# Diels-Alder Reactivity of Pyrano[3,4-*b*]indol-3-ones. Part 4.[1] Synthesis of the Carbazole Alkaloids Carbazomycin A and B and Hyellazole

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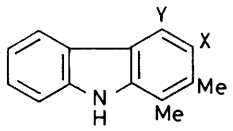
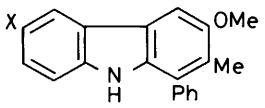
The first synthesis of the carbazole alkaloids carbazomycins A and B (**1**) is described. The key step is the regioselective Diels-Alder reaction between 1-methylpyrano[3,4-*b*]indol-3-one (**4**) and ethyl trimethylsilyl propynoate to give ethyl 1-methyl-3-trimethylsilylcarbazole-2-carboxylate (**6**). The ester and trimethylsilyl groups in carbazole (**6**) are converted into methyl and methoxy groups respectively, and the final oxygen substituent is introduced, after protection of the carbazole nitrogen, by bromination, lithiation, formation of the corresponding borate, and oxidation. The carbazole alkaloid hyellazole (**3a**) is synthesised by a similar route from 1-phenylpyrano[3,4-*b*]indol-3-one.

The carbazomycins (**1**), isolated from *Streptovertcillium*, are the first antibiotics which contain the carbazole nucleus. The structure of carbazomycin B (**1b**) was determined by extensive $^1H$ and $^{13}C$ n.m.r. studies, and was unequivocally confirmed to be 4-hydroxy-3-methoxy-1,2-dimethylcarbazole (**1b**) by an *X*-ray crystallographic analysis.[2] Carbazomycin A was postulated to be 3,4-dimethoxy-1,2-dimethylcarbazole (**1a**), by analogy with carbazomycin B, together with spectroscopic analysis, and chemical conversion of carbazomycin B into carbazomycin A with diazomethane. Carbazomycin B was found to be active against certain types of phytopathogenic fungi, and also showed rather weak antibacterial and anti-yeast activities. Carbazomycin A, however, showed only very weak antifungal and antibacterial activity.[2a] Since the isolation of carbazomycins A and B in 1980, another six members of the carbazomycin family, designated as carbazomycins C–H, have recently been isolated from the same *Streptomyces* species.[3]

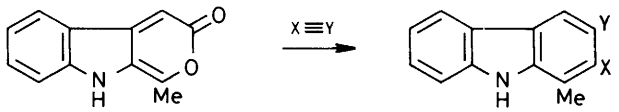



(**1a**) X = Y = OMe (carbazomycin A)
(**1b**) X = OMe, Y = OH (carbazomycin B)
(**2a**) X = H, Y = OMe (3-deoxycarbazomycin)
(**2b**) X = OMe, Y = H (4-deoxycarbazomycin)




(**3a**) X = H (hyellazole)
(**3b**) X = Cl (6-chlorohyellazole)

Although carbazomycins A and B were isolated nearly 10 years ago, these relatively simple compounds have not yet been synthesised, and this fact highlights the drawbacks of existing routes to polysubstituted carbazoles.[4,5] The synthesis of both 3- and 4-deoxycarbazomycins (**2a**) and (**2b**) has, however, recently been reported,[6,7] although the key step in the two syntheses, involving the Diels–Alder reaction of 3-vinylindoles with dimethyl acetylenedicarboxylate, was reported to proceed in very low yield.




(**4**) (**5**)

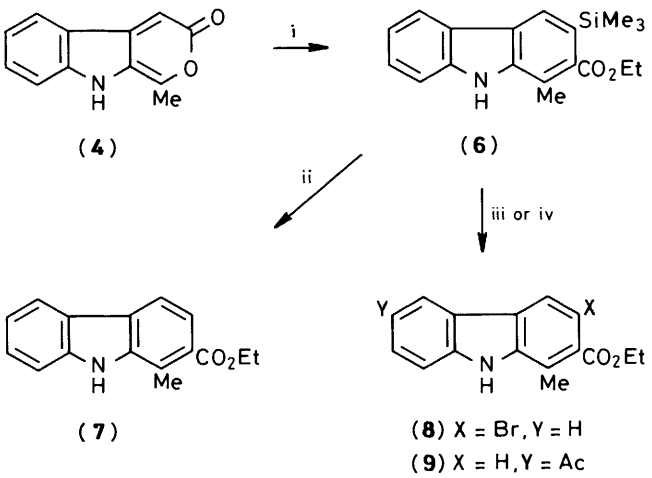
**Scheme 1.**

Two closely related carbazole alkaloids are hyellazole (**3a**) and its 6-chloro derivative (**3b**), isolated from the blue-green algae *Hyella caespitos*.[8] The structures of these carbazoles were determined by spectroscopic means and in the case of 6-chlorohyellazole (**3b**) confirmed by an *X*-ray crystallographic analysis.[8] Both hyellazole (**3a**) and 6-chlorohyellazole (**3b**) have been previously synthesised.[9] We have recently described a versatile route to carbazoles (**5**) based on the Diels–Alder reaction of pyrano[3,4-*b*]indol-3-ones, *e.g.* (**4**), with alkynes (Scheme 1), and have studied in detail the steric and electronic effects which influence the regiochemistry of the cycloaddition.[10] We now report the full details of the application of this chemistry to the first synthesis of the carbazomycins A and B, and of hyellazole.[11,12]

## Results and Discussion

*Synthesis of the Carbazomycins.*—In order to simplify the synthesis of the carbazomycins (**1**), 3-methoxy-1,2-dimethylcarbazole (4-deoxycarbazomycin) (**2b**) was selected as the initial target. 1,2,3-Trisubstituted carbazoles can readily be assembled by the pyranoindole methodology described in Scheme 1, and it was planned to introduce the 4-hydroxy or -methoxy substituent present in the carbazomycins in the later stages of the synthesis.

In principle, deoxycarbazomycin (**2b**) could be synthesised in a single step by Diels–Alder reaction of the 1-methylpyranoindolone (**4**) with 1-methoxypropyne. However, it was established earlier[10] that the pyranoindole (**4**) does not undergo Diels–Alder reaction with electron-rich alkynes. Therefore the substituents on the alkyne obviously need to be carefully chosen, such that they will enable the Diels–Alder reaction with the pyranoindole (**4**) to work, and also be easily transformed into the required groups at the 2- and 3-positions in the natural products. Knowing that at least one electron-withdrawing group on the acetylenic dienophile was necessary, one possibility would be to utilise the Diels–Alder reaction of pent-2-yn-




**Scheme 2.** *Reagents:* i, $EtO_2CC{\equiv}CSiMe_3$, PhBr, reflux; ii, aqueous $CF_3CO_2H$, heat; iii, NBS, MeCN; iv, AcCl, $AlCl_3$, $CH_2Cl_2$

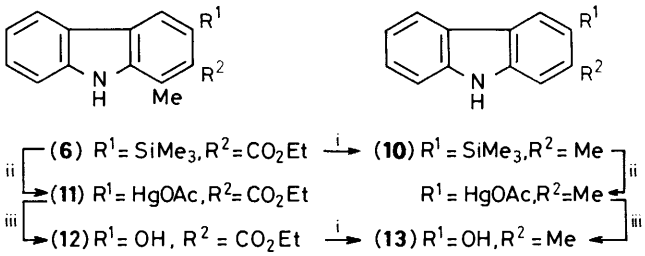
4-one with the pyranoindole (**4**), in which the acetyl group in the Diels–Alder adduct, could be transformed into an oxygen functionality by a Baeyer-Villiger oxidation. Although this approach looks attractive, our previous studies on the Diels–Alder reaction of the pyranoindole (**4**) have shown that such an unsymmetrical alkyne, which bears an electron-withdrawing group, and a second simple alkyl group, reacts to give the major product with the electron-withdrawing group at the 2-position of the carbazole. With this in mind, ethyl 3-trimethylsilylpropynoate[13] was chosen as the alkyne component in the Diels–Alder reaction with the pyranoindole (**4**). The silylated alkyne was chosen for a number of reasons. Firstly, it was expected that the alkyne would add in a highly regioselective manner to give the carbazole adduct with the ester group in the 2-position and the trimethylsilyl group in the 3-position, and secondly, it was hoped that the bulky trimethylsilyl group would not only help direct the orientation of cycloaddition in the required sense, but also be a potential hydroxy group, with the ester to become the 2-methyl group on reduction.

Ethyl 3-trimethylsilylpropynoate was prepared by lithiation of ethyl propiolate followed by quenching with trimethylsilyl chloride, although now the alkyne is commercially available. The Diels–Alder reaction of the pyranoindole (**4**) with the silylalkyne in refluxing bromobenzene was, indeed, highly regioselective, and gave the required trisubstituted carbazole (**6**) in 77% yield. Although on a small scale (100—200 mg) the Diels–Alder reaction of the pyranoindole (**4**) with the silylalkyne gave a very good yield (70—80%) of the carbazole (**6**), on a multi-gram scale (4—6 g) the reaction was found to be slightly lower yielding (50—55%). The regiochemistry of this selective Diels–Alder reaction was proved by protodesilylation of (**6**) with aqueous trifluoroacetic acid, to give the known[14] ethyl 1-methylcarbazole-2-carboxylate (**7**) in 86% yield (Scheme 2).

The Diels–Alder reaction of the pyranoindole (**4**) with 3-trimethylsilylpropanal in refluxing bromobenzene was also found to be completely regioselective and gave 1-methyl-3-trimethylsilylcarbazole-2-carbaldehyde in 39% yield. This reaction was less clean and lower yielding than the corresponding reaction with ethyl 3-trimethylsilylpropynoate probably as a result of the thermal instability of the acetylenic aldehyde.

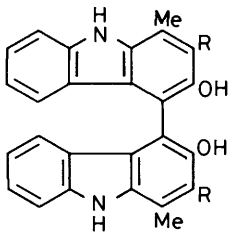
The 3-trimethylsilylcarbazole (**6**) prepared by the Diels–Alder reaction described above is potentially a very useful intermediate as the silicon group can be substituted by a variety of electrophiles.[15] For example treatment of the carbazole (**6**) with *N*-bromosuccinimide (NBS) in acetonitrile resulted in *ipso*-bromodesilylation to give specifically the 3-bromo derivative (**8**) in excellent yield (97%). Acetylation of carbazole (**6**) under Friedel–Crafts conditions, however, gave no products resulting from *ipso*-attack. Instead substitution occurred at the 6-position, together with loss of the trimethylsilyl group, which presumably occurred during the acidic work-up, to give the 6-acetyl derivative (**9**) in 55% yield together with the desilylated carbazole (**7**) (39%) (Scheme 2).

