

A Convenient Synthesis of Azolo-fused 2H-[1]Benzopyrans

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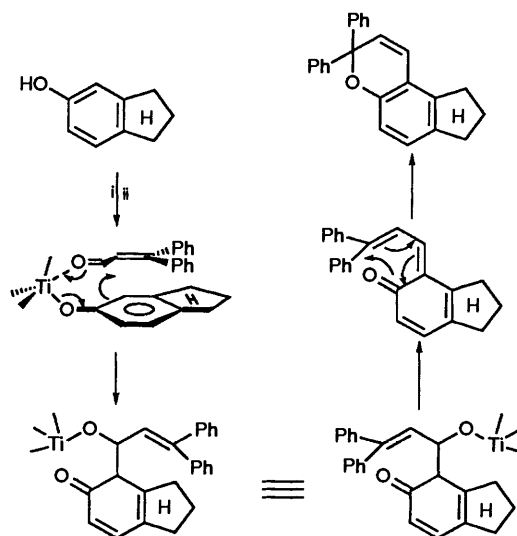
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The synthesis of substituted 7,7-diphenyl-7H-pyrano[3,2-*e*]benzazoles **2a-f** and 7,7-diphenyl-7H-pyrano[2,3-*g*]benzazoles **4a-d** is described. Thus, suitable titanium(IV) phenolates reacted with β -phenylcinnamaldehyde in refluxing aprotic non-polar solvents. Electrocyclisation of *o*-quinone allides generated *in situ* gives regiospecifically the title compounds. Stoichiometric amounts of heterocyclic phenol, titanium tetraethoxide and the carbonyl compound, have been found to give better results. In this series, substitution on the α position leads to the formation of the regioisomer. The method could be also extended to the formation of 8,8-diphenyl-8H-pyrano[2,3-*e*]benzazole **8**. A side reaction between the desired pyran and a second molecule of heterocyclic phenol was observed. This condensation product **9** was isolated and characterized in the case of the imidazole derivative, and a mechanism for its formation is proposed.

In recent years, 2H-[1]benzopyrans (2H-chromenes and their benzo derivatives) have been the subject of a fair amount of interest. They are an important class of oxygenated heterocyclic compounds¹ to which research has been devoted in connection with their photochromic properties² established by R. S. Becker³ and the biological activities^{4,5} of natural occurring chromenes.

During our study in the field of 2,2-diaryl-2H-chromenes which by molecular tailoring could be used to produce a wide range of different photochromic properties, related compounds annelated with azole systems were investigated. Indeed, the photochromic behaviour is strictly related to the aryl groups attached to the chromene.⁶

The synthesis of 2,2-disubstituted 2H-chromenes may be approached either by the preparation of another related ring system (mainly chromanones or coumarins) with subsequent variation of functionality^{7,8} or by *O*-alkylation of a free phenol followed by cyclisation onto the aromatic ring. The Kabbe synthesis⁹ gave poor yields¹⁰ of 2,2-diarylchroman-4-one starting with benzophenone derivatives and two additional steps (reduction and dehydration) are required to prepare the chromene. Thus, the second approach based on the thermal Claisen rearrangement of prop-2-ynyl ethers, is preferred and widely employed.^{11,12} This appeared particularly attractive because of ready availability of the starting phenols and chloro- or hydroxy-alkynes. Unfortunately, our attempts to prepare the desired target molecules were unsuccessful, despite varying the acidic conditions (toluene-*p*-sulfonic acid, sulfuric acid, trichloroacetic acid, acidic alumina).



Scheme 1 Reagents: i, Ti(OEt)₄; ii, Ph₂C=CHCHO

Sartori *et al.*,¹³ opened up new prospects for the preparation of 2,2-dialkyl-2H-chromenes which have been prepared by reaction of metal phenolates and α,β -unsaturated carbonyl compounds. However, the examples cited therein do not ensure the generality of this route, particularly concerning the heteroannellated 2,2-diaryl-2H-chromenes. Thus, the purpose of the present work was to set up a general method for building such pyrano[2,3]benzoazole frameworks, *i.e.* the three possible azolo-fused 2,2-diphenyl-2H-[1]benzopyran isomers (**I**, **II**, **III**) with the phenyl groups α to the pyran oxygen.

