Diels–Alder Reactions of Pyrano[3,4-*b*]indol-3-ones and a 2-Benzopyran-3-one with Hetero Substituted Olefins: Generation of Carbazole and Naphthalene Derivatives by Elimination instead of Dehydrogenation

Peter I. Van Broeck, Philippe E. Van Doren, Suzanne M. Toppet and Georges J. Hoornaert *
Departement Scheikunde, K.U. Leuven, Celestijnenlaan 200 F, B-3001 Leuven (Belgium)

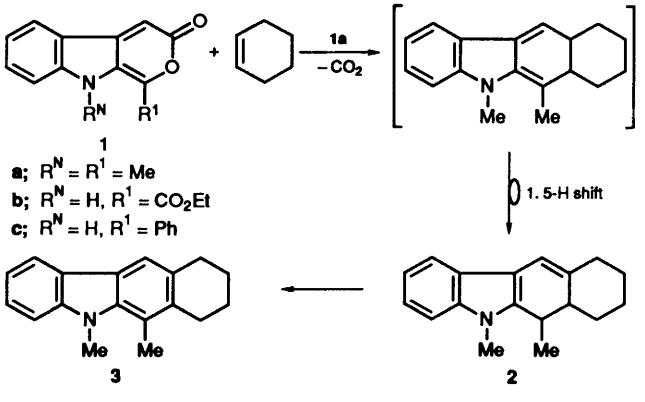
Pyrano[3,4-*b*]indol-3-ones are shown to undergo cycloaddition with electron-rich olefins. However, after loss of CO_2 from the adducts, the intermediate indole-2,3-quindodimethanes are not dehydrogenated—after a 1,5-sigmatropic hydrogen shift—to yield the expected heterosubstituted carbazoles. Rather, aromatisation arising from elimination of the hetero substituent takes place and other carbazoles are formed. In the same way, a hydroxyethylated naphthalenic compound was obtained from the adduct of 6,7-dimethoxy-1-methyl-2-benzopyran-3-one with 3,4-dihydrofuran. The hetero substituent is only conserved in cycloadditions of enamides with pyrano[3,4-*b*]indol-3-ones.

Recently, we reported that pyrano[3,4-*b*]indol-3-ones reacted with a series of electron-poor olefins to give stable substituted 1,2-dihydrocarbazoles.[1,2] The formation of these compounds involved cycloaddition of the starting materials, subsequent CO_2-extrusion from the adduct followed by a 1,5-sigmatropic hydrogen shift in an intermediate indole-2,3-quinodimethane.

The continued interest[3] in Diels–Alder reactions of pyrano[3,4-*b*]indol-3-ones prompted us to study the reaction of the pyranoindolone system and a 2-benzopyran-3-one with electron-rich dienophiles and related 2π-components.

Results and Discussion

1,9-Dimethylpyrano[3,4-*b*]indol-3-one **1a** when heated in neat cyclohexene gave a large amount of 6,6a,7,8,9,10-hexahydro-5,6-dimethylbenzo[*b*]carbazole **2** which could, as expected from earlier predictions,[1,2] be dehydrogenated to the corresponding 7,8,9,10-tetrahydrobenzo[*b*]carbazole **3**.



