 g (55%), colorless prisms, mp 251 °C (toluene). IR: 3050 w, 2920 m, 2880 w, 1608 m, 1556 s cm⁻¹. 1H NMR (CDCl₃): δ 1.44 (s, 3 H, Me), 1.63-1.69 and 2.01-2.35 (2 m, 4 H, 1-CH₂, 2-CH₂), 2.72 (t, J = 7.0 Hz, 2 H, 3-CH₂), 7.24-7.26 (t, J = 7.0 Hz, 1 H, 9-H), 7.33-7.38 and 7.41-7.56 (2 m, 7 H, 10-H, 11-H, 5 Ph H), 8.56 (dd, J = 7.0+2.0 Hz, 1 H, 8-H). Anal. calcd for C₂₂H₁₉NO₃ (359.43): C, 76.86 H, 5.89 N, 3.90. Found: C, 76.86 H, 5.89 N, 3.90.
5-Butyl-4-hydroxy-11b-methyl-1,2,3,11b-tetrahydro-6H-pyrido[3,2,1-jk]carbazole-6-one (6e):
Method A: This compound was obtained from tetrahydrocarbazole 3a (2.81 g, 15 mmol) and diethyl n-butylmalonate (5e) (3.24 g, 15 mmol) using the procedure and work-up described for 6a. The yield was 0.69 g (15%).

Method B: An intimate mixture of tetrahydrocarbazole 3a (1.85 g, 10 mmol) and bis-(2,4,6-trichlorophenyl) n-butylmalonate (5d) (5.19 g, 10 mmol) was heated to 200 °C for 20 minutes without solvent. The product was cooled to room temperature and digested with hexane several times to remove 2,4,6-trichlorophenol. The remaining solid was filtered by suction, washed with hexane and dried under reduced pressure at 40 °C. The yield was 2.16 g (70%), colorless powder, mp 198 °C (methanol). IR: 1705 m, 1680 s, 1650 s cm⁻¹

11b-Methyl-5-nitro-5-phenyl-1,2,3,11b-tetrahydro-pyrido[3,2,1-jk]carbazole-4,6(5H)-dione (8): To a solution of 2-phenyl-tetrahydropyridocarbazalone 6a (1.98 g, 6 mmol) in glacial acetic acid (20 mL), concentrated nitric acid (8.0 mL) was added slowly with stirring at room temperature. The reaction mixture was kept at room temperature for 12 hours to afford a solid product, which was filtered by suction, washed with water (50 mL) and dried under reduced pressure at 40 °C. The yield was 2.10 g (92%), yellow prisms, mp 145 °C (cyclohexane). IR: 3051 w, 2964 m, 2861 w, 1647 s, 1624 s, 1587 m cm⁻¹. ¹H NMR (CDCl₃): δ 0.91 (t, J = 7.0 Hz, butyl-CH₃), 1.23 (s, 3 H, Me), 1.35-2.30 (m, 4 H, 1-CH₂, 2-CH₂, 2 butyl-CH₂), 7.10-7.50 (m, 3 H, 9-H, 10-H, 11-H), 8.33 (dd, J = 7.0+1.5 Hz, 8-H), 10.80 (s, br, 1 H, OH). Anal. calcd for C₂₂H₁₈N₂O₄ (374.40): C, 70.58; H, 4.85; N, 7.48. Found: C, 70.96; H, 5.04; N, 7.30.

5-Chloro-11b-methyl-5-phenyl-1,2,3,11b-tetrahydro-pyrido[3,2,1-jk]carbazole-4,6(5H)-dione (9): To a suspension of 2-phenyl-tetrahydropyridocarbazalone 6a (1.98 g, 6 mmol) in dioxane (20 mL), sulfuryl chloride (1.0 g = 0.6 mL, 7.4 mmol) was added dropwise, keeping the temperature at 50 °C. After further 10 minutes at this temperature, the reaction mixture was poured onto ice-water (300 mL) and brought to pH = 4–6 with 2 M aqueous sodium hydroxide solution. The solid was filtered by suction, washed with water (50 mL) and dried under reduced pressure at 40 °C. The yield was 1.87 g (87%), yellow prisms, mp 158 °C (cyclohexane). IR: 1705 m, 1680 s, 1650 s cm⁻¹. ¹H NMR (DMSO-d₆): δ 1.44 (s, 3 H, Me), 2.08-2.36 (m, 4 H, 1-CH₂, 2-CH₂, 2 butyl-CH₂), 8.37-8.50 (m, 3 H, 9-H, 10-H, 11-H), 11-H), 8.58 (dd, J = 7.0+1.5 Hz, 8-H). Anal. calcd for C₂₂H₁₈ClN₂O₄ (347.45): C, 75.97; H, 4.76; N, 4.03. Found: C, 75.97; H, 4.76; N, 4.03.