Results and Discussion

The synthesis of the new compounds was achieved by the one-pot method outlined in Scheme 1. The reaction involves the formation of the titanium(IV) salt of the heterocyclic phenol which reacts with the α,β -unsaturated carbonyl compound. Subsequent cyclisation of the *o*-quinone allide generated *in situ* leads to the chromene moiety. The desired compounds were initially purified by flash chromatography. The solids obtained were recrystallised from appropriate solvents and fully characterized by ¹H, ¹³C NMR and electronic spectroscopy. The ¹H NMR spectrum for each compound displayed a doublet

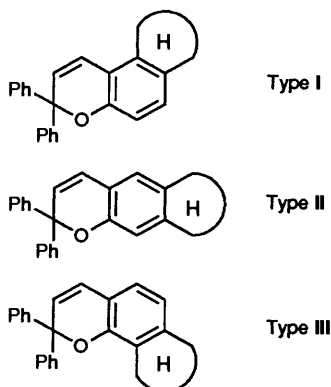
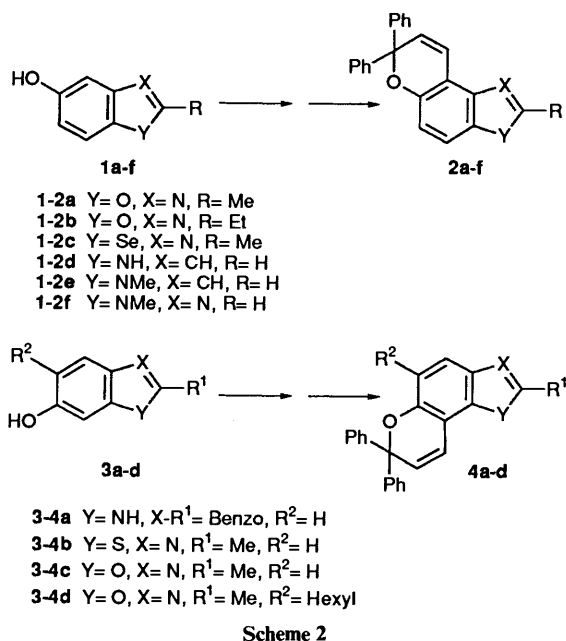


Table 1 Reaction conditions in the preparation of azolo-fused 2*H*-[1]benzopyrans

Phenolic substrate ^a				Molar ratio ^b	Time of reaction ^c (h)	Solvent	Compd.	Yield ^d (%)
	Y	X	R					
1a	O	N	Me	1:0.25:1.5	10 (3)	Toluene	2a	28 (42)
1a	O	N	Me	1:0.25:1	11 (3)	Toluene	2a	37
1a	O	N	Me	1:1:1	3 (0.5)	Toluene	2a	56
1a	O	N	Me	2:2:1	3 (0.5)	Toluene	2a	34 (18)
1b	O	N	Et	1:1:1	3 (0.5)	Toluene	2b	49
1c	Se	N	Me	1:1:1	4.5 (1)	Xylene	2c	33
1d	NH	CH	H	1:1:1	4 (0.5)	Toluene	2d	46
1e	NMe	CH	H	1:1:1	3.5 (0.5)	Toluene	2e	41
1f	NMe	N	Me	2:2:1	4 (0.5)	Xylene	2f	30 (15)
1f	NMe	N	Me	1:1:1	5 (1.5)	Toluene	2f	36
1f	NMe	N	Me	1:1:1	4 (0.5)	Xylene	2f	45

	Y	X	R ¹	R ²					
3a	NH		Benzo	H	1:1:1	3.5 (0.5)	Toluene	4a	31
3b	S	N	Me	H	1:1:1	3 (0.5)	Toluene	4b	44
3c	O	N	Me	H	1:1:1	3 (0.5)	Toluene	4c	42
3d	O	N	Me	n-Hexyl	1:1:1	4 (1)	Toluene	4d	23
5					1:1:1	4.5 (0.5)	Toluene	6	19
7					1:1:1	4 (0.5)	Xylene	8	21

^a See Schemes 2 and 4. ^b The molar ratio between phenolic substrate/Ti^{IV}/β-phenylcinnamaldehyde. ^c The values in parentheses refer to the time required for the complex formation. ^d Calculated on pure isolated compound based on β-phenylcinnamaldehyde, values in parentheses refer to yield based on starting phenol.

**Scheme 2**

integrating for one proton, centred at δ 6.2 with a coupling constant of 10 Hz which is typical for the proton α to the quaternary carbon of the pyran ring. Indeed, the presence of two phenyl groups causes a downfield shift in comparison with *gem*-dimethyl analogues.¹ The chemical shift (*ca.* δ 82) of the sp^3 carbon atom is also characteristic.¹⁴ The experimental data are reported in the corresponding section, and the conditions of reaction (solvent, time of reaction, molar ratio of reagents) are listed in Table 1.

