NEW REACTIVITY OF STABLE INDOLE-2,3-QUINODIMETHANE EQUIVALENTS: [4 + 2]-CYCLOADDITION, CYCLOREVERSION, SIGMATROPIC REARRANGEMENT, AND ELIMINATION PROCESSES IN THE REACTIONS OF 1,4-DIMETHYLPYRANO[3,4-b]INDOL-3-ONE AND 1-METHYLPYRIDO[3,4-b]INDOL-3-ONE WITH CC-DIENOPHILES

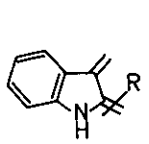
Houshang Erfanian-Abdoust and **Ulf Pindur***

Department of Chemistry and Pharmacy, University of Mainz, Saarstrasse 21, D-6500 Mainz 1, Federal Republic of Germany

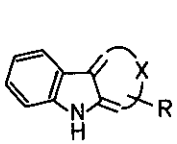
Abstract —— The reactions of 1,4-dimethylpyrano[3,4-b]indol-3-one (**1a**) with tetracyanoethylene and N-phenylmaleimide give the variously functionalized carbazole derivatives **3-7** and **9-12** via [4 + 2]cycloaddition, [4 + 2]cycloreversion, and some sigmatropic rearrangements. The Diels-Alder reactions of 1-methylpyrido[3,4-b]indol-3-one (**1b**) with several CC-dienophiles also give rise to the interesting carbazoles **14-18**. In the latter case, the primarily formed cycloadducts can be isolated and, in reactions of **1b** with unsymmetrical dienophiles, the products are formed in high regioselectivities.

The utilization of indole-2,3-quinodimethanes **I** and their respective derivatives as *in situ* generated reactive intermediates to function as enophiles in the regio- and stereocontrolled annellations of indoles via [4 + 2]cycloaddition has now gained practical significance and has been applied in efficient syntheses of carbazoles and alkaloids[1]. However, several of the integrated heterocyclic equivalents of **I**, namely **II**, are thermally extremely stable compounds which can also be employed in Diels-Alder reactions[1]. In this series, the use of pyrano[3,4-b]indol-3-ones of the type **1a** as stable cyclic analogs of indole-2,3-quinodimethanes in highly regio- and stereocontrolled [4 + 2]cycloadditions to furnish functionalized carbazole derivatives is now well established[1-8]. However, the synthetic applications of these types of compounds as well as their aza-analogs[2], the pyrido[3,4-b]indol-3-ones (X = NH) have not yet been evaluated sufficiently with regard to the scope and limitations of the methodology. Only sparse information on the influence of the selective functionalities in the reactant pairs which favor or block the Diels-Alder process or induce particular further reactions, for

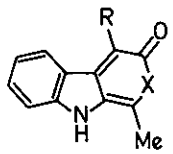
example, is available. In continuation of our investigations on the reactivity of 4π-indole synthons for molecular design by way of cycloaddition reactions, we now report on some new and surprising results from the Diels-Alder reactions of **1a** with tetracyanoethylene (TCNE) or N-phenylmaleimide (NPMI) as well as those of the aza-analog **1b** with several CC-dienophiles. In these reactions, the possibility for the stabilization of the primary cycloadducts via selective fragmentation (cycloreversion), elimination, and/or sigmatropic rearrangement, respectively, plays a significant role.