1
a; $R^N = R^1 = Me$
b; $R^N = H$, $R^1 = CO_2Et$
c; $R^N = H$, $R^1 = Ph$

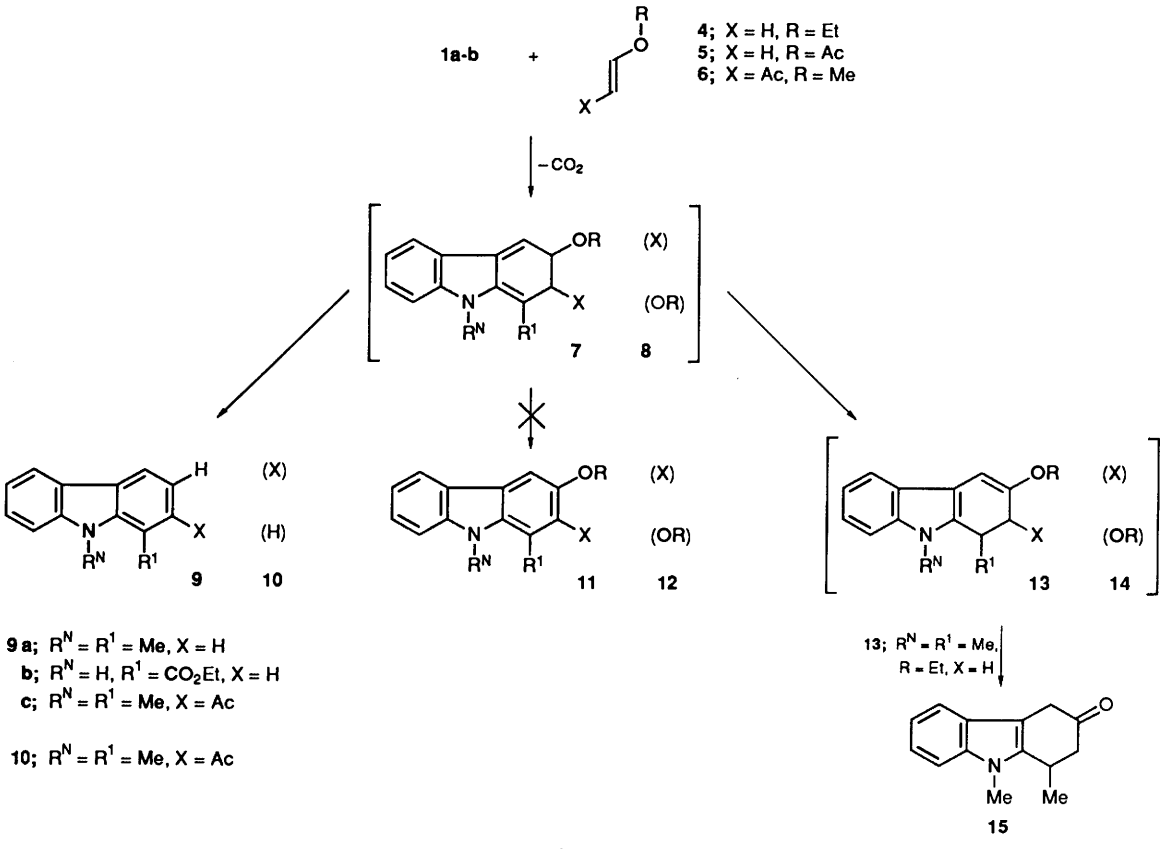
3 2

Scheme 1

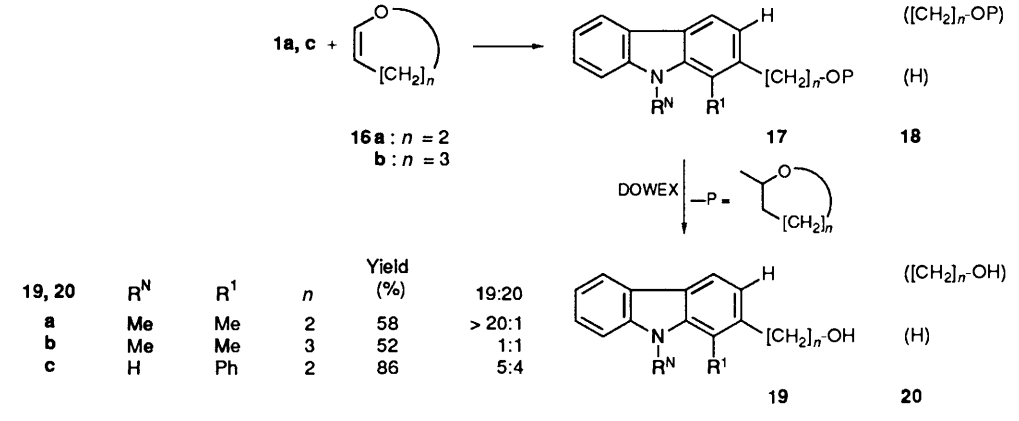
The observed high yield of the carbazolic compound **3** in the reaction of pyranoindolone **1a** with cyclohexene contrasts with the results obtained by Moody *et al.* in the reactions of pyranoindolones with unactivated acetylenic compounds such as hept-1-yne and diphenylacetylene to yield little if any carbazole.[3] Furthermore, the same authors observed no cycloaddition of the pyranoindolone system with electron-rich acetylenes. Because of this lack of reactivity, a more elaborate (5 steps) sequence rather than a simple Diels–Alder reaction of 1-phenylpyrano[3,4-*b*]indol-3-one with 1-methoxypropyne had to be used for the synthesis of the alkaloid hyellazole.[4]