5-Bromo-11b-methyl-5-phenyl-1,2,3,11b-tetrahydro-pyrido[3,2,1-jk]carbazole-4,6(5H)-dione (10): To a solution of 2-phenyl-tetrahydropyridocarbazalone 6a (1.98 g, 6 mmol) in dioxane (20 mL), a solution of bromine (0.96 g, 6 mmol) in chloroform (5 mL) of was slowly added. The reaction mixture was stirred at room temperature for 20 minutes and then extracted with water. The organic layer was dried with sodium sulfate and taken to dryness under reduced pressure. The solid was digested with cyclohexane, filtered by suction and dried at reduced pressure at room temperature. The yield was 2.20 g (89%), pale yellow crystals, mp 150 °C (cyclohexane). IR: 2970 w, 1710 m, 1685 s, 1640 s, 1590 cm⁻¹. Anal. calcd for C₂₁H₁₃BrN₂O₂ (408.30): C, 64.72; H, 4.44; N, 3.43. Found: C, 64.53; H, 4.76; N, 3.37.

4-Chloro-11b-methyl-5-phenyl-1,2,3,11b-tetrahydro-6H-pyrido[3,2,1-jk]carbazol-6-one (11a): A mixture of 2-phenyl-tetrahydropyridocarbazalone 6a (1.00 g, 3 mmol) and phosphoryl chloride (10 mL) was heated under reflux for 4 hours. The resulting solution was poured onto ice/water (100 mL) and brought to pH = 4–6 with 2 M aqueous sodium hydroxide solution. The solid was filtered by suction, washed with water (50 mL) and dried under reduced pressure at 40 °C. The yield was 0.72 g (69%), grayish prisms, mp 191 °C (ethanol). IR: 2950 w, 1710 m, 1675 s, 1610 m, 1555 s cm⁻¹. ¹H NMR (CDCl₃): δ 1.45 (s, 3 H, Me), 2.13-2.38 (m, 4 H, 1-CH₂, 2-CH₂, 2 butyl-CH₂), 7.10-7.50 (m, 3 H, 9-H, 10-H, 11-H), 8.33 (dd, J = 7.0+1.5 Hz, 8-H), 10.80 (s, br, 1 H, OH). Anal. calcd for C₂₂H₁₈ClN₂O₄ (363.85): C, 72.63; H, 4.99; N, 3.85. Found: C, 72.72; H, 5.06; N, 3.81.

4-Chloro-11b-methyl-5-phenyl-1,2,3,11b-tetrahydro-6H-pyrido[3,2,1-jk]carbazol-6-one (11b): A mixture of 8-chloro-2-phenyltetrahydropyridocarbazalone 6c (1.10 g, 3 mmol) and phosphoryl chloride (10 mL) was heated under reflux for 4 hours. The excess phosphoryl chloride was removed under reduced pressure, the
residue was poured on ice/water (200 mL) and then brought to pH = 4–6 with 2 M aqueous sodium hydroxide solution. The resulting solid was filtered by suction, washed with water (50 mL) and dried under reduced pressure at room temperature. The yield was 0.94 g (82%), colorless prisms, mp 175 °C (ethanol). IR: 2950 w, 2920 w, 1663 s, 1630 m, 1600 w, 1585 m cm

filtered by suction, washed with cold water (50 mL) and dried under reduced pressure at room temperature. The precipitate was filtered by suction, washed with a small amount of water and dried under reduced pressure. The yield was 53 mg (56%), light yellow prisms, mp 236 °C (dimethylformamide/methanol). IR: 3215 w, 3198 w, 3055 w, 2948 w, 2928 w, 2661 w, 1655 s, 1622 s, 1579 m, 1558 m cm


ted under reflux for 12 hours, then cooled to room temperature and poured onto ice/water (100 mL). The resulting precipitate was filtered by suction, washed with water (50 mL) and dried under reduced pressure at room temperature. The yield was 1.00 g (94%), colorless prisms, mp 202 °C (ethanol). IR: 2940 w, 1670 s, 1630 m, 1600 w, 1580 m cm


dissolved inorganic material was removed by filtration and the solvent of the filtrate was removed under reduced pressure. The solid residue was poured on ice/water (200 mL) and then brought to pH = 4–6 with 2 M aqueous sodium hydroxide solution. The resulting solid was filtered by suction, washed with water (50 mL) and dried under reduced pressure at room temperature. The yield was 0.94 g (82%), colorless prisms, mp 175 °C (ethanol). IR: 2950 w, 2920 w, 1663 s, 1630 m, 1600 w, 1580 m cm

Found: C, 69.17; H, 4.57; N, 3.61.