I

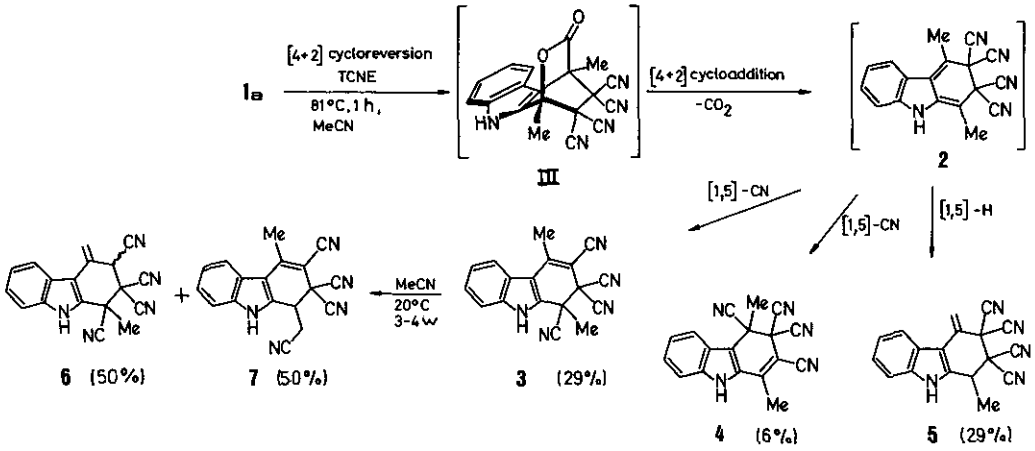


II

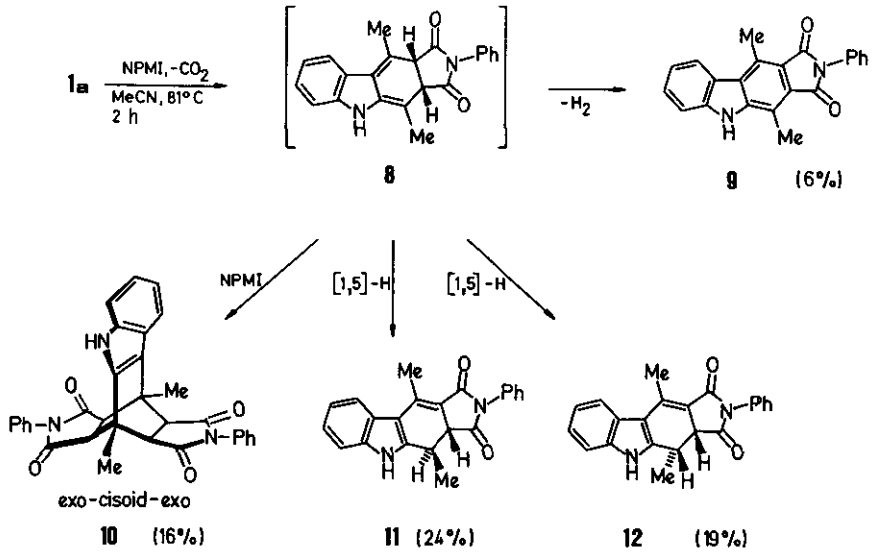


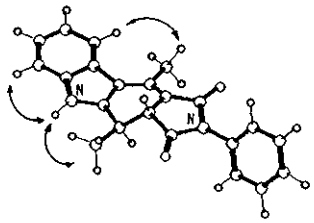
1	R	X
a	Me	O
b	H	NH

The 1-monomethyl derivative of **1a** (R = H), for example, does not react with TCNE to form characterizable products as a result of its lower enophilicity as a diene component[8]. In contrast, compound **1a** itself, which has a higher HOMO energy than the monomethyl derivative (MNDO calculations[8-10]), reacts with TCNE to form a number of novel hydrocarbazole derivatives **3-7**[11]. According to the mechanism established for cycloadditions of pyrano[3,4-b]indole derivatives[1,2], **1a** reacts in the first step via [4 + 2]cycloaddition to form the bicyclic bridged lactone **III**, which then undergoes a subsequent cycloreversion by extrusion of CO_2 as a good leaving group. The 2,3-dihydrocarbazole **2** thus formed cannot undergo stabilization by simple β-elimination to furnish the corresponding thermodynamically more stable, fully aromatic carbazole derivative. This has been demonstrated by others and by us in several reactions of pyrano[3,4-b]indol-3-ones with CC-dienophiles which result in the introduction of good leaving groups into molecules of the type **2**[1,4,8]. Thus, the reactive indole-2,3-quinodimethane **2** undergoes other thermally allowed stabilization processes by way of several sigmatropic rearrangements. Hence, [1,5]-cyanotropic shifts lead to the novel cyclic annellated vinylindoles **3** and **4** whereas a [1,5]-prototopic shift gives rise to the new carbazole derivative **5**, respectively. The regioselectivities of the rearrangements to furnish **3** and **5** (the major products) can be attributed to the larger HOMO coefficients at C1 as compared to C4 in compound **2**. The isolated pure compound **3** rearranges in acetonitrile at 20 °C within 3-4 weeks via a formal [1,3]-H shift and a further cyano group migration to give the tetra- and dihydrocarbazoles **6** (which cannot be completely separated from **3** by FC) and **7**. For a mechanistic discussion of the seldomly occurring [1,3]-H shift, see Ref.[10].

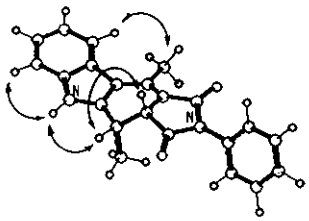


The Diels-Alder reaction of **1a** with N-phenylmaleimide (NPMI) also produces several new carbazole derivatives **9**–**12** in a one-pot procedure. The primarily formed tetracyclic indole-2,3-quinodimethane intermediate **8** is transformed by four different processes, each of which involves the generation of a more highly resonance-stabilized [b]annellated indole derivative. Thus, spontaneous dehydrogenation of **8** yields the carbazole derivative **9** (which cannot be completely separated from **11** by MPLC) while a tandem Diels-Alder sequence of **8** with a further molecule of NPMI results directly in the stereoselective formation of the novel barrelene derivative **10**[6]. A further stabilization process of **8** comprises formal antara- and suprafacial [1,5]-H shifts to yield **11** and **12** (see also Fig. 1 for the stereochemistry).