Returning to the synthesis of carbazomycins A and B, the 3-trimethylsilyl group in carbazole (**6**) needed to be converted into an oxygen function, and the ester into a methyl group, steps which, in principle, could be carried out in either order. Reduction of the 2-ester group in carbazole (**6**) with lithium aluminium hydride in refluxing tetrahydrofuran (THF) gave the expected 1-methyl-3-trimethylsilylcarbazol-2-ylmethanol in good yield together with a small amount of 1,2-dimethyl-3-trimethylsilylcarbazole (**10**) (4%). Formation of the carbazole (**10**) in the above reduction was not expected, although it was fortuitous, as it implied that the 2-ester group in carbazole (**6**) could be converted directly into the required methyl group in a single step. This transformation was achieved simply by carrying out the reduction at a higher temperature, and heating a mixture of the carbazole (**6**) with an excess of lithium aluminium hydride in refluxing dioxane for 18 h to give directly the dimethylcarbazole (**10**) in virtually quantitative yield on a multi-gram scale (Scheme 3).




**Scheme 3.** *Reagents*: i, $LiAlH_4$, dioxane, reflux; ii, $Hg(OAc)_2$, AcOH; iii, borane–THF, then alkaline peroxide work-up

The conversion of simple arylsilanes into the corresponding aryl trifluoroacetates with lead(IV) trifluoroacetate in trifluoroacetic acid has been reported in the literature.[16] However, when either of the carbazoles (**6**) or (**10**) was subjected to these conditions extremely rapid decomposition of the starting material was observed, presumably owing to the instability of the electron-rich carbazole ring system to the powerful oxidising conditions. The transformation of the 3-trimethylsilyl group in carbazoles (**6**) and (**10**) to the corresponding 3-hydroxy group was therefore accomplished by a two-step sequence employing milder oxidising conditions. Treatment of the carbazole (**6**) with mercury(II) acetate in acetic acid at room temperature resulted in rapid mercuriodesilylation[17] to give the arylmercury compound (**11**), which precipitated out of the reaction mixture and was isolated simply by filtration to give analytically pure material in 60% yield. Hydroboration[18] of the 3-mercuriocarbazole (**11**) with an excess of borane–THF complex gave the corresponding arylborane which was oxidised *in situ* with alkaline hydrogen peroxide to give the 3-hydroxycarbazole (**12**) in 76% yield (Scheme 3). Reduction of the 2-ester group in the carbazole (**12**) to give the corresponding methyl group, with lithium aluminium hydride in refluxing dioxane proved difficult, since a large excess of the reducing agent had to be used and even after 54 h only moderate yields (30—42%) of the required product (**13**) could be obtained. A second product was also formed in the reaction, in low yield, and based on its



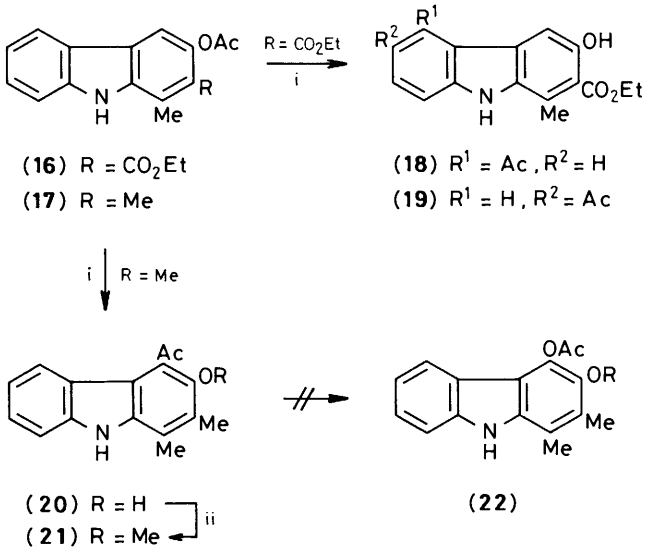
(14) R = Me
(15) R = $CO_2Et$

spectroscopic data this was tentatively assigned as the 4,4′-bicarbazole (**14**).

Although the reduction of the 2-ester in carbazole (**12**) gave only moderate yields of the required carbazole (**13**), this compound could be obtained in good yield from 1,2-dimethyl-3-trimethylsilycarbazole (**10**). Thus, mercurio-desilylation of the carbazole (**10**) gave the arylmercury compound (66%), which was hydroborated and oxidised as before to give the hydroxycarbazole (**13**) in 85% yield (Scheme 3). Therefore, although two routes have been developed for the synthesis of 3-hydroxy-1,2-dimethylcarbazole (**13**), both from carbazole (**6**), the higher yielding sequence requires reduction of the 2-ester group in carbazole (**6**) to be carried out before conversion of the 3-trimethylsilyl group into the hydroxy function.

It was envisaged that the 3-hydroxy group in the carbazoles (**13**) and (**12**) could be used to direct the introduction of the extra hydroxy group present at C-4 in the carbazomycins. Several methods for the introduction of the 4-oxygen substituent were therefore attempted on both carbazoles (**13**) and (**12**) in parallel. Radical oxidation of the hydroxycarbazoles (**13**) and (**12**), with either Fremy's salt[19] or benzoyl t-butyl nitroxide,[20] to give the corresponding *ortho*-quinones, was unsuccessful and in both cases led to the formation of a complex mixture of products. The mass spectrum of the product mixture resulting from the radical oxidation of the carbazole (**13**) gave a molecular ion corresponding to a dimer of the starting carbazole, but the $^1H$ n.m.r. spectrum of the product mixture was very complex. The $^1H$ n.m.r. spectrum of the product mixture resulting from the oxidation of the carbazole (**12**) was also very complex, although the mass spectrum gave a molecular ion of 285, which corresponds to the mass of the desired *ortho*-quinone. The products from these radical oxidations were very difficult to purify since they were all extremely polar and virtually insoluble in most organic solvents. Other attempts to introduce the extra hydroxy group at C-4 in the carbazoles (**13**) and (**12**) using oxidants such as manganese(IV) oxide[21] or dibenzoyl peroxide[22] resulted in either complete decomposition of the hydroxycarbazoles or the formation of the dimeric 4,4′-bicarbazoles respectively. Although the required C-4 aryl radical is presumably generated in the reaction of the hydroxycarbazoles (**13**) and (**12**) with dibenzoyl peroxide, the rate of dimerisation of the aryl radical is obviously much faster than the rate of coupling with another benzoyl radical, and hence the 4,4′-bicarbazoles (**14**) and (**15**) are formed in good yield.

Since all the direct oxidation methods for introducing the C-4 oxygen in carbazoles (**13**) and (**12**) were unsuccessful, attention was focussed on introducing other groups at C-4 which could subsequently be converted into a hydroxy function. Accordingly, 4-acetylation of the hydroxycarbazoles (**12**) and (**13**) was attempted *via* Fries rearrangement[23] of the corresponding *O*-acetyl derivatives (**16**) and (**17**). The *O*-acetylcarbazoles were prepared in high yield by acetylation of the hydroxycarbazoles (**12**) and (**13**) with acetic anhydride in pyridine. Fries rearrangement of the carbazole (**16**) with aluminium trichloride in refluxing tetrachloroethane did not give the desired *ortho*-rearrangement product; instead, three other products were formed in low yields. The deacylated carbazole (**12**) was isolated in 12% yield, together with the carbazoles (**18**) (6%) and (**19**) (28%) resulting from rearrangement of the acetyl group to the 5- and 6-positions of carbazole respectively (Scheme 4). In contrast, Fries rearrangement of the dimethylcarbazole (**17**) with aluminium trichloride in refluxing tetrachloroethane gave the required *ortho*-rearrangement product (**20**) in 50% yield (Scheme 4). The yield of this reaction, however, could not consistently be reproduced and appeared to be dependent on the quality of the aluminium trichloride used. The use of freshly sublimed aluminium trichloride usually resulted in a lower yield of the required carbazole (**20**), together with the formation of other rearranged products. Attempts to modify the reaction conditions by conducting the Fries rearrangement of carbazole (**17**) with aluminium trichloride in solvents such as carbon disulphide or dichloroethane simply resulted in the recovery of the starting carbazole.



(16) R = $CO_2Et$
(17) R = Me
(18) $R^1$ = Ac, $R^2$ = H
(19) $R^1$ = H, $R^2$ = Ac
(20) R = H
(21) R = Me
(22)

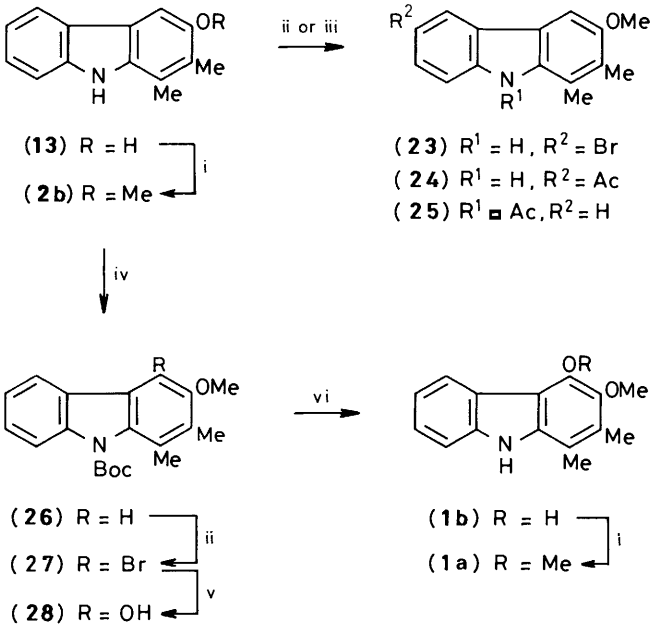
**Scheme 4.** *Reagents:* i, $AlCl_3$, $Cl_2CHCHCl_2$, reflux; ii, MeI, $K_2CO_3$, acetone, reflux

The 4-acetylcarbazole (**20**) was methylated with iodomethane in the presence of potassium carbonate, to give the 3-methoxy derivative (**21**) in 81% yield (Scheme 4). It now remained only to convert the 4-acetyl group in carbazole (**21**) into the acetoxy compound (**22**) by a Baeyer-Villiger oxidation, followed by hydrolysis of the acetate to give carbazomycin B. The Baeyer-Villiger oxidation of carbazole (**21**), however, proved difficult and under a variety conditions simply resulted in the formation of decomposition products.