The results obtained with cyclohexene prompted us to test the reactivity of the pyranoindolones **1a–b** with enol systems such as ethyl vinyl ether **4**, vinyl acetate **5** and 4-methoxybut-3-en-2-one **6**. These compounds and other heterosubstituted olefins, *e.g.* enamides, could yield polyfunctionalised carbazoles with protected hydroxy or amino groups. However, the major products isolated from the reaction of the pyranoindolones **1a** and **1b** with the enol ether **4** were, respectively, 1,9-dimethylcarbazole **9a** and ethyl carbazole-1-carboxylate **9b**, in each of which the ether group was absent. Reaction of the pyranoindolone **1a** with compound **5** also gave the 1,9-dimethylcarbazole **9a** in high yield (97%). Reaction of pyranoindolone **1a** with compound **6** provided the 2-acetyl-1,9-dimethylcarbazole **9c** and its 3-acetyl isomer **10** in a ratio of *ca.* 1:1. Compounds of type **9**, **10** probably arise from alcohol or acetic acid elimination from the intermediate indole-2,3-quinodimethanes **7**, **8** which fail to give (after rearrangement and dehydrogenation) the expected products of type **11**, **12**. The isolation of 1,2-dihydro-1,9-dimethylcarbazol-3(4*H*)-one **15** from the reaction of the pyranoindolone **1a** with the enol ether **4** may arise from a 1,5-hydrogen migration step, followed by hydrolysis of the corresponding 1,2-dihydrocarbazole **13**. The reactions with ethyl vinyl ether gave no information about the ratio of the intermediates **7**, **8**. However reaction of the pyranoindolones **1a** and **1c** with the cyclic enol ethers dihydrofuran **16a** and dihydropyran **16b** produced either one **17a** or two regioisomeric carbazoles **17b**, **c** and **18b**, **c** substituted at the 2- or 3-position with a protected hydroxyalkyl group. This protection by, respectively, a tetrahydrofuranyl group and a tetrahydropyranyl group is due to the excess of dienophile reacting with the hydroxyalkylated carbazoles **19**, **20** primarily formed by an elimination process. Removal of these groups and isolation of the alcohols **19** and **20** was possible *via* methanol elution of the compounds **17** and **18** on an activated Dowex column. The regiochemistry of the addition could be deduced from the *J* values for 4-H, 3-H or 2-H in compounds **19**, **20**. However, we feel that more experiments are required to explain the observed regiochemical behaviour. In the above experiments, avoidance of elimination in favour of dehydrogenation was not achieved by the use of a catalyst such as palladium-on-charcoal.[5]

A comparable and unavoidable elimination took place in the reaction of the pyranoindolone **1a** with *trans*-β-nitrostyrene. The 1,9-dimethyl-2- (or 3)-phenylcarbazoles **21** and **22** obtained

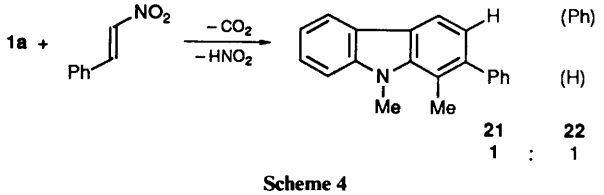


Scheme 2



19, 20	R^N	R^1	n	Yield (%)	19:20
a	Me	Me	2	58	> 20:1
b	Me	Me	3	52	1:1
c	H	Ph	2	86	5:4

Scheme 3

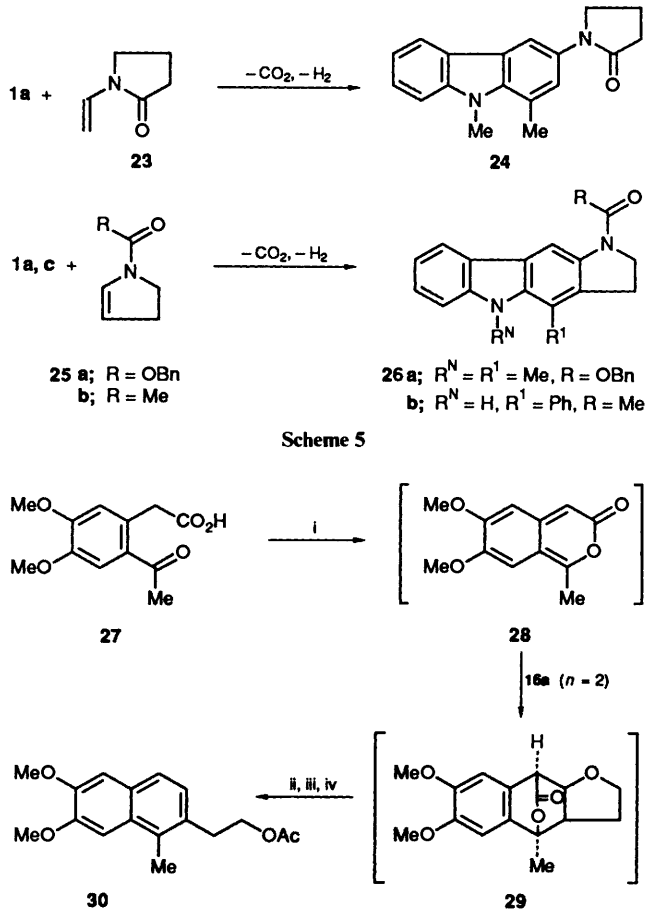


Scheme 4

(Scheme 4) were identical with those produced during the reaction of the pyranoindolone and styrene.[1]