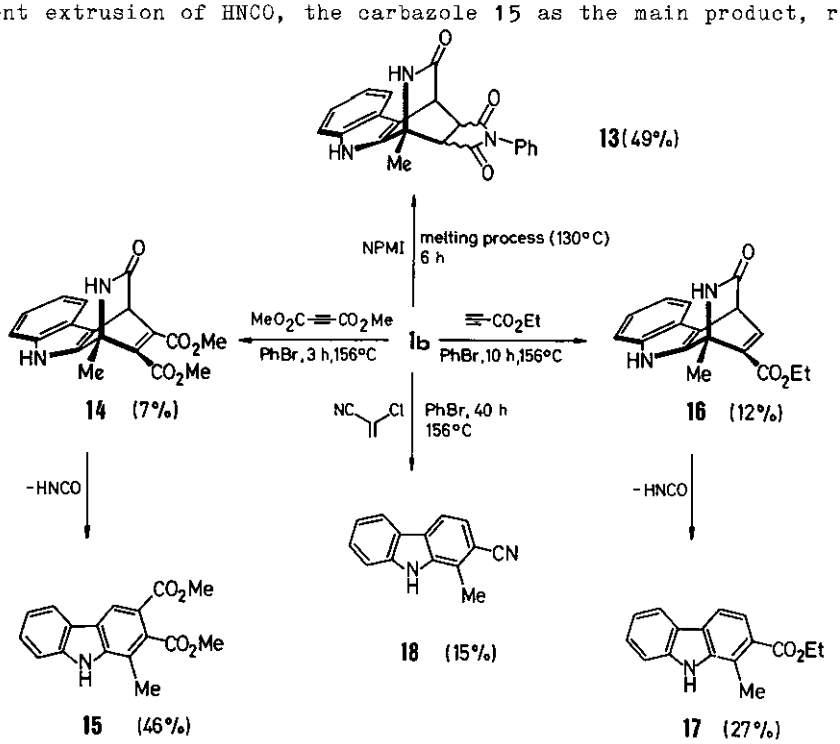
11



12

Fig. 1. Geometry-optimized molecular structures of compounds **11** and **12** (computer simulation, modified force field calculations) for describing the diagnostically important $^1H,^1H$-NOE's.

In the course of further investigations, we examined the outcome of Diels-Alder reactions of 1-methylpyrido[3,4-b]indol-3-one (**1b**)[2] with several acceptor-substituted CC-dienophiles. The results demonstrated that, in general, **1b** is less enophilic than **1a** or the monomethyl derivative of **1a** (R = H)[8]. Thus, **1b** only reacts with NPMI under drastic conditions (melting of the two reactants) to form the primary Diels-Alder adduct **13**[12]. As a result of the presence of the less effective leaving group HNCO (instead of CO_2), the [4 + 2]cycloaddition step stops at the first stage. Dimethyl acetylenedicarboxylate reacts with **1b** under less forcing conditions to furnish the bicyclic bridged pyridone derivative **14** and, after subsequent extrusion of HNCO, the carbazole **15** as the main product, respectively.



In the same way but with high regioselectivity, **1b** also reacts with the less dienophilic ethyl propiolate to yield **16** and **17** or with 2-chloropropenenitrile (α-chloroacrylonitrile) to form the 2-cyano-1-methylcarbazole **18**[8] in high regioselectivity via [4 + 2]cycloaddition, HNCO extrusion, and HCl elimination.

The reactions of **1b** with methyl acrylate and ethyl phenylpropiolate did not give characterizable products, probably as a consequence of the lower dienophilicities of the CC-enes[8]. According to our own MNDO calculations[9] on the parent compound of **1b**, the regiochemistries of the reactions with unsymmetrical CC-dienophiles can be predicted both under frontier orbital and under charge control[10]. The regiochemistries in these cases are in the opposite sense as compared to those of the cycloadditions of **1a** and the 1-methyl derivative (R = H) with the respective CC-dienophiles[4,8]. Hence, the diene **1b** is a useful synthon for the highly selective generation of carbazoles bearing an acceptor group at the 2-position.

In summary, the present results demonstrate that the product spectra obtained from the cycloaddition reactions of **1a** with CC-dienophiles are principally controlled by the driving forces of the stabilization of the primarily formed [4 + 2]-cycloadducts. In the cases of the cycloaddition reactions of **1b**, the primarily formed cycloadducts can be isolated in three cases as a result of the higher product stabilities of the bridged bicyclic systems. The Diels-Alder reactions of **1b** with unsymmetrical dienophiles produce functionalized carbazole derivatives in high regioselectivities.