In a parallel approach, the introduction of other groups at C-4 in deoxycarbazomycin (**2b**) was investigated. Deoxycarbazomycin (**2b**) was prepared in excellent yield (95%) by methylation of the corresponding hydroxycarbazole (**13**) with iodomethane in the presence of potassium carbonate (Scheme 5). It was envisaged that electrophilic substitution in deoxycarbazomycin (**2b**) would be directed to the 4-position by the 3-methoxy group, thus allowing the introduction of a variety of electrophiles at C-4. However, experimentally, it was found that electrophilic bromination of carbazole (**2b**), with NBS in acetonitrile, occurred at C-6 and not C-4, and gave the 6-bromocarbazole (**23**) in 82% yield. Similarly, Friedel–Crafts acetylation of the carbazole (**2b**) gave the 6-acetyl derivative (**24**) (52%) together with a small amount of the *N*-acetylcarbazole (**25**) (39%).

In order to deactivate the 6-position of the carbazole (**2b**) to

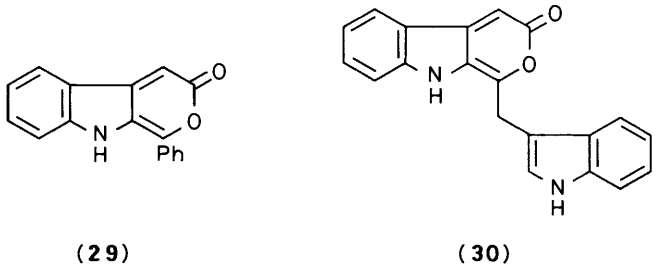
electrophilic attack it was decided to protect the carbazole-nitrogen with the electron-withdrawing butyloxycarbonyl (Boc) group. The Boc group was introduced in high yield (95%) simply by treating the carbazole (**2b**) with di-t-butyl oxydiformate in the presence of 4-dimethylaminopyridine (DMAP),[24] and bromination of the resulting *N*-t-butyloxycarbonylcarbazole (**26**) with *N*-bromosuccinimide gave the *required* 4-bromo derivative (**27**) in excellent yield (95%) (Scheme 5). Treatment of the bromide (**27**) with t-butyl-lithium in THF at −78 °C, followed by reaction with trimethyl borate, and alkaline hydrogen peroxide work-up gave the 4-hydroxycarbazole (**28**) in 73% yield, together with the carbazole (**26**) (22%) resulting from protonation of the aryl-lithium (Scheme 5). The t-butyloxycarbonyl group was removed in excellent yield simply by heating[25] the carbazole (**28**) to 180—190 °C to give carbazomycin B (**1b**) (98%), methylation of which gave carbazomycin A (**1a**) (94%). The $^1H$ and $^{13}C$ n.m.r. and mass spectral data for the synthetic carbazomycins agreed well with those described in the literature[2a] although the melting point of the synthetic carbazomycin A (**1a**) [m.p. 143—146 °C colourless plates (from dichloromethane–hexane)] was much higher than the literature value [lit.,[2a] m.p. 51—52.5 °C pale yellow needles (from ethyl acetate–hexane)]. In view of this vast difference in the melting point the structure of our synthetic carbazomycin A was confirmed by an *X*-ray crystallographic analysis.




**Scheme 5.** *Reagents*: i, MeI, $K_2CO_3$, acetone, reflux; ii, NBS, MeCN; iii, AcCl, $AlCl_3$, $CH_2Cl_2$; iv, $(Boc)_2O$, DMAP, MeCN; v, Bu$^t$Li, THF, −78 °C; $B(OMe)_3$, then alkaline peroxide work-up; vi, 180—190 °C

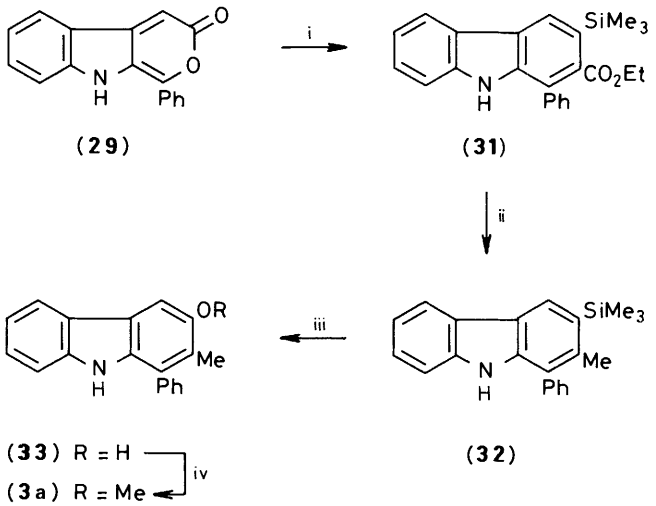
*Synthesis of Hyellazole.* The 1,2,3-substitution pattern found in hyellazole (**3a**) closely resembles that found in deoxycarbazomycin (**2b**), the only difference being the 1-phenyl group present in hyellazole. Hence the hyellazole molecule should be available from a Diels–Alder reaction of the 1-phenylpyranoindole (**29**) and ethyl trimethylsilylpropynoate followed by a similar series of functional group interconversions.

Preparation of the known 1-phenylpyranoindole (**29**) in the usual way, by reaction of indol-3-ylacetic acid with benzoic anhydride in the presence of boron trifluoride–diethyl ether was unsuccessful and instead resulted in the formation of the pyranoindole (**30**) as the only isolable product in low yield (13%). Initial attempts to prepare the 1-phenylpyranoindole (**29**) by the literature method,[26] involving the reaction of indol-3-ylacetic acid with benzoic acid in the presence of polyphosphoric acid, simply resulted in the formation of polymeric material. However, it was found that the pyranoindole (**29**) could be obtained by the above reaction if the polyphosphoric acid used was only half the concentration of that recommended in the published procedure.




(**29**) (**30**)

The Diels–Alder reaction of the pyranoindole (**29**) with ethyl 3-trimethylsilylpropynoate, in refluxing bromobenzene, gave regiospecifically the carbazole (**31**) (40—62%) (Scheme 6). Reduction of the carbazole ester (**31**) with an excess of lithium aluminium hydride in refluxing dioxane gave the 2-methylcarbazole (**32**) in excellent yield (92%). Mercurio-desilylation of the carbazole (**32**) with mercury(II) acetate gave the corresponding arylmercury compound which, without purification, was treated with an excess of borane–THF complex, followed by alkaline hydrogen peroxide work-up to give the 3-hydroxycarbazole (**33**) in 41% yield from carbazole (**32**). Finally, methylation of the hydroxy group in carbazole (**32**) gave hyellazole (**3a**) (92%). The $^1H$ n.m.r. and mass spectral data of the synthetic hyellazole closely matched those described in the literature.[8]




**Scheme 6.** *Reagents:* i, $EtO_2CC{\equiv}CSiMe_3$, PhBr, reflux; ii, $LiAlH_4$, dioxane, reflux; iii, $Hg(OAc)_2$, AcOH; then borane–THF and alkaline peroxide work-up; iv, MeI, $K_2CO_3$, acetone, reflux

## Experimental

For general points see ref. 10.

*Ethyl 1-Methyl-3-trimethylsilyl-9H-carbazole-2-carboxylate* (**6**).—A mixture of the pyranoindole (**4**) (6.02 g, 30.25 mmol) and ethyl 3-(trimethylsilyl)propynoate (5.66 g, 33.3 mmol) in bromobenzene (450 ml) was heated under reflux under nitrogen for 48 h. The solvent was evaporated and the residue chromatographed (dichloromethane–light petroleum) to give the *title compound* (**6**) (5.21 g, 53%), m.p. 191—194 °C (Found: C,

70.2; H, 7.1; N, 4.25. $C_{19}H_{23}NO_2Si$ requires C, 70.1; H, 7.1; N, 4.3%); $\nu_{max.}$(Nujol) 3 358, 1 699, 1 466, 1 263, 1 055, and 841 $cm^{-1}$; $\delta_H$(500 MHz; $CDCl_3$) 0.39 (9 H, s), 1.44 (3 H, t, *J* 7.1 Hz), 2.53 (3 H, s), 4.45 (2 H, q, *J* 7.1 Hz), 7.24—7.27 (1 H, m), 7.39—7.42 (2 H, m), 8.11 (1 H, d, *J* 8 Hz), 8.18 (1 H, s, 4-H), and 8.21 (1 H, br, NH); *m/z* 325 ($M^+$, 17%), 310(100), and 282 (89).

*Ethyl* 1-*Methyl*-9H-*carbazole*-2-*carboxylate* (**7**).—Ethyl 1-methyl-3-trimethylsilyl-9*H*-carbazole-2-carboxylate (**6**) (51 mg, 0.16 mmol) was dissolved in trifluoroacetic acid–water (2:1; 6 ml) and the mixture heated at 70 °C for 2 h and then allowed to stand at room temperature for 12 h. The reaction mixture was then diluted with water (50 ml) and extracted with ether. The combined ether extracts were washed with half saturated aqueous sodium hydrogen carbonate until the washings remained basic, and then washed with water and brine and dried ($MgSO_4$). The solvent was evaporated and the residue chromatographed to give the title compound (**7**) (34 mg, 86%). m.p. 127—127.5 °C (lit.,[14] m.p. 126—127 °C), $\nu_{max.}$(Nujol) 3 387, 1 695, 1 626, 1 500, 1 288, 1 258, 1 155, 1 055, 754, 745, and 733 $cm^{-1}$; $\delta_H$(250 MHz; $CDCl_3$) 1.43 (3 H, t, *J* 7 Hz), 2.8 (3 H, s), 4.41 (2 H, q, *J* 7Hz), 7.19—7.29 (1 H, m), 7.40—7.49 (2 H, m), 7.82 (1 H, d, *J* 8 Hz), 7.91 (1 H, d, *J* 8 Hz), 8.07 (1 H, d, *J* 7.8 Hz), and 8.23 (1 H, br, NH); *m/z* 253 ($M^+$, 100%), 224 (18), 208 (39), and 180 (27).