Somewhat more successful results were obtained with enamides such as *N*-vinylpyrrolidone **23** or *N*-(benzyloxycarbonyl)- and *N*-acetyl-4,5-dihydropyrrole **25a**, **b** instead of enol ethers: the cycloadditions proceeded regioselectively and no elimination products were observed. Thus, reaction of the pyranoindolone **1a** and *N*-vinylpyrrolidone in the presence of a dehydrogenating catalyst gave a moderate yield of 1,9-dimethyl-3-(2-oxopyrrolidin-1-yl)carbazole **24** (2-H and 4-H, ^{1}H NMR signals at 7.43 and 7.97). The reaction of the pyranoindolone **1a** with compound **25a** and of the pyranoindolone **1c** with compound **25b** gave the *N*-acylated 2,3-dihydropyrrolo[3,2-*b*]carbazoles **26a** and **26b** (Scheme 5). The regiochemistry of the addition is assumed to be comparable with that observed for compound **24**. This is an agreement with the pronounced broadening of the 9-H and 10-H NMR signal as a result of the effect of the 1-benzyloxycarbonyl group in compound **26a**.

6,7-Dimethoxy-1-methyl-2-benzopyran-3-one **28** generated *in situ* from the *o*-acetylphenylacetic acid **27** in refluxing acetic anhydride as dehydrating agent,[6] showed a similar behaviour to that of the pyran[3,4-*b*]indol-3-ones **1**. The intermediate adduct **29** formed with dihydrofuran decomposed to a hydroxyethylated naphthalene derivative of which the alcohol function was further acetylated to yield the naphthalenic compound **30** (Scheme 6). However, the Diels–Alder reaction



Scheme 6 *Reactants and conditions:* i, Ac_2O, reflux; ii, $-CO_2$; iii, elimination (deprotection); iv, acetylation.

of 2-benzopyran-3-one **28** with *N*-vinylpyrrolidone yielded a complex mixture.

Experimental

IR spectra were recorded as thin films between NaCl plates or as solids in KBr pellets on a Perkin-Elmer 297 spectrometer. ^1H NMR spectra were recorded on a Bruker WM 250 spectrometer using Me_4Si as standard: *J* Values are in Hz. ^{13}C NMR spectra were all recorded on a Bruker WM 250 spectrometer operating at 62.5 MHz and using 90 and 135 DEPT pulse sequences to aid in assignment. Mass spectra were recorded on a Kratos MS 50 instrument operating at 70 eV and 150–250 °C as required. Exact mass measurements were performed at a resolution 10 000. M.p.s were taken on a Reichert-Jung Thermovar apparatus and are uncorrected. MN-Kieselgel 60 (70–230 mesh) or aluminium oxide (Fluka, type 507 C neutral) and chloroform stabilised with 2-methylbut-2-ene were used for chromatographic separations. All solvents and reagents were dried and purified by standard procedures. All cycloadditions were performed under nitrogen or *in vacuo*. Pyrano[3,4-*b*]indol-3-ones **1**,[7] phenylacetic acid derivative **27**[8] and *N*-acyl-4,5-dihydropyroles **25a–b**[9] were prepared as previously described.

Reaction of 1,9-*Dimethylpyrano*[3,4-b]*indol*-3-*one* **1a** *with Cyclohexene.*—A mixture of the pyranoindolone **1a** (0.43 g, 2 mmol) and cyclohexene (4 cm^3) was degassed by subsequent freeze–pump–thaw cycles; it was then heated in a sealed tube for 3 days at 120 °C. The excess of dienophile was evaporated under reduced pressure and the residue was chromatographed on silica gel (toluene–$CHCl_3$, 1:1) to give a mixture of 6,6a,7,8,9,10-hexahydro-5,6-dimethylbenzo[*b*]carbazole **2** and the corresponding 7,8,9,10-tetrahydrobenzo[*b*]carbazole **3** in a ratio of 3:1. Compound **2** was completely converted into the product **3** within a week.

For compound **2** δ_H(250 MHz; $CDCl_3$) 1.25 (3 H, d, *J* 7.5), 1.75 (7 H, m), 3.20 (3 H, m), 3.53 (3 H, s), 7.00 (3 H, m), 7.10 (1 H, br s) and 7.35 (1 H, m).