EXPERIMENTAL

Melting points were measured in open capillary tubes on a Büchi SMP 20 apparatus and are uncorrected. Nmr spectra were recorded on a Bruker WM 400 spectrometer with TMS as internal standard (δ, ppm). EI mass spectra were obtained on a Varian MAT 711 instrument operating at 70 eV. Elemental analyses were performed with a Carlo Erba Strumentazione apparatus. All reactions were performed in highly pure, anhydrous solvents and under inert gas atmospheres. Flash chromatography was performed on Merck silica gel (0.040-0.063 mm) with petroleum ether (40-60 °C)/ethyl acetate as eluent. The constitutions and relative configurations of all compounds (except for the configurations of **6** and **13**) were elucidated by various high resolution ^{1}H- and ^{13}C-nmr techniques (e.g. 400 MHz $^{1}H,^{1}H$-NOE experiments, selective homodecoupling, 100.6 MHz ^{13}C-nmr APT techniques, gated and DEPT experiments).

Procedure for the Synthesis of Compounds 3, 4, 5, 6, and 7. 1,4-Dimethylpyrano[3,4-b]indol-3-one (**1a**) (426 mg, 2 mmol) was suspended in 25 ml of acetonitrile and treated with a solution of TCNE (384 mg, 3 mmol) in 10 ml of acetonitrile (syringe technique). The reaction mixture was heated at 81 °C for 2.5 h. After concentration under vacuum, the mother liquor was separated by flash chromatography [elution with petroleum ether (40-60 °C)/ethyl acetate, 6/4]. After 3 days compound **3** has precipitated from the concentrated eluate (first precipitation) and after 3-4 weeks compounds **6** and **7** (1:1) have been formed quantitatively in this eluate (second precipitation).

1,4-Dimethyl-1,2,2,3-tetracyano-1,2-dihydro-9H-carbazole (3). Yield: 0.172 g (29%); slightly greenish crystals; mp 218 °C (petroleum ether/ethyl acetate); ^{1}H-nmr (CD_3CN): 2.13 (s, 3H, C1-CH_3), 2.77 (s, 3H, C4-CH_3), 7.33 (ddd, ^3J = 7.44 Hz, ^3J = 7.76 Hz, ^4J = 1.20 Hz, 1H, C6-H), 7.39 (ddd, ^3J = 7.71 Hz, ^3J = 7.69 Hz, ^4J = 1.20 Hz, 1H, C7-H), 7.60 (d, ^3J = 8.21 Hz, 1H, C8-H), 7.87 (d, ^3J = 7.96 Hz, 1H, C5-H), 10.86 (s, 1H, NH); EI-ms: m/z = 297 ($M^{+\cdot}$, 70%), 282 ($M^{+\cdot}$ - CH_3, 18%), 270 ($M^{+\cdot}$ - HCN, 42%), 255 ($M^{+\cdot}$ - CH_3 - HCN, 100%). Anal. Calcd for $C_{18}H_{11}N_5$ (297.32): C, 72.72; H, 3.73; N, 23.56. Found: C, 72.70; H, 3.69; N, 23.44.

1,4-Dimethyl-2,3,3,4-tetracyano-3,4-dihydro-9H-carbazole (4). Yield: 0.036 g (6%); slightly yellowish crystals; mp 222 °C (petroleum ether/ethyl acetate); ^{1}H-nmr (CD_3CN): 2.45 (s, 3H, C4-CH_3), 2.69 (s, 3H, C1-CH_3), 7.28 (dd, ^3J = 7.34 Hz, ^3J = 7.65 Hz, 1H, C6-H), 7.48 (dd, ^3J = 7.63 Hz, ^3J = 7.64 Hz, 1H, C7-H), 7.60 (d, ^3J = 8.90 Hz, 1H, C8-H), 7.92 (d, ^3J = 8.16 Hz, 1H, C5-H), 9.34 (s, 1H, NH); EI-ms: m/z = 297 ($M^{+\cdot}$, 100%), 270 ($M^{+\cdot}$ - HCN, 17%). Anal. Calcd for $C_{18}H_{11}N_5$ (297.32): C, 72.72; H, 3.73; N, 23.56. Found: C, 72.55; H, 3.69; N, 23.40.

1-Methyl-4-methylene-2,2,3,3-tetracyano-1,2,3,4-tetrahydro-9H-carbazole (5). Yield: 0.172 g (29%); light greenish crystals; mp 218-219 °C (petroleum ether/ ethyl acetate); ^{1}H-nmr (CD_3CN): 1.86 (d, ^3J = 6.81 Hz, 3H, C1-CH_3), 4.28 (q, ^3J = 6.81 Hz, 1H, C1-H), 5.98 (d, ^2J = 2.62 Hz, 1H, CH_2), 6.26 (d, ^2J = 2.62 Hz, 1H, CH_2), 7.27 (ddd, ^3J = 7.24 Hz, ^3J = 7.55 Hz, ^4J = 1.30 Hz, 1H, C6-H), 7.34 (ddd, ^3J = 7.72 Hz, ^3J = 7.19 Hz, ^4J = 1.30 Hz, 1H, C7-H), 7.52 (dd, ^3J = 7.43 Hz, ^4J = 1.30 Hz, 1H, C8-H), 7.84 (d, ^3J = 7.40 Hz, 1H, C5-H), 10.03 (s, 1H, NH); EI-ms: m/z = 297 ($M^{+\cdot}$, 11%), 58 (100%). Anal. Calcd for $C_{18}H_{11}N_5$ (297.32): C, 72.72; H, 3.73; N, 23.56. Found: C, 72.59; H, 3.70; N, 23.49.