1-*Methyl*-3-*trimethylsilyl*-9H-*carbazole*-2-*carbaldehyde*.—A mixture of the pyranoindole (**4**) (136 mg, 0.68 mmol) and 3-(trimethylsilyl)propynal (131 mg, 1.04 mmol) in bromobenzene (10 ml) was heated under reflux for 28 h. The solvent was evaporated and the residue chromatographed (dichloromethane–light petroleum) to give the *title compound* (74 mg, 39%), m.p. 207—210 °C (Found: $M^+$, 281.1240. $C_{17}H_{19}NOSi$ requires *M*, 281.1236; $\nu_{max.}$(Nujol) 3 291, 1 656, 1 330, 1 319, 1 307, 1 248, 1 227, 842, and 733 $cm^{-1}$; $\delta_H$(250; MHz; $CDCl_3$) 0.36 (9 H, s), 2.80 (3 H, s), 7.06—7.14 (1 H, m), 7.26—7.34 (2 H, m), 7.96 (1 H, d, *J* 7.6 Hz), 8.08 (2 H, br, NH and 4-H), and 10.62 (1 H, s, CHO); *m/z* 281 ($M^+$, 8%), 266 (100), and 236 (5).

*Ethyl* 3-*Bromo*-1-*methyl*-9H-*carbazole*-2-*carboxylate* (**8**.—*N*-Bromosuccinimide (52 mg, 0.29 mmol) was added in one portion to a stirred solution of ethyl 1-methyl-3-trimethylsilyl-9*H*-carbazole-2-carboxylate (**6**) (95 mg, 0.29 mmol) in acetonitrile (4 ml) and the reaction mixture stirred at room temperature for 16 h. It was then evaporated and the residue chromatographed (dichloromethane–light petroleum) to give the *title compound* (**8**) (94 mg, 97%), m.p. 203—207 °C (Found: $M^+$, 331.0206. $C_{16}H_{14}BrNO_2$ requires *M*, 331.0208); $\nu_{max.}$(Nujol) 3 327, 1 711, 1 442, 1 325, 1 282, 1 263, 1 159, 1 015, 749, and 736 $cm^{-1}$; $\delta_H$[250 MHz; $(CD_3)_2CO$] 1.40 (3 H, t, *J* 7 Hz), 2.55 (3 H, s), 4.44 (2 H, q, *J* 7 Hz), 7.22 (1 H, ~t, *J* 7.5 Hz), 7.44 (1 H, ~t, *J* 7.5 Hz), 7.55 (1 H, d, *J* 7.5 Hz), 8.17 (1 H, d, *J* 7.5 Hz), 8.24 (1 H, s, 4-H), and 10.64 (1 H, br, NH); *m/z* 333/331 ($M^+$, 100%), 305/304 (14), 303/302 (13), and 288/286 (43).

*Ethyl* 6-*Acetyl*-1-*methyl*-9H-*carbazole*-2-*carboxylate* (**9**).—A solution of acetyl chloride (15 mg, 0.19 mmol) in dry dichloromethane (1 ml) was added to a stirred suspension of aluminium trichloride (51 mg, 0.38 mmol) in dichloromethane (1 ml) at room temperature. After 10 min a solution of the carbazole (**6**) (62 mg, 0.19 mmol) in dichloromethane (4 ml) was added in one portion and the reaction mixture stirred for 22 h. Dilute hydrochloric acid (2M; 10 ml) was then added and the mixture extracted with dichloromethane. The combined extracts were washed with brine, dried ($Na_2SO_4$), and evaporated and the residue chromatographed (ether–light petroleum) to give (i) ethyl 1-methyl-9*H*-carbazole-2-carboxylate (**7**) (19 mg, 39%) identical ($^1H$ n.m.r. and t.l.c. properties) with an authentic sample whose preparation was described above; and (ii) the *title compound* (**9**) (31 mg, 55%), m.p. 220—223 °C (Found: C, 73.0; H, 5.7; N, 4.7. $C_{18}H_{17}NO_3$ requires C, 73.2; H, 5.8; N, 4.7%); $\nu_{max.}$(Nujol) 3 317, 1 689, 1 663, 1 615, 1 602, 1 305, 1 253, and 1 146 $cm^{-1}$; $\delta_H$(250 MHz; $CDCl_3$) 1.44 (3 H, t, *J* 7 Hz), 2.72 (3 H, s), 2.82 (3 H, s), 4.41 (2 H, q, *J* 7 Hz), 7.48 (1 H, d, *J* 8.7 Hz), 7.86 (1 H, d, *J* 8.2 Hz), 7.96 (1 H, d, *J* 8.2 Hz), 8.10 (1 H, dd, *J* 8.7 Hz and 1.7 Hz), 8.62 (1 H, br, NH), and 8.71 (1 H, d, *J* 1.7 Hz); *m/z* 295 ($M^+$, 100%), 280 (99), 266 (10), 252 (17), and 250 (26).

1-*Methyl*-3-*trimethylsilyl*-9H-*carbazol*-2-*ylmethanol*.—Lithium aluminium hydride (28 mg, 0.74 mmol) was added to a solution of the carbazole (**6**) (123 mg, 0.38 mmol) in dry THF (5 ml) under nitrogen, and the mixture heated under reflux for 36 h. The excess of lithium aluminium hydride was destroyed by careful addition of water (0.5 ml) after which solid sodium hydrogen carbonate was added until a white grannular precipitate resulted. The mixture was diluted with ether (50 ml), filtered through Celite, and the filtrate dried ($MgSO_4$) and evaporated. Chromatography of the residue gave (i) 1,2-*dimethyl*-3-*trimethylsilyl*-9H-*carbazole* (**10**) (4 mg, 4%), data given below; (ii) recovered starting material (**6**) (18 mg, 15%); and (iii) the *title compound* (75 mg, 70%), m.p. 204—205 °C (Found: C, 71.7; H, 7.5; N, 4.85. $C_{17}H_{21}NOSi$ requires C, 72.0; H, 7.5; N, 4.9%); $\nu_{max.}$(Nujol) 3 556, 3 279, 1 248, 983, 836, 744, and 731 $cm^{-1}$; $\delta_H$(250 MHz; $CDCl_3$) 0.43 (9 H, s), 1.73 (1 H, br s, OH), 2.63 (3 H, s), 4.97 (2 H, br d, *J* 4.5 Hz, $OCH_2$), 7.19—7.26 (1 H, m), 7.36—7.47 (2 H, m), 8.03 (1 H, br, NH), 8.07 (1 H, d, *J* 8.1 Hz), and 8.09 (1 H, s, 4-H); *m/z* 283 ($M^+$, 48%), 268 (100), 252 (24), and 250 (52).

1-2-*Dimethyl*-3-*trimethylsilyl*-9H-*carbazole* (**10**).—Lithium aluminium hydride (3.1 g, 81.6 mmol) was added to a solution of the carbazole (**6**) (4.40 g, 13.5 mmol) in dry dioxane (400 ml) and the mixture heated under reflux under nitrogen for 18 h. The reaction mixture was allowed to cool and then poured into ether (300 ml). The excess of lithium aluminium hydride was destroyed by careful addition of water (*ca.* 15 ml) (**CAUTION**) after which solid sodium hydrogen carbonate was added until a white grannular precipitate resulted. The mixture was filtered through Celite, the filtrate concentrated under reduced pressure and the residue chromatographed (ether–light petroleum) to give the *title compound* (**10**) (3.59 g, 98%), m.p. 140—145 °C (Found: C, 76.1; H, 8.0; N, 5.1. $C_{17}H_{21}NSi$ requires C, 76.3; H, 7.9; N, 5.2%); $\nu_{max.}$(Nujol) 3 477, 1 328, 1 259, 1 244, 1 011, 863, 841, 750, and 734 $cm^{-1}$; $\delta_H$(250 MHz, $CDCl_3$) 0.42 (9 H, s), 2.46 (3 H, s), 2.56 (3 H, s), 7.21 (1 H, ddd, *J* 7.4, 7.4 and 1.4 Hz), 7.33—7.44 (2 H, m), 7.90 (1 H, br, NH), and 8.32—8.08 (2 H, m, 4-H and 5-H); *m/z* 267 ($M^+$, 64%), 252 (100), and 236 (12).

*Ethyl* 3-*Acetoxymercurio*-1-*methyl*-9H-*carbazole*-2-*carboxylate* (**11**).—Ethyl 1-methyl-3-trimethylsilyl-9*H*-carbazole-2-carboxylate (**6**) (1.174 g, 3.61 mmol) was added to a stirred solution of mercury(II) acetate (1.152 g, 3.61 mmol) in acetic acid (22 ml) in one portion and the reaction mixture stirred for 8 h. It was then diluted with ether (20 ml) and the resulting white solid filtered off, washed with ethanol (2 × 5 ml) and ether (2 × 5 ml), and dried *in vacuo* to give the *title compound* (**11**), (1.111 g, 60%), m.p. > 300 °C (Found: C, 42.1; H, 3.2; N, 2.65. $C_{18}H_{17}HgNO_4$ requires C, 42.2; H, 3.3; N, 2.7%); $\nu_{max.}$(Nujol) 3 257, 1 706, 1 628, 1 610, 1 330, 1 255, and 1 049 $cm^{-1}$; $\delta_H$[250 MHz; $(CD_3)_2SO$] 1.36 (3 H, t, *J* 7.7 Hz), 1.95 (3 H, s), 2.66 (3 H, s), 4.35 (2 H, q, *J* 7.7 Hz), 7.19 (1 H, ~t, *J* 8 Hz), 7.45 (1 H, ~t, *J* 8 Hz), 7.55 (1 H, br d, *J* 8 Hz), 8.04—8.14 (2 H, m), and 11.41 (1 H, s, NH).

*Ethyl* 3-*Hydroxy*-1-*methyl*-9H-*carbazole*-2-*carboxylate* (**12**).—Borane–tetrahydrofuran complex (1M; 34.5 ml, 34.5

mmol) was added to a stirred solution of ethyl 3-acetoxymercurio-1-methyl-9*H*-carbazole-2-carboxylate (**11**) (1.103 g, 2.15 mmol) in dry THF (80 ml) under nitrogen. After 35 min, a mixture of hydrogen peroxide (30%; 12 ml) and sodium hydroxide (2M; 12 ml) was carefully added and the reaction mixture stirred for a further 10 min. It was then acidified with dilute hydrochloric acid (1M), diluted with water (200 ml), and extracted with ether. The ethereal extracts were washed with water and brine, dried ($MgSO_4$), and concentrated and the residue chromatographed (dichloromethane–light petroleum) to give the *title compound* (**12**) (402 mg, 76%), m.p. 202.5—203.5 °C (Found: C, 71.3; H, 5.5; N, 5.1. $C_{16}H_{15}NO_3$ requires C, 71.4; H, 5.6; N, 5.2%); $\nu_{max.}$(Nujol) 3 340, 2 493, 1 651, 1 423, 1 373, 1 323, and 749 $cm^{-1}$; $\delta_H$[500 MHz; $(CD_3)_2CO$] 1.45 (3 H, t, *J* 7 Hz), 2.77 (3 H, s), 4.48 (2 H, q, *J* 7 Hz), 7.13 (1 H, ddd, *J* 7.5, 7.5 and 1 Hz), 7.41 (1 H, ddd, *J* 7.5, 7.5 and 1 Hz), 7.47 (1 H, br d, *J* 7.5 Hz), 7.49 (1 H, s, 4-H), 8.06 (1 H, br d, *J* 7.5 Hz), 10.15 (1 H, br, NH), and 10.37 (1 H, s, OH); *m/z* 269 ($M^+$, 35%), 223 (100), 195 (22), and 167 (25).