For compound **3** (0.46 g, 93%); m.p. 160 °C (MeOH) (Found: C, 86.6; H, 7.6; N, 5.5. $C_{18}H_{19}N$ requires C, 86.7; H, 7.7; N, 5.6%); δ_H(250 MHz; $CDCl_3$) 1.85 (4 H, m), 2.63 (3 H, s), 2.83 (2 H, t, *J* 6), 2.97 (2 H, td, *J* 6 and 1), 4.00 (3 H, s), 7.25 (3 H, m), 7.65 (1 H, d, *J* 1) and 7.97 (1 H, m); *m/z* 249 (M^+, 100%) and 234 (22)).

Reaction of Pyrano[3,4-b]*indol*-3-*ones* **1a** *and* **1b** *with Ethyl Vinyl Ether* **4** *and Reaction of the Pyranoindolone* **1a** *with Vinyl Acetate* **5** *and* 4-*Methoxybut*-3-*en*-2-*one* **6**: *General Procedure.*—A degassed mixture of the pyranoindolone **1a** or **1b** (1.5 mmol) and dienophiles **4**, **5** or **6** (5 cm^3) with toluene (3 cm^3) was heated in a sealed tube during 5 days at 80 °C for ethyl vinyl ether, or during 3 days at 120 °C for compounds **5** and **6**. The residue obtained after evaporation was chromatographed on silica gel ($CHCl_3$) to give 1,9-dimethylcarbazole (**9a**) or ethyl carbazole-1-carboxylate **9b** for reactions of compounds **4** and **5**. The 1,2-dihydro-1,9-dimethylcarbazole-3(4*H*)-one **15** was also isolated in the reaction of compound **4** with **1a**. A 1:1 mixture of 2-acetyl-1,9-dimethylcarbazole **9c** and its 3-acetyl isomer **10** was obtained from the reaction of compound **6**. They could be separated by HPLC.

For compound **9a** (44% with ethyl vinyl ether and 97% with vinyl acetate); m.p. 110 °C (MeOH) (lit.,[10] 108–109 °C; δ_H(250 MHz; $CDCl_3$) 2.60 (3 H, s), 3.80 (3 H, s), 6.8–7.4 (5 H, m) and 7.7–8.0 (2 H, m); *m/z* 195 (M^+, 100%), 180 (11) and 165 (4).

For compound **9b** (0.18 g, 50%); m.p. 102 °C (hexane) (Found: M^+, 239.0949. $C_{15}H_{13}NO_2$ requires *M*, 239.0946); ν_{max}(NaCl)/cm^{-1} 1680 (CO_2Et); δ_H(250 MHz; $CDCl_3$) 1.50 (3 H, t, *J* 7.5), 4.50 (2 H, q, *J* 7.5), 7.25 (1 H, t, *J* 7), 7.27 (1 H, td, *J* 7 and 1.5), 7.45 (1 H, td, *J* 7 and 1.5), 7.50 (1 H, dd, *J* 7 and 1.5), 8.10 (2 H, dd, *J* 7 and 1.5), 8.28 (1 H, dd, *J* 7 and 1.5) and 9.95 (1 H, br s); δ_C 167.5 (CO), 140.4 (C), 139.6 (C), 127.3 (CH), 126.5 (CH), 125.3 (CH), 124.6 (C), 122.5 (C), 120.4 (CH), 119.9 (CH), 118.4 (CH), 111.9 (C), 111.1 (CH), 60.9 (CH_2) and 14.4 (CH_3); *m/z* 239 (M^+, 68%), 193 (100), 165 (33) and 139 (14).

For compound **9c** (0.16 g, 45%); m.p. 87 °C (MeOH) (Found: M^+, 237.1154. $C_{16}H_{15}NO$ requires *M*, 237.1154); ν_{max}(NaCl)/cm^{-1} 1685 (CO); δ_H(250 MHz; $CDCl_3$) 2.67 (3 H, s), 2.90 (3 H, s), 4.12 (3 H, s), 7.2–7.5 (4 H, m), 8.00 (1 H, d, *J* 7.5) and 8.10 (1 H, s); δ_C 203.5 (CO), 143.3 (C), 140.8 (C), 138.1 (C), 126.7 (CH), 125.7 (C), 122.2 (C), 120.5 (CH and C), 119.7 (CH), 119.4 (CH), 117.3 (CH), 109 (CH), 33.4 (CH_3), 30.8 (CH_3) and 16.8 (CH_3); *m/z* 237 (M^+, 91%), 222 (90) and 194 (42).

For compound **10** (0.16 g, 45%); m.p. 163 °C (MeOH); δ_H(250 MHz; $CDCl_3$) 2.67 (3 H, s), 2.85 (3 H, s), 4.10 (3 H, s), 7.2–7.5 (3 H, m), 7.69 (1 H, s), 8.12 (1 H, d, *J* 7.5) and 8.55 (1 H, s); δ_C 197.6 (CO), 142.5 (C), 142.2 (C), 128.9 (C and CH), 126.3 (CH), 123.3(C), 123.2 (C), 120.1 (C and CH), 120 (CH), 119.8 (CH), 109 (CH), 32.2 (CH_3), 26.5 (CH_3) and 20.3 (CH_3).