1-Methyl-4-methylene-1,2,2,3-tetracyano-1,2,3,4-tetrahydro-9H-carbazole (6). Product **6** was characterized by ^{1}H-nmr spectroscopy in a mixture with product **7**; ^{1}H-nmr (CD_3CN): 2.04 (s, 3H, C1-CH_3), 5.39 (s, 1H, C3-H), 5.59 (d, ^2J = 2.25 Hz, 1H, CH_2), 5.81 (d, ^2J = 2.25 Hz, 1H, CH_2), 7.26 (t, J = 7.44 Hz, 1H, C6-H), 7.37 (dd, ^3J = 7.46 Hz, ^3J = 7.38 Hz, 1H, C7-H), 7.74 (d, ^3J = 8.45 Hz, 1H, C8-H), 7.76 (d, ^3J = 8.74 Hz, 1H, C5-H), 10.19 (s, 1H, NH).

1-Cyanomethyl-4-methyl-2,2,3-tricyano-1,2-dihydro-9H-carbazole (7). Yield: 0.303 g (50%; calculated from the rearrangement reaction of **3**); colorless crystals; mp >350 °C (petroleum ether/ethyl acetate); ^{1}H-nmr (DMSO-d_6): 2.71 (s, 3H, C4-CH_3), 3.70 (dd, ^2J = 14.30 Hz, ^3J = 7.58 Hz, 1H, CH_2CN), 3.77 (dd, ^2J = 14.30 Hz, ^3J = 7.80 Hz, 1H, CH_2CN), 5.02 (dd, ^3J = 7.91 Hz, ^3J = 7.73 Hz, 1H, C1-H), 7.21 (ddd, ^3J = 7.59 Hz, ^3J = 7.62 Hz, ^4J = 0.90 Hz, 1H, C6-H), 7.30 (ddd, ^3J = 8.07 Hz, ^3J = 7.17 Hz, ^4J = 0.81 Hz, 1H, C7-H), 7.56 (d, ^3J = 8.14 Hz, 1H, C8-H), 7.79 (d, ^3J = 8.03 Hz, 1H, C5-H), 12.54 (s, 1H, NH); EI-ms: m/z = 297 ($M^{+\cdot}$, 31%), 282 ($M^{+\cdot}$ - CH_3, 27%), 270 ($M^{+\cdot}$ - HCN, 49%), 255 ($M^{+\cdot}$ - CH_3 - HCN, 100%). Anal. Calcd for $C_{18}H_{11}N_5$ (297.32): C, 72.72; H, 3.73; N, 23.56. Found: C, 72.59; H, 3.69; N, 23.66.

Procedure for the Synthesis of Compounds 9, 10, 11, and 12. 1,4-Dimethylpyrano[3,4-b]indol-3-one (**1a**) (0.426 g, 2 mmol) was suspended in 30 ml of acetonitrile, the suspension was heated to boiling, and treated with a solution of N-phenylmaleimide (0.80 g, 4.6 mmol) in 15 ml of acetonitrile (syringe technique). The reaction mixture was then heated at 81 °C for a total of 2.5 h. Compounds **10** and **11** were obtained by fractional recrystallization of the precipitate. Compound **12** was isolated by evaporation of the reaction mixture under vacuum and flash chromatography of the residue [elution with petroleum ether (40-60 °C)/ethyl acetate, 6/4]. In spite of the use of various separation methods (flash chromatography, MPLC, and fractional crystallization), compound **9** could only be characterized in a mixture with product **11**.

4,10-Dimethyl-2-phenyl-5H-pyrrolo[3,4-b]carbazole-1,3-dione (9). ^{1}H-nmr (DMSO-d_6): 2.82 (s, 3H, C4-CH_3), 3.05 (s, 3H, C10-CH_3), 7.27 (t, ^3J = 7.59 Hz, 1H, C8-H), 7.47 (mc, 6H, carbazole C7-H, phenyl C2-H to C6-H), 7.61 (d, ^3J = 8.13 Hz, 1H, C6-H), 8.19 (d, ^3J = 7.94 Hz, 1H, C9-H), 12.07 (s, 1H, NH); EI-ms: m/z = 340 ($M^{+\cdot}$, 50%).