*Lithium Aluminium Hydride Reduction of Ethyl 3-Hydroxy-1-methyl-9H-carbazole-2-carboxylate* (**12**).—Lithium aluminium hydride (161 mg, 4.2 mmol) was added to a solution of the carbazole (**12**) (95 mg, 0.35 mmol) in dry dioxane (40 ml) and the reaction mixture heated under reflux under nitrogen for 36 h. More $LiAlH_4$ (90 mg, 2.37 mmol) was added and the reaction mixture heated under reflux for a further 18 h. It was allowed to cool and then diluted with ether (30 ml). The excess of lithium aluminium hydride was destroyed by careful addition of water (**CAUTION**) after which solid sodium hydrogen carbonate was added until a white grannular precipitate resulted. The mixture was then filtered through Celite, the filtrate concentrated under reduced pressure, and the residue chromatographed (ether–light petroleum) to give (i) 3-hydroxy-1,2-dimethyl-9*H*-carbazole (**13**) (31 mg, 42%), m.p. 245—249 °C (decomp.), (Found: C, 79.5; H, 6.4; N, 6.6. $C_{14}H_{13}NO$ requires C, 79.6; H, 6.2; N, 6.6%); $\nu_{max.}$(Nujol) 3 433, 3 306, 1 466, 1 436, 1 299, 1 265, 1 249, 1 061, 767, and 751 $cm^{-1}$; $\delta_H$[250 MHz; $(CD_3)_2CO$] 2.30 (3 H, s), 2.47 (3 H, s), 7.04 (1 H, ~t, *J* 7.7 Hz), 7.25 (1 H, ~t, *J* 7.7 Hz), 7.38 (1 H, s, 4-H), 7.40 (1 H, d, *J* 7.7 Hz), 7.86—7.91 (2 H, m, OH and 5-H), and 9.90 (1 H, br, NH); *m/z* 211 ($M^+$, 100%), 196 (16), 182 (3), 180 (6), and 167 (10); and (ii) 3,3′-*dihydroxy*-1,1′,2,2′-*tetramethyl*-4,4′-*bi*-9H-*carbazole* (**14**), m.p. darkens *ca.* 200 °C (Found: $M^+$, 420.1842. $C_{28}H_{24}N_2O_2$ requires *M*, 420.1838); $\nu_{max.}$($CHCl_3$) 3 539, 3 476, 1 458, and 1 359 $cm^{-1}$; $\delta_H$[270 MHz; $(CD_3)_2CO$] 2.45 (6 H, s), 2.65 (6 H, s), 6.45 (2 H, s, 2 × OH), 6.52 (2 H, ~t, *J* 8 Hz), 6.64 (2 H, d, *J* 8 Hz), 7.05 (2 H, ~t, *J* 8 Hz), 7.34 (2, H, d, *J* 8 Hz), and 10.00 (2 H, br, 2 × NH); *m/z* 420 ($M^+$, 100%), 211 (27), and 210 (23).

3-*Acetoxymercurio*-1,2-*dimethyl*-9H-*carbazole*.—1,2-Dimethyl-3-trimethylsilyl-9*H*-carbazole (**10**) (3.143 g, 11.77 mmol) was added to a stirred solution of mercury(II) acetate (3.76 g, 11.79 mmol) in acetic acid (50 ml) in one portion. After *ca.* 2 min the reaction mixture was diluted with ether (100 ml) and the resulting white solid immediately filtered off, washed with ether (50 ml), water (50 ml), and again with ether (25 ml), and dried *in vacuo* to give the *title compound* (3.527 g, 66%), m.p. > 300 °C, (Found:C, 42.0; H, 3.2; N, 3.1. $C_{16}H_{15}HgNO_2$ requires C, 42.3; H, 3.3; N, 3.1%); $\nu_{max.}$(Nujol) 3 325, 1 603, 1 363, 1 320, 1 245, 736, and 689 $cm^{-1}$; $\delta_H$[250 MHz; $(CDCl_3)_2SO$] 1.95 (3 H, s), 2.45 (3 H, s), 2.53 (3 H, s), 7.10 (1 H, ~t, *J* 7.7 Hz), 7.32 (1 H, ~t, *J* 7.7 Hz), 7.45 (1 H, d, *J* 7.7 Hz), 7.85 (1 H, s, 4-H), 7.94 (1 H, d, *J* 7.7 Hz), and 11.01 (1 H, br, NH).

3-*Hydroxy*-1,2-*dimethyl*-9H-*carbazole* (**13**).—Borane-tetrahydrofuran complex (1M; 124 ml, 124 mmol) was added to a stirred solution of 3-acetoxymercurio-l,2-dimethyl-9*H*-carbazole (3.527 g, 7.77 mmol) in dry THF (220 ml) under nitrogen. After 40 min a mixture of hydrogen peroxide (30%; 43 ml) and sodium hydroxide (2M; 43 ml) was carefully added and the reaction mixture stirred for a further 5 min. The reaction mixture was then acidified with dilute hydrochloric acid (1M), diluted with water (200 ml), and extracted with ether. The ethereal extracts were washed with water and brine, dried ($MgSO_4$), and concentrated and the residue chromatographed (dichloromethane–light petroleum) to give the title compound (**13**) (1.392 g, 85%) identical ($^1H$ n.m.r. and t.l.c.) with the sample described above.

*Reaction of 3-Hydroxy-1,2-dimethyl-9H-carbazole* (**13**) *with Dibenzoyl Peroxide*.—Dibenzoyl peroxide (22 mg, 0.09 mmol) was added to stirred solution of the carbazole (**13**) (19.4 mg, 0.09 mmol) in chloroform (8 ml) at room temperature. The reaction mixture immediately became light brown. After the mixture had been stirred for 10 min, dilute aqueous sodium sulphite (5%; 20 ml) was added to it and the whole extracted with ether. The combined organic extracts were washed with dilute aqueous sodium hydrogen carbonate, water, and brine, dried ($MgSO_4$), and concentrated go give a dark brown oil which was chromatographed (dichloromethane) to give the 4,4′-bicarbazole (**14**) (17 mg, 88%), identical ($^1H$ n.m.r. and t.l.c.) with the sample described above.

*Reaction of Ethyl 3-Hydroxy-1-methyl-9H-carbazole-2-carboxylate* (**12**) *with Dibenzoyl Peroxide*.—Dibenzoyl peroxide (17 mg, 0.07 mmol) was added to stirred solution of the carbazole (**12**) (19 mg, 0.07 mmol) in chloroform (10 ml) at room temperature. The reaction mixture immediately became light brown. After the mixture had been stirred for 10 min, dilute aqueous sodium sulphite (10%; 2 ml) was added to it and the whole extracte with ether. The combined organic extracts were washed with dilute aqueous sodium hydrogen carbonate, water, and brine, dried ($MgSO_4$), and concentrated to give a brown oil which was chromatographed (dichloromethane–ether) to give 2,2′-*bisethoxycarbonyl*-3,3′*dihydroxy*-1,1′-*dimethyl*-4,4′-*bi*-9*H*-*carbazole* (**15**) (14 mg, 74%), m.p. darkens *ca.* 240 °C (Found: $M^+$, 536.1933. $C_{32}H_{28}N_2O_6$ requires *M*, 536.1947); $\nu_{max.}$(Nujol) 3 323, 1 615, 1 622, 1 395, 1 374, 1 323, 1 256, 1 164, 1 143, and 746 $cm^{-1}$; $\delta_H$[270 MHz; $(CD_3)_2CO$] 1.48 (6 H, t, *J* 7 Hz), 2.80 (6 H, s), 4.51 (4 H, q, *J* 7 Hz), 6.60 (2 H, ~t, *J* 7.6 and Hz), 6.74 (2 H, d, *J* 7.6 Hz), 7.18 (2 H, ~t, *J* 7.6 Hz), 7.39 (2 H, d, *J* 7.6 Hz), 10.26 (2 H, br, 2 × NH), and 10.33 (2 H, s, 2 × OH); *m/z* 536 ($M^+$, 93%), 490 (100), and 444 (57).

*Ethyl 3-Acetoxy-1-methyl-9H-carbazole-2-carboxylate* (**16**).—Acetic anhydride (0.5 ml) followed by 4-dimethylaminopyridine (5 mg, 0.04 mmol) were added to a stirred solution of the carbazole (**12**) (81 mg, 0.30 mmol) in pyridine (2 ml) and the reaction mixture was stirred for 12 h. Water (2 ml) was then added and the mixture stirred for a further 15 min. It was then diluted with water and extracted with ether. The organic extracts were washed with dilute hydrochloric acid (2M; 25 ml), aqueous sodium hydrogen carbonate (half saturated; 50 ml), water, and brine, dried ($MgSO_4$), and concentrated to give a white solid which was chromatographed (dichloromethane–light petroleum) to give the *title compound* (**16**) (93 mg, 99%), m.p. 72— 74 °C (Found: C, 69.4; H, 5.5; N, 4.45. $C_{18}H_{17}NO_4$ requires C, 69.4; H, 5.5; N, 4.5%); $\nu_{max.}$(Nujol) 3 350, 1 764, 1 749, 1 719, 1 456, 1 367, 1 287, 1 262, 1 249, 1 228, and 1 058 $cm^{-1}$; $\delta_H$(270 MHz; $CDCl_3$) 1.40 (3, H, t, *J* 7.2 Hz), 2.36 (3 H, s), 2.45 (3 H, s), 4.41 (2 H, q, *J* 7.2 Hz), 7.12 (1 H, ddd, *J* 7.1, 7.1 and 1.4 Hz), 7.32—7.42 (2 H, m), 7.45 (1 H, s, 4-H), 7.69 (1 H, br d, *J* 7.8 Hz), and 8.30 (1 H, br, NH); *m/z* 311 ($M^+$, 16%), 269 (34), 223 (100), 195 (11), and 167 (17).