For compound **15** (0.06 g, 18%) (Found: M^+, 213.1151. $C_{14}H_{15}NO$ requires *M*, 213.1154); ν_{max}(NaCl)/cm^{-1} 1720 (CO); δ_H(250 MHz; $CDCl_3$) 1.27 (3 H, d, *J* 7.5), 2.55 (1 H, dd, *J* 13.5 and 2), 2.99 (1 H, dd, *J* 13.5 and 7.5), 3.47 (1 H, pd, *J* 7.5 and 2), 3.48 (1 H, d, *J* 20), 3.67 (3 H, s), 3.69 (1 H, d, *J* 20), 7.12 (1 H, t, *J* 8), 7.25 (2 H, m) and 7.42 (1 H, d, *J* 8); δ_C 209.7 (CO), 138.2 (C), 137.6 (C), 126.1 (C), 121.6 (CH), 119.3 (CH),

117.6 (CH), 109 (CH), 104.8 (C), 46.9 (CH_2), 36.5 (CH_2), 29.1 (CH_3), 28.4 (CH) and 21.5 (CH_3); *m/z* 213 (M^+, 84%), 185 (46) and 170 (100).

Reaction of 1,9-*Dimethylpyrano*[3,4-b]*indol*-3-*one* **1a** *with* 3,4-*Dihydrofuran* **16a** *or* 3,4-*Dihydro*-2H-*pyran* **16b** *and of* 1-*Phenylpyrano*[3,4-b]*indol*-3-*one* **1b** *with Dienophile* **16a**: *General Procedure*.—A degassed mixture of the pyranoindolone **1a** or **1b** (1 mmol), the dienophile **16a** or **16b** (5 cm^3), palladium-on-charcoal (0.04 g) and toluene (3 cm^3) was heated in a sealed tube during 4 days at 120 °C. The residue obtained after evaporation was chromatographed on silica gel (2% EtOAc–98% $CHCl_3$) to give a tetrahydrofuranyl ether **17a**, **c**; **18a**, **c** or a tetrahydropyranyl ether **17b**, **18b** which could be deprotected on an activated Dowex column (25 g Dowex, eluent MeOH) to give the hydroxyalkylated carbazoles **19**, **20**.

For compound **19a** (0.14 g, 58%); m.p. 125 °C (toluene) (Found: M^+, 239.1311. $C_{16}H_{17}NO$ requires *M*, 239.1310); ν_{max}(KBr)/cm^{-1} 3290 (OH); δ_H(250 MHz; $CDCl_3$) 1.63 (1 H, br s), 2.75 (3 H, s), 3.07 (2 H, t, *J* 8), 3.85 (2 H, t, *J* 8), 4.03 (3 H, s), 7.02 (1 H, d, *J* 8), 7.18 (1 H, m), 7.30 (1 H, d, *J* 8), 7.43 (1 H, m), 7.83 (1 H, d, *J* 8) and 7.99 (1 H, d, *J* 8); δ_C 142.3 (C), 140.9 (C), 134.6 (C), 125.4 (CH), 122.8 (C), 122.7 (C), 122 (CH), 119.6 (CH), 119.1 (C), 118.9 (CH), 117.7 (CH), 108.7 (CH), 63.3 (CH_2), 37.2 (CH_2), 33.2 (CH_3) and 15 (CH_3); *m/z* 239 (M^+, 49%), 208 (100) and 193 (8).

Compounds **19b** and **20b** were obtained as a 1:1 mixture (0.13 g, 52%) which could be separated by HPLC.

For compound **19b** (0.07 g, 27%); m.p. 80–82 °C (toluene) (Found: M^+, 253.1472. $C_{17}H_{19}NO$ requires *M*, 253.1467); ν_{max}(KBr)/cm^{-1} 3325 (OH); δ_H(250 MHz; $CDCl_3$) 1.40 (1 H, br s), 1.90 (2 H, p, *J* 7), 2.75 (3 H, s), 2.90 (2 H, t, *J* 7), 3.70 (2 H, t, *J* 7), 4.06 (3 H, s), 7.06 (1 H, d, *J* 8), 7.2–7.4 (3 H, m), 7.86 (1 H, d, *J* 8) and 8.00 (1 H, d, *J* 8); δ_C 142.4 (C), 141 (C), 138.5 (C), 125.3 (CH), 123 (C), 122.3 (C), 121.5 (CH), 119.6 (CH), 118.9 (CH), 118.5 (C), 117.6 (CH), 108.6 (CH), 62.6 (CH_2), 34.1 (CH_2), 33.3 (CH_3), 30.5 (CH_2) and 14.9 (CH_3); *m/z* 253 (M^+, 33%), 222 (15), 208 (100) and 194 (12).