4,10-Dimethyl-2,14-diphenyl-3ac,4,5,10ac-tetrahydro-11-anti-H-4,10t-epipyrrolopyrrolo-[3,4-b]carbazole-1,3,13,15-tetraone (10). Yield: 0.165 g (16%); colorless needles; mp 326-328 °C (acetonitrile); ^{1}H-nmr (acetone-d_6): 2.28 (s, 3H, C4-CH_3), 2.52 (s, 3H, C10-CH_3), 3.38 (d, ^3J = 7.91 Hz, 2H, C3a-H, C12-H), 3.48 (d, ^3J = 7.91 Hz, 2H, C10a-H, C11-H), 6.47

(dd, ^3J = 6.87 Hz, ^4J = 2.31 Hz, 4H, C2'-H, C2"-H, C6'-H, C6"-H), 7.02 (dd, ^3J = 7.04 Hz, ^3J = 7.46 Hz, 1H, C8-H), 7.08 (dd, ^3J = 8.12 Hz, ^3J = 7.10 Hz, 1H, C7-H), 7.19 (mc, 6H, C3'-H, C3"-H, C4'-H, C4"-H, C5'-H, C5"-H), 7.39 (d, ^3J = 8.05 Hz, 1H, C6-H), 7.64 (d, ^3J = 7.91 Hz, 1H, C9-H), 10.58 (s, 1H, NH); EI-ms: m/z = 515 ($M^{+\cdot}$, 50%), 343 (100%). Anal. Calcd for $C_{32}H_{25}N_3O_4$ (515.57): C, 74.55; H, 4.89; N, 8.15, Found: C, 74.45; H, 4.73; N, 8.10.

4α,10-Dimethyl-2-phenyl-3aα,4β-dihydropyrrolo[3,4-b]-1,3,5-H-carbazole-1,3-dione (11) and its Enantiomer. Yield: 0.164 g (24%); slightly yellowish crystals; mp 307 °C (acetonitrile); ^{1}H-nmr (DMSO-d_6): 1.76 (d, $^3J_{4\alpha\text{-Me},4\beta}$ = 6.62 Hz, 3H, C4-CH_3), 2.80 (d, $^5J_{3a\alpha,10\text{-Me}}$ = 1.20 Hz, 3H, C10-CH_3), 3.43 (dd, $^3J_{4\beta,4\alpha\text{-Me}}$ = 6.62 Hz, $^3J_{3a\alpha,4\beta}$ = 15.50 Hz, 1H, C4β-H), 3.65 (dd, $^3J_{3a\alpha,4\beta}$ = 15.50 Hz, $^5J_{3a\alpha,10\text{-Me}}$ = 1.20 Hz, 1H, C3aα-H), 7.13 (mc, 2H), 7.33 (d, ^3J = 7.33 Hz, C2'-H, C6'-H), 7.48 (mc, 4H), 7.78 (d, ^3J = 7.13 Hz, 1H, C9-H), 11.90 (s, 1H, NH) and the other enantiomer; EI-ms: m/z = 342 ($M^{+\cdot}$, 72%), 326 ($M^{+\cdot}$ - 16, 27%), 149 (100%). Anal. Calcd for $C_{22}H_{18}N_2O_2$ (342.34): C, 77.17; H, 5.30; N, 8.18. Found: C, 77.10; H, 5.25; N, 8.15.

4β,10-Dimethyl-2-phenyl-3aα,4α-dihydropyrrolo[3,4-b]-1,3,5-H-carbazole-1,3-dione (12) and its Enantiomer. Yield: 0.130 g (19%); slightly yellowish crystals; mp 306 °C (petroleum ether/ethyl acetate); ^{1}H-nmr (DMSO-d_6): 1.10 (d, $^3J_{4\beta\text{-Me},3a\alpha}$ = 7.00 Hz, 3H, C4β-CH_3), 2.82 (d, $^5J_{3a\alpha,10\text{-Me}}$ = 2.0 Hz, 3H, C10-CH_3), 3.50 (dd, $^3J_{4\alpha,4\beta\text{-Me}}$ = 7.10 Hz, $^3J_{4\alpha,3a\alpha}$ = 7.20 Hz, 1H, C4α-H), 4.23 (dd, $^3J_{3a\alpha,4\beta}$ = 7.20 Hz, $^5J_{3a\alpha,10\text{-Me}}$ = 2.0 Hz, 1H, C3α-H), 7.13 (mc, 2H), 7.33 (d, ^3J = 7.85 Hz, 2H, C2'-H, C6'-H), 7.43 (mc, 2H), 7.50 (dd, ^3J = 7.76 Hz, ^3J = 7.33 Hz, 2H), 7.79 (d, ^3J = 7.07 Hz, 1H, C9-H), 11.99 (s, 1H, NH) and the other enantiomer; EI-ms: m/z = 342 ($M^{+\cdot}$, 100%). Anal. Calcd for $C_{22}H_{18}N_2O_2$ (342.34): C, 77.17; H, 5.30; N, 8.18. Found: C, 77.11; H, 5.25; N, 8.09.