3-*Acetoxy*-1,2-*dimethyl*-9H-*carbazole* (**17**).—Acetic anhydride (1 ml) was added to a stirred solution of 3-hydroxy-1,2-dimethyl-9*H*-carbazole (**13**) (262 mg, 1.24 mmol) in pyridine (4 ml) and the reaction mixture stirred for 6 h. Water (2 ml) was added and the mixture stirred for a further 15 min. It was then diluted with water and extracted with ether. The organic extracts were washed with dilute hydrochloric acid (2M; 50 ml), aqueous sodium hydrogen carbonate (half saturated; 50 ml), water, and brine, dried ($MgSO_4$), and concentrated to give a white solid which was chromatographed (dichloromethane–light petroleum) to give the *title compound* (**17**) (289 mg, 92%),m.p. 202—204 °C (Found: C, 75.6; H, 6.0; N, 5.4. $C_{16}H_{15}NO_2$ requires C, 75.9; H, 6.0; N, 5.5%); $\nu_{max.}$(Nujol) 3 393, 1 738, 1 459, 1 376, 1 317, 1 236, 1 218, and 754 $cm^{-1}$; $\delta_H$(250 MHz; $CDCl_3$) 2.24 (3 H, s), 2.40 (3 H, s), 2.46 (3 H, s), 7.19 (1 H, ddd, *J* 7, 7 and 1.9 Hz), 7.34—7.45 (2 H, m), 7.57 (1 H, s), 7.90 (1 H, br, NH), and 7.94 (1 H, br d, *J* 7 Hz); *m/z* 253 ($M^+$, 26%) and 211 (100).

*Fries Rearrangement of Ethyl* 3-*Acetoxy*-1-*methyl*-9H-*carbazole*-2-*carboxylate* (**16**).—Tetrachloroethane (6 ml) was added to a well mixed mixture of aluminium trichloride (83 mg, 0.62 mmol) and the carbazole (**16**) (83 mg, 0.27 mmol) under nitrogen and the reaction mixture was heated under reflux for 20 min. After cooling to room temperature the mixture was poured into dilute hydrochloric acid (1M; 20 ml) and the aqueous mixture extracted with ethyl acetate. The combined extracts were washed with water and brine, dried ($MgSO_4$), and concentrated to give a yellow–green solid which was chromatographed (ether–light petroleum) to give (i) ethyl 3-hydroxy-1-methyl-9*H*-carbazole-2-carboxylate (**12**) (10 mg, 12%) identical ($^1H$ n.m.r. and t.l.c.) with the sample described above; (ii) *ethyl* 5-*acetyl*-3-*hydroxy*-1-*methyl*-9H-*carbazole*-2-*carboxylate* (**19**) (5 mg, 6%), m.p. 193—200 °C (Found: $M^+$, 311.156. $C_{18}H_{17}NO_4$ requires *M*, 311.1158); $\nu_{max.}$(Nujol) 3 429, 1 657, 1 329, 1 274, 1 246, 1 219, 1 194, and 1 135 $cm^{-1}$; $\delta_H$[270 MHz; $(CD_3)_2CO$] 1.47 (3 H, t, *J* 7.1 Hz), 2.73 (3 H, s), 2.82 (3 H, s), 4.51 (2 H, q, *J* 7.1 Hz), 7.29 (1 H, ~t, *J* 7.8 Hz), 7.56 (1 H, s, 4-H), 8.16 (1 H, d, *J* 7.8 Hz), 8.39 (1 H, d, *J* 7.8 Hz), 10.38 (1 H, s, OH), and 10.48 (1 H, br, NH); *m/z* 311 ($M^+$, 44%), and 265 (100); and (iii) *ethyl* 6-*acetyl*-3-*hydroxy*-1-*methyl*-9H-*carbazole*-2-*carboxylate* (**19**) (23 mg, 28%), m.p. 268—270 °C (Found: $M^+$, 311.1156. $C_{18}H_{17}NO_4$ requires *M*, 311.1158); $\nu_{max.}$(Nujol) 3 331, 1 664, 1 655, 1 625, 1 603, 1 589, 1 328, 1 273, and 1 247 $cm^{-1}$; $\delta_H$[270 MHz; $(CD_3)_2CO$] 1.45 (3 H, t, *J* 7.1 Hz), 2.65 (3 H, s), 2.78 (3 H, s), 4.49 (2 H, q, *J* 7.1 Hz), 7.52 (1 H, d, *J* 8.5 Hz), 7.63 (1 H, s, 4-H), 8.08 (1 H, dd, *J* 8.5 and 1.5 Hz), 8.82 (1 H, d, *J* 1.5 Hz), 10.39 (1 H, s, OH), and 10.59 (1 H, br, NH); *m/z* 311 ($M^+$, 34%) and 265 (100).

4-*Acetyl*-3-*hydroxy*-1,2-*dimethyl*-9H-*carbazole* (**20**).—Tetrachloroethane (4 ml) was added to a well mixed mixture of aluminium trichloride (70 mg, 0.52 mmol) and carbazole (17) (60 mg, 0.24 mmol) under nitrogen and the reaction mixture heated under reflux for 1.5 h. After cooling to room temperature the mixture was poured into dilute hydrochloric acid (1M; 20 ml) and the aqueous mixture extracted with ethyl acetate. The combined extracts were washed with water and brine, dried ($MgSO_4$), and concentrated to give a yellow-green solid which was chromatographed (ether–light petroleum) to give the *title compound* (**20**) (30 mg, 50%), m.p. 215—220 °C (Found: $M^+$, 253.1108. $C_{16}H_{15}NO_2$ requires *M*, 253.1103); $\nu_{max.}$($CHCl_3$) 3 474, 3 440, 1 617, 1 460, 1 359, 1 311, 1 273, and 1 234 $cm^{-1}$; $\delta_H$(250 MHz; $CDCl_3$) 2.37 (3 H, s), 2.53 (3 H, s), 2.88 (3 H, s), 7.21 (1 H, ~t, *J* 8 Hz), 7.40 (1 H, ~t, *J* 8 Hz), 7.50 (1 H, d, *J* 8 Hz), 7.98 (1 H, d, *J* 8 Hz), 8.10 (1 H, br, NH), and 11.91 (1 H, s, OH); *m/z* 253 ($M^+$, 100%), 238 (66), 235 (14), and 211 (26).

4-*Acetyl*-3-*methoxy*-1,2-*dimethyl*-9H-*carbazole* (**21**).—A mixture of the carbazole (**20**) (20 mg, 0.08 mmol), potassium carbonate (60 mg, 0.43 mmol), and methyl iodide (0.5 ml) in acetone (5 ml) was heated under reflux under nitrogen for 5 h. The mixture was evaporated and the residue dissolved in water (10 ml) and extracted with ether. The ether extracts were washed with water and brine, dried ($MgSO_4$), and concentrated to give a yellow oil which was chromatographed (dichloromethane–light petroleum) to give the *title compound* (**21**) (17 mg, 81%) as a pale yellow oil (Found: $M^+$, 267.1254. $C_{17}H_{17}NO_2$ requires *M*, 267.1259); $\nu_{max.}$($CHCl_3$) 3 475, 1 693, 1 390, 1 298, and 1 188 $cm^{-1}$; $\delta_H$[250 MHz; $(CD_3)_2CO$] 2.37 (3 H, s), 2.52 (3 H, s), 2.68 (3 H, s), 3.73 (3 H, s), 7.07 (1 H, ~t, *J* 8 Hz), 7.33 (1 H, ~t, *J* 8 Hz), 7.47 (1 H, d, *J* 8 Hz), 7.79 (1 H, d, *J* 8 Hz), and 10.24 (1 H, br, NH); *m/z* 267 ($M^+$, 100%), 252 (84), 237 (11), 234 (11), and 224 (16).

3-*Methoxy*-1,2-*dimethyl*-9H-*carbazole* (4-*Deoxycarbazomycin*) (**2b**).—A mixture of 3-hydroxy-1,2-dimethyl-9*H*-carbazole (**13**) (526 mg, 2.49 mmol), potassium carbonate (5.0 g, 36.2 mmol), and methyl iodide (5 ml) in acetone (60 ml) was heated under reflux under nitrogen for 6 h. The mixture was evaporated and ether (100 ml) added to the residue. The potassium salts were filtered off, the filtrate concentrated, and the residue chromatographed (dichloromethane–light petroleum) to give the title compound (**2b**) (533 mg, 95%), m.p. 120—121 °C (lit.,[2a] m.p. 129—130 °C, lit.,[6] m.p. 129—131 °C) (Found: C, 80.0; H, 6.8; N, 6.2. Calc. for $C_{15}H_{15}NO$: C, 80.0; H, 6.7; N, 6.2%); $\nu_{max.}$(Nujol) 3 414, 1 456, 1 426, 1 309, 1 255, 1 210, 1 163, 1 146, 1 113, 1 102, 764, 751, and 731 $cm^{-1}$; $\delta_H$[500 MHz; $(CD_3)_2CO$)] 2.29 (3 H, s), 2.48 (3 H, s), 3.91 (3 H, s), 7.09 (1 H, ddd, *J* 7.5, 7.5 and 1 Hz), 7.28 (1 H, ddd, *J* 7.5, 7.5 and 1 Hz), 7.44 (1 H, br d, *J* 7.5 Hz), 7.50 (1 H, s, 4-H), 8.01 (1 H, br d, *J* 7.5 Hz), and 9.95 (1 H, br, NH); *m/z* 225 ($M^+$, 93%), 210 (100), 194 (4), 180 (18), and 167 (14).

6-*Bromo*-3-*methoxy*-1,2-*dimethyl*-9H-*carbazole* (**23**).—A solution of *N*-bromosuccinimide (30 mg, 0.17 mmol) in acetonitrile (1 ml) was added to a stirred solution of the carbazole (**2b**) (38 mg, 0.17 mmol) in acetonitrile (4 ml) over 1 min and the mixture stirred at room temperature for 2 min. The solvent was evaporated and the residue chromatographed (ether–light petroleum) to give the *title compound* (**23**) (42 mg, 82%), m.p. 201—207 °C (Found: C, 59.4; H, 4.6; Br, 26.1, N, 4.5; $C_{15}H_{14}BrNO$ requires C, 59.2; H, 4.6; Br, 26.3, N, 4.6%); $\nu_{max.}$($CHCl_3$) 3 477, 1 460, 1 287, 1 208, and 1 107 $cm^{-1}$; $\delta_H$(270 MHz; $CDCl_3$) 2.34 (3 H, s), 2.46 (3 H, s), 3.93 (3 H, s), 7.29 (1 H, d, *J* 8.3 Hz), 7.31 (1 H, s, 4-H), 7.43 (1 H, dd, *J* 8.3 and 2 Hz), 7.79 (1 H, br, NH), and 8.11 (1 H, d, *J* 2 Hz); *m/z* 305/303 ($M^+$, 100%), 290/288 (79), 274 (3), 260 (7), 225 (11), 210 (12), 209 (9), and 180 (18).