For compound **20b** (0.06 g, 25%); m.p. 120–122 °C (toluene); ν_{max}(KBr)/cm^{-1} 3350 (OH); δ_H(250 MHz; $CDCl_3$) 1.40 (1 H, br s), 1.90 (2 H, p, *J* 7), 2.80 (3 H, s), 2.90 (2 H, t, *J* 7), 3.70 (2 H, t, *J* 7), 4.06 (3 H, s), 7.06 (1 H, d, *J* 2), 7.2–7.4 (3 H, m), 7.75 (1 H, d, *J* 2) and 8.00 (1 H, d, *J* 8); δ_C 141.7 (C), 138.1 (C), 132.1 (C), 129.3 (CH), 125.2 (CH), 123.5 (C), 122.5 (C), 120 (C), 119.6 (CH), 118.4 (CH), 117.2 (CH), 108.2 (CH), 62.2 (CH_2), 34.6 (CH_2), 31.9 (CH_3), 31.5 (CH_2) and 19.9 (CH_3).

Compounds **19c** and **20c** were obtained as a 5:4 mixture (0.24 g, 85%) (Found: M^+, 287.1315. $C_{20}H_{17}NO$ requires *M*, 287.1310); ν_{max}(KBr)/cm^{-1} 3300 (OH).

For compound **19c** δ_H(250 MHz; $CDCl_3$) 1.59 (1 H, s), 3.03 (2 H, t, *J* 8), 3.90 (2 H, t, *J* 8), 7.17 (1 H, d, *J* 8), 7.2–7.55 (8 H, m), 7.97 (1 H, d, *J* 8), 8.05 (1 H, d, *J* 8) and 8.3 (1 H, br s).

For compound **20c**; δ_H(250 MHz; $CDCl_3$) 1.29 (1 H, br s), 2.90 (2 H, t, *J* 8), 3.69 (2 H, t, *J* 8), 7.25 (1 H, d, *J* 2), 7.3–7.6 (8 H, m), 7.8 (1 H, br s), 7.88 (1 H, d, *J* 2) and 8.04 (1 H, d, *J* 8); *m/z* 287 (M^+, 50%), 256 100), 242 (3) and 241 (7).

Reaction of the Pyranoindolone **1a** *with* trans-β-*Nitrostyrene*.—A degassed mixture of the pyranoindolone **1a** (0.21 g, 1 mmol), and *trans*-β-nitrostyrene (0.70 g, 4.7 mmol) and toluene (3 cm^3) was heated in a sealed tube for 18 h at 100 °C. The residue obtained after evaporation was chromatographed on silica gel with a gradient elution (100% $CHCl_3$ to 5% EtOAc–95% $CHCl_3$) to give the 1,9-dimethyl-2- (or 3)-phenylcarbazoles **21** and **22** in a 1:1 ratio (0.13 g, 48%) with the spectroscopic characteristics as described previously.[1]

Reaction of the Pyranoindolone **1a** *with* 1-*Vinylpyrrolidin*-2-*one* **23** *or* N-(*Benzyloxycarbonyl*)-4,5-*dihydropyrrole* **25a** *and of* 1-*Phenylpyrano*[3,4-b]*indol*-3-*one* **1c** *with* N-*Acetyl*-4,5-*dihydropyrrole* **25b**: *General Procedure*.—A mixture of the pyranoindolone **1a** (2 mmol), the pyrrolidinone **23** (5 cm^3) or 4,5-dihydropyrrole **25a** (2 cm^3) and a mixture of pyranoindolone **1c** (0.26 g, 1 mmol), with the dienophile **25b** (3 cm^3), palladium-on-charcoal (0.04 g) and toluene (3 cm^3) was degassed and heated in a sealed tube during 5, 4 and 2 days respectively at 120 °C. The residue obtained after evaporation was chromatographed on deactivated aluminium oxide (6 cm^3 water/100 g aluminium oxide) (10% EtOAc–90% $CHCl_3$) to give 1,9-dimethyl-3-(2-oxopyrrolidin-1-yl)carbazole **24** or the *N*-acylated 2,3-dihydropyrrolo[3,2-*b*]carbazoles **26**.