4-Methyl-2-phenyl-4,5,10,10a-tetrahydro-3aH-4,10-azaethanopyrrolo[3,4-b]carbazole-1,3,11-trione (13). 1-Methylpyrido[3,4-b]indol-3-one (**1b**) (0.1 g, 0.05 mmol) was heated with N-phenylmaleimide (0.197 g, 1.14 mmol) in a dry flask under an argon atmosphere at about 130 °C for 6 h. The residue was shaken four times with diethyl ether and the non-extractable remainder was boiled with acetone. The residues remaining after concentration of the diethyl ether and acetone extracts were combined and recrystallized from acetone. Yield: 0.091 g (49%); slightly yellowish crystals; decomposition above 250 °C; ^{1}H-nmr (acetone-d_6): 2.16 (s, 3H, C4-CH_3), 3.74 (d, $^3J_{3a,10a}$ = 7.51 Hz, 1H, C3a-H), 3.77 (dd, $^3J_{10a,3a}$ = 7.51 Hz, $^3J_{10a,10}$ = 2.92 Hz, 1H, C10a-H), 4.45 (d, $^3J_{10,10a}$ = 2.92 Hz, 1H, C10-H), 6.13 (d, ^3J = 7.46 Hz, 2H, C2'-H, C6'-H), 7.12 (mc, 5H, C3'-H, C4'-H, C5'-H, C7-H,

C8-H), 7.40 (d, ^3J = 7.98 Hz, 1H, C6-H), 7.56 (d, ^3J = 7.73 Hz, 1H, C9-H), 7.64 (s, 1H, 12-NH), 10.73 (s, 1H, 5-NH); EI-ms: m/z = 371 ($M^{+\cdot}$, 44%), 174 (100%). Anal. Calcd for $C_{22}H_{17}N_3O_3$ (371.39): C, 71.15; H, 4.61; N, 11.31. Found: C, 70.98; H, 4.58; N, 11.28.

Procedure for the Synthesis of Compounds 14 and 15. 1-Methylpyrido[3,4-b]indol-3-one (**1b**) (0.13 g, 0.65 mmol) was suspended in 15 ml of bromobenzene, the suspension was heated to boiling under an argon atmosphere, and treated with a solution of dimethyl acetylenedicarboxylate (0.2 ml, 1.63 mmol) in 2 ml of bromobenzene (syringe technique). The reaction mixture was heated at 156 °C for 3 h and then concentrated under vacuum. The products **14** and **15** were isolated using flash chromatography (elution with petroleum ether/ethyl acetate, 7/3).

Dimethyl 1-Methyl-3-oxo-2,3,4,9-tetrahydro-1H-1,4-ethenopyrido[3,4-b]indole-10,11-dicarboxylate (14). Yield: 0.015 g (7%); colorless crystals; mp 118-119 °C (petroleum ether/ethyl acetate); ^{1}H-nmr (CD_3CN): 2.65 (s, 3H, C1-CH_3), 3.67 (s, 3H, $COOCH_3$), 3.78 (s, 3H, $COOCH_3$), 5.68 (s, 1H, C4-H), 7.24 (mc, 1H, C6-H or C7-H), 7.54 (mc, 3H, 2-NH, C8-H, and C7-H or C6-H), 8.11 (d, ^3J = 7.96 Hz, 1H, C5-H), 9.61 (s, 1H, NH); EI-ms: m/z = 340 ($M^{+\cdot}$, 9%), 281 ($M^{+\cdot}$ - $COOCH_3$, 56%), 149 (100%): Anal. Calcd for $C_{18}H_{16}N_2O_5$ (340.33): C, 63.53; H, 4.74; N, 8.23. Found: C, 63.45; H, 4.70; N, 8.18.

Dimethyl 1-Methyl-9H-carbazole-2,3-dicarboxylate (15). Yield: 0.090 g (46%); colorless crystals; mp 182 °C (petroleum ether/ethyl acetate); ^{1}H-nmr (DMSO-d_6): 2.49 (s, 3H, C1-CH_3), 3.84 (s, 3H, $COOCH_3$), 3.85 (s, 3H, $COOCH_3$), 7.25 (dd, ^3J = 7.38 Hz, ^3J = 7.30 Hz, 1H, C6-H), 7.48 (dd, ^3J = 7.49 Hz, ^3J = 7.28 Hz, 1H, C7-H), 7.58 (d, ^3J = 8.12 Hz, 1H, C8-H), 8.26 (d, ^3J = 7.76 Hz, 1H, C5-H), 8.66 (s, 1H, C4-H), 11.84 (s, 1H, NH); EI-ms: m/z = 297 ($M^{+\cdot}$, 95%), 266 ($M^{+\cdot}$ - OCH_3, 63%), 207 ($M^{+\cdot}$ - $COOCH_3$ - OCH_3, 100%), 179 ($M^{+\cdot}$ - 2 $COOCH_3$, 51%). Anal. Calcd for $C_{17}H_{15}NO_4$ (297.31): C, 68.68; H, 5.09; N, 4.71. Found: C, 68.79; H, 5.01; N, 4.75.