6-*Acetyl*-3-*methoxy*-1,2-*dimethyl*-9H-*carbazole* (**24**).—A solution of acetyl chloride (15 mg, 0.19 mmol) in dry dichloromethane (1 ml) was added to a stirred suspension of aluminium trichloride (51 mg, 0.38 mmol) in dichloromethane (1 ml) at room temperature. After 10 min a solution of the carbazole (**2b**) (42 mg, 0.19 mmol) in dichloromethane (2 ml) was added in one portion and the mixture stirred for 20 min. Dilute hydrochloric acid (2M; 10 ml) was added and the mixture extracted with ethyl acetate. The combined extracts were washed with brine, dried ($MgSO_4$), and evaporated and the residue chromatographed (ether–light petroleum) to give (i) 9-acetyl-3-methoxy-1,2-dimethyl-9*H*-carbazole (**25**) (18 mg, 36%) as a colourless oil, $\nu_{max.}$($CHCl_3$) 1 696, 1 415, 1 365, and 1 248 $cm^{-1}$; $\delta_H$(270 MHz; $CDCl_3$) 2.31 (3 H, s), 2.37 (3 H, s), 2.58 (3 H, s), 3.95 (3 H, s), 7.28 (1 H, s, 4-H), 7.31—7.45 (2 H, m), 7.88 (1 H, d, *J* 7.8 Hz), and 8.04 (1 H, d, *J* 7.8 Hz); *m/z* 267 ($M^+$, 33%), 225

(55), 210 (55), 85 (66), and 83 (100); and (ii) the *title compound* (**24**) (26 mg, 52%), m.p. 285—286 °C (Found: C, 76.4; H, 6.4; N, 5.2. $C_{17}H_{17}NO_2$ requires C, 76.4; H, 6.4; N, 5.2%); $\delta_H$[270 MHz; $(CD_3)_2CO$] 2.28 (3 H, s), 2.49 (3 H, s), 3.62 (3 H, s), 3.93 (3 H, s), 7.48 (1 H, d, *J* 8 Hz), 7.66 (1 H, s), 7.99 (1 H, dd, *J* 8 and 1.6 Hz), 8.77 (1 H, d, *J* 1.6 Hz), and 10.43 (1 H, br, NH); *m/z* 267 ($M^+$, 97%) and 252 (100).

*t-Butyl 3-Methoxy-1,2-dimethyl-9H-carbazole-9-carboxylate* (**26**).—A solution of di-t-butyl oxydiformate (296 mg, 1.36 mmol) in acetonitrile (1 ml) was added to a stirred solution of the carbazole (**2b**) (153 mg, 0.68 mmol) in acetonitrile (3 ml) under nitrogen. 4-Dimethylaminopyridine (83 mg, 0.68 mmol) was added in one portion and the reaction mixture stirred for 16 h. It was then evaporated and the residue chromatographed (dichloromethane–light petroleum) to give the *title compound* (**26**) (211 mg, 95%), m.p. 113—114 °C (Found: C, 73.9; H, 7.2; N, 4.25. $C_{20}H_{23}NO_3$ requires C, 73.8; H, 7.1; N, 4.3%); $\nu_{max.}$(Nujol) 1 729, 1 295, and 1 151 $cm^{-1}$; $\delta_H$[270 MHz; $(CD_3)_2CO$] 1.67 (9 H, s), 2.28 (3 H, s), 2.37 (3 H, s), 3.93 (3 H, s), 7.31 (1 H, ~t, *J* 8 Hz), 7.42 (1 H, ~t, *J* 8 Hz), 7.51 (1 H, s, 4-H), 8.01 (1 H, br d, *J* 8 Hz), and 8.05 (1 H, br d, *J* 8 Hz); *m/z* 325 ($M^+$, 41%), 269 (97), 225 (73), and 57 (100).

*t-Butyl 4-Bromo-3-methoxy-1,2-dimethyl-9H-carbazole-9-carboxylate* (**27**).—*N*-Bromosuccinimide (52 mg, 0.29 mmol) was added to a stirred solution of carbazole (**26**) (94) mg, 0.29 mmol) in acetonitrile (4 ml) and the mixture stirred at room temperature in the dark for 16 h. It was then evaporated and the residue chromatographed (dichloromethane–light petroleum) to give the *title compound* (**27**) (111 mg, 95%), m.p. 153—157 °C (Found: C, 59.75; H, 5.5; Br, 19.9; N, 3.5; $C_{20}H_{22}BrNO_3$ requires C, 59.4; H, 5.5; Br, 19.8; N, 3.5%); $\nu_{max.}$(Nujol) 1 723, 1 379, 1 368, 1 313, 1 250, 1 147, 1 097, 774, and 752 $cm^{-1}$; $\delta_H$[270 MHz;$(CD_3)_2CO$] 1.68 (9 H, s), 2.34 (3 H, s), 2.42 (3 H, s), 3.83 (3 H, s), 7.40 (1 H, ~t, *J* 7.8 Hz), 7.53 (1 H, ~t, *J* 7.8 Hz), 8.09 (1 H, br d, *J* 7.8 Hz), and 8.74 (1 H, br d, *J* 7.8 Hz); *m/z* 405/403 ($M^+$, 2%), 349/347 (5), 305/303 (10), 290/288 (14), 149 (28), and 57 (100).

*t-Butyl 4-Hydroxy-3-methoxy-1,2-dimethyl-9H-carbazole-9-carboxylate* (**28**).—A solution of the carbazole (**27**) (50 mg, 0.12 mmol) in THF (2.5 ml) was cooled to −78 °C under nitrogen. t-Butyl-lithium in hexane (1.7M; 0.08 ml, 0.136 mmol) was added over 30 s, to give a yellow solution. After 10 min trimethyl borate (14 mg, 0.135 mmol, 15 μl) was added and the mixture allowed to warm to 0 °C over 2 h. A mixture of hydrogen peroxide (30%; 0.2 ml) and sodium hydroxide (2M; 0.2 ml) was carefully added and the mixture stirred for a further 2 min. The reaction mixture was then acidified with dilute hydrochloric acid (1M), diluted with water (20 ml), and extracted with ether. The ethereal extracts were washed with water and brine, dried ($MgSO_4$), and concentrated and the residue chromatographed (dichloromethane–light petroleum) to give (i) t-butyl 3-methoxy-1,2-dimethyl-9*H*-carbazole-9-carboxylate (**26**) (9 mg, 22%) identical ($^1H$ n.m.r. and t.l.c.) with the previous sample whose preparation was described above; and (ii) the *title compound* (**28**) (31 mg, 73%), m.p. 151—154 °C (Found: C, 70.5; H, 7.1; N, 3.95. $C_{20}H_{23}NO_4$ requires C, 70.4; H, 6.8; N, 4.1%); $\nu_{max.}$(Nujol) 3 382, 1 703, 1 451, 1 372, 1 290, 1 254, 1 159, 1 143, and 1 001 $cm^{-1}$; $\delta_H$[270 MHz; $(CD_3)_2CO$] 1.67 (9 H, s), 2.26 (3 H, s), 2.33 (3 H, s), 3.76 (3 H, s), 7.30 (1 H, ~t, *J* 8 Hz), 7.38 (1 H, ~t, *J* 8 Hz), 8.01 (1 H, br d, *J* 8 Hz), 8.23 (1 H, br d, *J* 8 Hz) and 8.42 (1 H, s, OH); *m/z* 341 ($M^+$, 23%); 285 (53), 270 (6), 241 (45), 226 (10), and 57 (93).

*4-Hydroxy-3-methoxy-1,2-dimethyl-9H-carbazole* (*Carbazomycin B*) (**1b**).—The carbazole (**28**) (26 mg, 76 μmol) was heated neat at 180—190 °C (oil bath temperture) under a nitrogen atmosphere for 20 min and then cooled to give the title compound (**1b**) (18 mg, 98%), m.p. 162—164 °C (from dichloromethane–hexane) (lit.,[2a] 158.5—160 °C), $\nu_{max.}$($CHCl_3$) 3 534, 3 477, 1 644, 1 615, 1 503, 1 455, 1 415, 1 393, 1 323, 1 301, 1 244, 1 147, 1 084, and 1 006 $cm^{-1}$; $\delta_H$(270 MHz; $CDCl_3$) 2.37 (3 H, s), 2.40 (3 H, s), 3.83 (3 H, s), 6.05 (1 H, s, OH), 7.22 (1 H, ~t, *J* 6.9 Hz), 7.32—7.42 (2 H, m), 7.77 (1 H, br, NH), and 8.25 (1 H, br d, *J* 7.8 Hz); *m/z* 241 ($M^+$, 57%), 226 (100), and 198 (14).

*3,4-Dimethoxy-1,2-dimethyl-9H-carbazole* (*Carbazomycin A*) (**1a**).—A mixture of carbazomycin B (**1b**) (12 mg, 50 μmol), potassium carbonate (101 mg, 0.73 mmol) and methyl iodide (0.6 ml) in acetone (2 ml) was heated under reflux under nitrogen for 3.5 h. The mixture was evaporated and ether (10 ml) added. The potassium carbonate was filtered off and the filtrate concentrated and the residue chromatographed (ether–light petroleum) to give the title compound (**1a**) (11.8 mg, 94%), m.p. 143—146 °C, (from dichloromethane–hexane) (lit.,[2a] 51—52.5 °C), $\nu_{max.}$($CHCl_3$) 3 476, 1 612, 1 500, 1 455, 1 397, 1 318, 1 294, 1 166, 1 150, 1 089, 1 052, 1 008, 973, and 880 $cm^{-1}$; $\delta_H$[270 MHz; $(CD_3)_2CO$] 2.33 (3 H, s), 2.43 (3 H, s), 3.82 (3 H, s), 4.04 (3 H, s), 7.12 (1 H, ~t, *J* 7.6 Hz), 7.30 (1 H, ~t, *J* 7.6 Hz), 7.43 (1 H, br d, *J* 7.6 Hz), 8.16 (1 H, br d, *J* 7.6 Hz), and 10.05 (1 H, br, NH); $\delta_C$(125.76 MHz; $CDCl_3$) 12.6, 13.6, 60.5, 61.0, 110.2, 113.5, 114.5, 119.5, 122.5, 122.9, 125.1, 128.8, 136.4, 139.4, 144.5, and 146.0; *m/z* 255 ($M^+$, 100%), 240 (86), 212 (13), 197 (27), 180 (4), and 167 (8).