For compound **24** (0.15 g, 27%); m.p. 201–202 °C (toluene) (Found: M^+, 278.1417. $C_{18}H_{18}N_2O$ requires *M*, 278.1419); ν_{max}(KBr)/cm^{-1} 1685 (CO); δ_H(250 MHz; $CDCl_3$) 2.17 (2 H, p, *J* 8), 2.64 (2 H, t, *J* 8), 2.81 (3 H, s), 3.92 (2 H, t, *J* 8), 4.02 (3 H, s), 7.19 (1 H, m), 7.32 (1 H, d, *J* 8), 7.43 (2 H, m), 7.97 (1 H, br d, *J* 2) and 8.02 (1 H, dd, *J* 8 and 1); δ_C 174 (CO), 142.1 (C), 137 (C), 131.4 (C), 125.7 (CH), 123.4 (C), 122.8 (C), 122.6 (CH), 120.6 (C), 120 (CH), 118.8 (CH), 110.5 (CH), 108.5 (CH), 49.9 (CH_2), 32.5 (CH_2), 32.1 (CH_3), 20.2 (CH_3) and 18.1 (CH_2); *m/z* 278 (M^+, 100%), 223 (34) and 195 (8).

For compound **26a** (0.25 g, 34%); m.p. 187–188 °C (MeOH–$CHCl_3$ 9:1) (Found: M^+, 370.1674. $C_{24}H_{22}N_2O_2$ requires *M*, 370.1681); ν_{max}(KBr)/cm^{-1} 1700 (CO); δ_H(250 MHz; $CDCl_3$) 2.59 (3 H, s), 3.09 (2 H, t, *J* 8), 3.96 (3 H, s), 4.09 (2 H, t, *J* 8), 5.32 (2 H, br s), 7.16 (1 H, t, *J* 8), 7.25 (1 H, d, *J* 8), 7.4–7.6 (6 H, m), 8.03 (1 H, br d), and 8.39 (1 H, br s); δ_C 152.9 (CO), 142.2 (C), 136.7 (C), 136.4 (C), 135 (C), 128.5 (CH), 128.3 (C), 128 (CH), 127.9 (CH), 125 (CH), 123.3 (C), 123.2 (C), 119.8 (CH), 118.5 (CH), 116.5 (C), 108.4 (CH), 103.6 (CH), 66.9 (CH_2), 47.6 (CH_2), 32.4 (CH_3), 27 (CH_2) and 15.4 (CH_3); *m/z* 370 (M^+, 19%), 235 (40), 220 (38) and 91 (100).

For compound **26b** obtained as an unstable oil (0.08 g, 25%) (Found: M^+, 326.1419. $C_{22}H_{18}N_2O$ requires *M*, 326.1419); ν_{max}(NaCl)/cm^{-1} 1715 (CO); δ_H(250 MHz; $CDCl_3$) 2.26 (3 H, s), 3.21 (2 H, t, *J* 8), 4.08 (2 H, t, *J* 8), 7.1–7.6 (8 H, m), 7.9 (1 H, br s), 8.1 (1 H, d, *J* 8) and 8.95 (1 H, s); *m/z* 326 (M^+, 100%), 283 (72), 254 (30) and 206 (8).

Reaction of 6,7-*Dimethoxy*-2-*benzopyran*-3-*one* **28** *with the Dienophile* **16a** *in Acetic Anhydride*.—A mixture of 2-acetyl-4,5-dimethoxyphenylacetic acid **27** (0.21 g, 0.88 mmol), the dienophile **16a** (3 cm^3) and acetic anhydride (freshly distilled over quinoline, 10 cm^3) was degassed and heated in a sealed tube for 2.5 h at 120 °C. The residue obtained after evaporation was chromatographed on silica gel with a gradient elution (100% $CHCl_3$ to 5% EtOAc–95% $CHCl_3$) to give a mixture of compounds **30** and a compound with the alkanol group protected by a tetrahydrofuranyl group. Deprotection on an activated DOWEX column and acylation with acetic anhydride yielded a pure hydroxyethylated naphthalenic compound **30** (0.18 g, 72%); m.p. 114 °C (MeOH) (Found: M^+, 288.1358. $C_{17}H_{20}O_4$ requires *M*, 288.1361); ν_{max}(KBr)/cm^{-1} 1750 (CO); δ_H(250 MHz; $CDCl_3$) 1.98 (3 H, s), 2.54 (3 H, s), 3.05 (2 H, t, *J* 8), 3.90 (3 H, s), 3.95 (3 H, s), 4.20 (2 H, t, *J* 8), 7.09 (1 H, s), 7.17 (1 H, d, *J* 9), 7.25 (1 H, s) and 7.5 (1 H, d, *J* 9); δ_C 171.1 (CO), 149.4 (C), 148.8(C), 130.9 (C), 130.5 (C), 128.5 (C), 128.3 (C), 126.8 (CH), 124.6 (CH), 106.8 (CH), 103.1 (CH), 64.6 (CH_2), 55.7 (CH_3), 33.5 (CH_2), 21 (CH_3) and 14.6 (CH_3); *m/z* 288 (M^+, 27), 228 (100) and 251 (42).

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