4-Azido-11b-methyl-5-phenyl-1,2,3,11b-tetrahydro-6H-pyrido[3,2,1-jk]carbazol-6-one (13): To a solution of 4-chloro-5-phenyl-tetrahydropyridocarbazolone 11a (1.16 g, 3 mmol) in dimethylformamide (10 mL), 1,2,4-triazole sodium (0.36 g, 3 mmol) was added and the resulting mixture was heated to 80 °C for 12 hours. Insoluble inorganic material was removed by filtration and the solvent of the filtrate was removed under reduced pressure. The solid residue was digested with water (50 mL), filtered by suction, washed with water (50 mL) and dried under reduced pressure at room temperature. The yield was 1.00 g (94%), colorless prisms, mp 202 °C cm


ting precipitate was filtered by suction, washed with cold water (50 mL) and dried under reduced pressure at room temperature. The yield was 1.00 g (88%), colorless prisms, mp 175 °C (ethanol). IR: 2950 w, 2920 w, 1663 s, 1625 s, 1591 m cm

Found: C, 75.86; H, 5.01; N, 14.64.

4-Azido-11b-methyl-5-phenyl-1,2,3,11b-tetrahydro-6H-pyrido[3,2,1-jk]carbazol-6-one (13): To a solution of 4-chloro-5-phenyl-tetrahydropyridocarbazolone 11a (1.16 g, 3 mmol) in ethanol (15 mL) and water (5 mL), sodium azide (0.26 g, 4 mmol) was added and the resulting mixture was heated to 80 °C for 12 hours. Insoluble inorganic material was removed by filtration and the solvent of the filtrate was removed under reduced pressure. The solid residue was digested with water (50 mL), filtered by suction, washed with water (50 mL) and dried under reduced pressure at room temperature. The yield was 0.94 g (82%), colorless prisms, mp 175 °C (ethanol). IR: 2950 w, 2920 w, 1663 s, 1630 m, 1600 w, 1580 m cm

4-Azido-11b-methyl-5-phenyl-1,2,3,11b-tetrahydro-6H-pyrido[3,2,1-jk]carbazol-6-one (13): To a solution of 4-chloro-5-phenyl-tetrahydropyridocarbazolone 11a (1.16 g, 3 mmol) in dimethylformamide (6 mL) was heated under reflux for 12 hours, then cooled to room temperature and poured onto ice/water (100 mL). The resulting precipitate was filtered by suction, washed with a small amount of water and dried under reduced pressure at 40 °C. The yield was 53 mg (56%), light yellow prisms, mp 236 °C (dimethylformamide/methanol). IR: 3215 w, 3198 w, 3055 w, 2948 w, 2928 w, 2661 w, 1655 s, 1622 s, 1579 s, 1558 m cm

4-Azido-11b-methyl-5-phenyl-1,2,3,11b-tetrahydro-6H-pyrido[3,2,1-jk]carbazol-6-one (13): To a solution of 4-chloro-5-phenyl-tetrahydropyridocarbazolone 11a (1.16 g, 3 mmol) in dimethylformamide (6 mL) was heated under reflux for 12 hours, then cooled to room temperature and poured onto ice/water (100 mL). The resulting precipitate was filtered by suction, washed with a small amount of water and dried under reduced pressure at 40 °C. The yield was 53 mg (56%), light yellow prisms, mp 236 °C (dimethylformamide/methanol). IR: 3215 w, 3198 w, 3055 w, 2948 w, 2928 w, 2661 w, 1655 s, 1622 s, 1579 s, 1558 m cm

References and Notes

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[3] (a) The Merck Index; Budavari, S., Ed.; Merck & Co Inc: Rahway, N J, USA, 1996; Vol 12, 9020; (b) ibid, 1476; (c) ibid, 10170; (d) ibid, 8377; (e) ibid, 6308.

Syntheses and Reactions of 5-Alkyl- and 5-Aryl-11b-Methyl-1,2,3,11b-tetrahydro-pyrido[3,2,1-\textit{jk}]carbazoles

Having a Strychnos Alkaloids Partial Structure