*1-(Indol-3-yl)methylpyrano*[3,4-b]*indol-3-one* (**30**).—Boron trifluoride–diethyl ether (3 ml) was added to a stirred solution of indol-3-ylacetic acid (1.75 g, 10 mmol) and benzoic anhydride (4.5 g, 19.9 mmol) in dry ether (3 ml) at room temperature over 10 min and the mixture stirred for 3 h. It was then diluted with ether (20 ml). The resulting dark red solid was filtered off, washed with ether (3 × 10 ml) and dilute aqueous sodium hydrogen carbonate (20 ml). The resulting brown gum was dissolved in acetone and directly pre-adsorbed onto silica and chromatographed (ether–methanol) to give the *title compound* (**30**) (206 mg, 13%), m.p. 218—220 °C (Found: $M^+$, 314.1056. $C_{20}H_{14}N_2O_2$ requires *M*, 314.1055); $\nu_{max.}$(Nujol) 3 337, 3 233, 1 689, 1 606, and 1 567 $cm^{-1}$ ± $\delta_H$[250 MHz; $(CD_3)_2CO$]4.27 (2 H, s), 6.56 (1 H, s), 6.95 (1 H, ~t, *J* 7.7 Hz), 6.99—7.10 (2 H, m), 7.25—7.38 (3 H, m), 7.49—7.58 (2 H, m), 7.99 (1 H, d, *J* 7.7 Hz), 10.74 (1 H, br, NH), and 11.00 (1 H, br, NH); *m/z* 314 ($M^+$, 69%), 285 (25), 257 (36), and 130 (100).

*1-Phenylpyrano*[3,4-b]*indol-3-one* (**29**).—Phosphorus pentoxide (15 g) was added in small portions to orthophosphoric acid (20 g) at room temperature and the mixture then heated at 110 °C for 2 h. The resulting polyphosphoric acid was allowed to cool to room temperature when a mixture of indol-3-ylacetic acid (1.75 g, 10 mmol) and benzoic acid (2.0 g, 16.4 mmol) was added and the contents of the flask mixed thoroughly. The mixture was heated slowly over 0.5 h to 90 °C and then maintained at this temperature for a further 0.5 h. After this the hot reaction mixture was poured into water (300 ml) (**CAUTION**) and the resulting orange precipitate filtered off, washed with water (2 × 50 ml), aqueous sodium hydrogen carbonate (half saturated; 4 × 50 ml), and again with water (2 × 50 ml). The solid was dried *in vacuo* and then chromatographed (ether–methanol) to give a bright red–orange solid which was triturated with ether–THF to give the *title compound* (**29**) (437 mg, 17%), m.p. 225—228 °C (lit.,[26] m.p. 231 °C) $\nu_{max.}$(Nujol) 3 320, 1 682, 1 639, 1 614, and 1 555 $cm^{-1}$; $\delta_H$[500 MHz; $(CD_3)_2SO$] 6.82 (1 H, s), 7.07 (1 H, ~t, *J* 8 Hz), 7.30 (1 H, d, *J* 8 Hz), 7.49—7.55 (2 H, m), 7.60 (2 H, ~t, *J* 8 Hz), 7.91 (2 H,

d, *J* 8 Hz), 8.05 (1 H, d, *J* 8 Hz), and 10.60 (1 H, br, NH); *m/z* 261 ($M^+$, 100%), 233 (41), and 204 (56).

*Ethyl 1-Phenyl-3-trimethylsilyl-9H-carbazole-2-carboxylate* (**31**).—A mixture of the pyranoindole (**29**) (23 mg, 0.09 mmol) and ethyl 3-(trimethylsilyl)propynoate (42 mg, 0.25 mmol) in bromobenzene (2 ml) was heated under reflux under nitrogen for 35 h and then evaporated. The residue was chromatographed (dichloromethane–light petroleum) to give the *title compound* (**31**) (21 mg, 62%), m.p. 166—169 °C (Found: C, 74.4; H, 6.3; N, 3.7. $C_{24}H_{25}NO_2Si$ requires C, 74.4; H, 6.5; N, 3.6%); $\nu_{max.}$ 3 396, 1 704, 1 257, 859, 838, 742, and 704 $cm^{-1}$; $\delta_H$(500 MHz; $CDCl_3$) 0.4 (9 H, s), 0.87 (3 H, t, *J* 7 Hz), 3.97 (2 H, q, *J* 7 Hz), 7.25 (1 H, ~t, *J* 8 Hz), 7.34 (1 H, d, *J* 8 Hz), 7.39—7.53 (6 H, m), 7.99 (1 H, br, NH), 8.14 (1 H, d, *J* 8 Hz), and 8.30 (1 H, s, 4-H); *m/z* 387 ($M^+$, 9%), 372 (100), and 344 (68).

*2-Methyl-1-phenyl-3-trimethylsilyl-9H-carbazole* (**32**).—A mixture of ethyl 1-phenyl-3-trimethylsilyl-9*H*-carbazole-2-carboxylate (**31**) (102 mg, 0.26 mmol) and lithium aluminium hydride (80 mg, 2.1 mmol) in dry dioxane (10 ml) was heated under reflux under nitrogen for 20 h. The reaction mixture was diluted with ether (50 ml) and the water (0.5 ml) carefully added, followed by solid sodium hydrogen carbonate until a light grey solid resulted. The mixture was filtered through Celite, the filtrate concentrated under reduced pressure, and the residue chromatographed (dichloromethane–hexane) to give the *title compound* (**32**) (80.2 mg, 92%) as a colourless oil (Found: $M^+$, 329.1596. $C_{22}H_{23}NSi$ requires *M*, 329.1600); $\nu_{max.}$($CCl_4$) 3 469, 1 600, 1 494, 1 467, 1 327, 1 250, 1 236, and 1 052 $cm^{-1}$; $\delta_H$(270 MHz; $CDCl_3$) 0.46 (9 H, s), 2.43 (3 H, s), 7.23 (1 H, ddd, *J* 7.5, 7.5 and 1.5 Hz), 7.27—7.39 (2 H, m), 7.42—7.61 (5 H, m), 7.68 (1 H, br NH), 8.11 (1 H, d, *J* 8 Hz), and 8.23 (1 H, s, 4-H); *m/z* 329 ($M^+$, 100%), 314 (54), 298 (4), 284 (5), 268 (2), 257 (16), and 254 (29).

*3-Hydroxy-2-methyl-1-phenyl-9H-carbazole* (**33**).—A solution of mercury(II) acetate (60 mg, 0.19 mmol) in acetic acid (2 ml) was added to 2-methyl-1-phenyl-3-trimethylsilyl-9*H*-carbazole (**32**) (61 mg, 0.19 mmol) in one portion. After 3 min ether (2 ml) was added to induce precipitation of the product; the product did not precipitate. The mixture was, therefore, concentrated under reduced pressure to give crude 3-acetoxymercurio-2-methyl-1-phenyl-9*H*-carbazole as a cream solid, which was throughly dried *in vacuo* for 20 h. The crude product was dissolved in THF (3 ml) and boron–tetrahydrofuran complex (1M; 3 ml, 3 mmol) added under nitrogen. After 40 min a mixture of hydrogen peroxide (30%; 0.5 ml) and sodium hydroxide (2M; 0.5 ml) was carefully added and the reaction mixture stirred for a further 2 min. It was then acidified with dilute hydrochloric acid (1M), diluted with water (20 ml), and extracted with ether. The ethereal extracts were washed with water and brine, dried ($MgSO_4$), and concentrated and the residue chromatographed (dichloromethane–light petroleum) to give the *title compound* (**33**) (20.8 mg, 41%), m.p. 176—180 °C (Found: C, 83.6; H, 5.5; N, 5.1. $C_{19}H_{15}NO$ requires C, 83.5; H, 5.5; N, 5.1%); $\nu_{max.}$($CHCl_3$) 3 605, 3 466, 3 340 br, 1 508, 1 490, 1 431, 1 315, 1 221, 1 123, and 1 108 $cm^{-1}$; $\delta_H$[250 MHz; $(CD_3)_2CO$] 2.17 (3 H, s), 7.06 (1 H, ~t, *J* 7.5 Hz), 7.24 (1 H, ~t, *J* 7.5 Hz), 7.34—7.56 (7 H, m), 7.94 (1 H, d, *J* 7.8 Hz), 8.05 (1 H, s, OH), and 9.43 (1 H, br, NH); *m/z* 273 ($M^+$, 100%).

*3-Methoxy-2-methyl-1-phenyl-9H-carbazole* (*Hyellazole*) (**3a**).—A mixture of 3-hydroxy-2-methyl-1-phenyl-9*H*-carbazole (**33**) (11.4 mg, 41.8 μmol), potassium carbonate (100 mg, 0.72 mmol), and methyl iodide (1.14 g, 8 mmol, 0.5 ml) in acetone (3 ml) was heated under reflux under nitrogen for 4 h. The reaction mixture was then diluted with ether (5 ml) and the potassium salts filtered off. Evaporation of the filtrate and chromatography of the residue (dichloromethane–hexane) gave the title compound (**3a**) (11 mg, 92%), m.p. 133—134 °C (lit.,[8] m.p. 133—134 °C), $\nu_{max.}$($CCl_4$) 3 473, 1 454, 1 423, 1 307, 1 208, 1 156, and 1 149 $cm^{-1}$; $\delta_H$[250 MHz; $(CD_3)_2CO$] 2.12 (3 H, s), 3.98 (3 H, s), 7.10 (1 H, ddd, *J* 7.3, 7.3 and 1 Hz), 7.26 (1 H, ddd, *J* 7.6, 7.6 and 1 Hz), 7.34—7.57 (6 H, m) 7.69 (1 H, s, 4-H), 8.07 (1 H, d, *J* 8 Hz), and 9.53 (1 H, br, NH); *m/z* 287 ($M^+$, 100%), 272 (50), 254 (14), 241 (7), and 181 (74).

## Acknowledgements

We thank the S.E.R.C. and May & Baker for a CASE award to (P. S.), the Royal Society of Chemistry for a Hickinbottom Fellowship (to C. J. M.), and Dr. P. Knowles for helpful discussions.

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*Received* 20*th April* 1989; *Paper* 9/01680E