Procedure for the Synthesis of Compounds 16 and 17. 1-Methylpyrido[3,4-b]indol-3-one (**1b**) (0.12 g, 0.6 mmol) was suspended in 15 ml of bromobenzene, the suspension was heated to boiling under an argon atmosphere, and treated with ethyl propiolate (1.2 ml, 10.6 mmol) (syringe technique). The reaction mixture was heated at 156 °C for a total of 10 h and then concentrated under vacuum. The products **16** and **17** were isolated using flash chromatography (elution with petroleum ether/ethyl acetate, 8/2).

Ethyl 1-Methyl-3-oxo-2,3,4,9-tetrahydro-1H-1,4-ethenopyrido[3,4-b]indole-11-carboxylate (16). Yield: 0.022 g (12%); colorless crystals; mp 176-177 °C (petroleum ether/ethyl acetate); ^{1}H-nmr (DMSO-d_6): 1.23 (t, ^3J = 7.08 Hz, 3H, $COOCH_2CH_3$), 2.74 (s, 3H, C1-CH_3), 4.15 (q, ^3J = 7.08 Hz, 2H, $COOCH_2CH_3$), 5.72 (d, ^3J = 12.40 Hz, 1H, C4-H), 7.20 (dd, ^3J = 6.74 Hz, ^4J = 2.15 Hz, 1H, C6-H), 7.54 (mc, 2H, C7-H, C8-H), 7.65 (s, 1H, 2-NH), 8.19 (d, ^3J = 7.83 Hz, 1H, C5-H), 8.67 (d, ^3J = 12.40 Hz, 1H, C10-H), 11.57 (s, 1H, 9-NH); EI-ms: m/z = 296 ($M^{+\cdot}$, 11%), 223 ($M^{+\cdot}$ - $COOC_2H_5$, 100%), Anal. Calcd for $C_{17}H_{16}N_2O_3$ (296.33): C, 68.91; H, 5.44; N, 9.45. Found: C, 68.98; H, 5.39; N, 9.39.

Ethyl 1-Methyl-9H-carbazole-2-carboxylate (17). Yield: 0.041 g (27%); colorless crystals; mp 120 °C (petroleum ether/ethyl acetate); ^{1}H-nmr (DMSO-d_6): 1.35 (t, ^3J = 7.09, 3H, $COOCH_2CH_3$), 2.78 (s, 3H, C1-CH_3), 4.32 (q, ^3J = 7.09 Hz, $COOCH_2CH_3$), 7.18 (dd, ^3J = 7.16 Hz, ^3J = 7.32 Hz, 1H, C6-H), 7.44 (dd, ^3J = 7.65 Hz, ^3J = 7.58 Hz, 1H, C7-H), 7.55 (d, ^3J = 8.15 Hz, 1H, C8-H), 7.64 (d, ^3J = 8.21 Hz, 1H, C4-H), 8.01 (d, ^3J = 8.21 Hz, 1H, C3-H), 8.14 (d, ^3J = 7.80 Hz, 1H, C5-H), 11.46 (s, 1H, NH); EI-ms: m/z = 253 ($M^{+\cdot}$, 100%), 224 ($M^{+\cdot}$ - C_2H_5, 26%), 208 ($M^{+\cdot}$ - OC_2H_5, 56%). Anal. Calcd for $C_{16}H_{15}NO_2$ (253.30): C, 75.87; H, 5.97; N, 5.53. Found: C, 75.79; H, 5.91; N, 5.56.

2-Cyano-1-methyl-9H-carbazole (18). 1-Methylpyrido[3,4-b]indol-3-one (**1b**) (0.12 g, 0.6 mmol) was suspended in 10 ml of bromobenzene, the suspension was heated to boiling under an argon atmosphere, and treated with α-chloroacrylonitrile (5 ml, 63 mmol) (syringe technique). The reaction mixture was heated at 156 °C for a total of 40 h and then concentrated under vacuum. The product **18** was isolated using flash chromatography (elution with petroleum ether/ethyl acetate, 17/3). Yield: 0.019 g (15%); colorless crystals; mp 154 °C (petroleum ether/ethyl acetate); ^{1}H-nmr (DMSO-d_6): 2.74 (s, 3H, C1-CH_3), 7.23 (dd, ^3J = 7.46 Hz, ^3J = 7.80 Hz, 1H, C6-H), 7.47 (d, ^3J = 8.08 Hz, 1H, C3-H or C4-H), 7.49 (dd, ^3J = 8.13 Hz, ^3J = 7.13 Hz, 1H, C7-H), 7.57 (d, ^3J = 8.18 Hz, 1H, C8-H), 8.13 (d, ^3J = 8.08 Hz, 1H, C4-H or C3-H), 8.20 (d, ^3J = 7.84 Hz, 1H, C5-H), 11.71 (s, 1H, NH); EI-ms: m/z = 206 ($M^{+\cdot}$, 5%), 71 (100%). Anal. Calcd for $C_{14}H_{10}N_2$ (206.25): C, 81.53; H, 4.89; N, 13.58. Found: C, 81.44; H, 4.82; N, 13.39.

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