The transition metal plays a fundamental role in coordinating both the phenolic substrate and the unsaturated carbonyl compound, inducing intramolecular irreversible reactions within the phenolate-reagent complex. Thus, the solvent and any species present in the reaction medium must not exclude the aldehyde from complex formation. The reaction

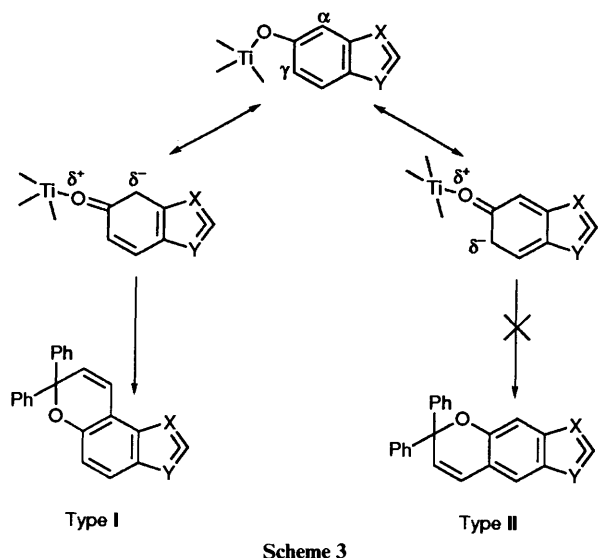
is also performed in an aprotic non-polar solvent (toluene or xylene) to accommodate the solubility of the starting heterocyclic phenol.

In order to optimize the reaction conditions, the ratio between the different reagents was allowed to vary, the pyranic ring formation being monitored by TLC (hydrolysis of an aliquot) and by liquid chromatography. In contrast to previous work,¹³ better results in terms of yield have been found using stoichiometric amounts of phenol, titanium tetraethoxide, and β-phenylcinnamaldehyde (see Table 1). Furthermore, shorter times are required for the preparation of the reaction organometallic complex using 1 equiv. of titanate. Thus, chromenes were obtained in increased yield by refluxing such suitable titanium(IV) phenolates with the aldehyde for 3–4 h, an important reduction from 7–8 h advocated in non-stoichiometric experiments.

Several heterocyclic phenols **1a–f** and **3a–f** (Scheme 2, Table 1) which represent the nitrogen-containing five-membered benzo fused aromatic heterocycles, *i.e.* benzoxazole, indole, benzoselenazole, benzothiazole, carbazole and benzimidazole, were tested in this approach to pyran ring formation. It seems that this route to heteroannulated chromenes has no limitations in terms of chemical structure of the starting phenol and could be readily extended to other heterocyclic analogues. This observation is significantly attractive since the value of heteroannulated benzopyrans^{1,2,15} both for their pharmacological and hi-tech uses has recently been recognised.

The method was found to be regioselective and the cyclisation occurs only on the position α to the heterocyclic junction, showing the importance of delocalisation and giving more carbanionic character at C- α relative to C- γ in which the aromatic character of the residual ring is disrupted (Scheme 3). All the phenols **1a–f** and **3a–d** give chromenes of Type I with this synthetic pathway and no trace of a linear chromene (Type II) was detected.

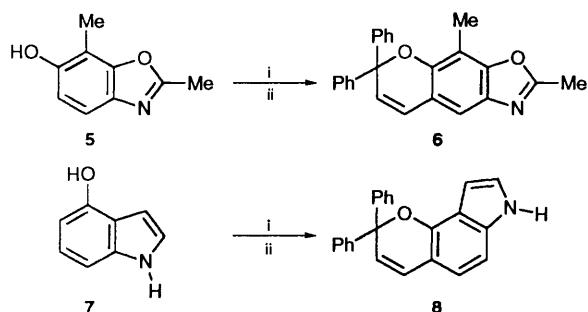
This example is of interest since it provides an illustration of the regioselectivity arising from resonance stabilisation. The ¹H NMR spectra of the angular isomer (Type I) displayed two doublets with a coupling constant of 8.6 (J^{1-3}) integrating each



for one proton and assigned to the two protons of the benzene ring; whereas it would be two singlets for the linear one (Type II) for this ring directly linked to the pyran moiety.

Nevertheless, the linear isomer could be obtained by suitable substitution of the starting phenol. We synthesized 6-hydroxy-2,7-dimethylbenzoxazole **5** in which the α position (C-7) is substituted by a methyl group; this was forced to cyclize in the other position affording the pyranic compound **6** (Scheme 4).

This method is also compatible with compounds bearing a hydroxy group at the α position, as shown with the cyclisation of 4-hydroxyindole **7** which leads to the formation of 8,8-diphenyl-8*H*-pyrano[2,3-*e*]indole **8** (Scheme 4). Thus, the formation of



Scheme 4 Reagents: i, Ti(OEt)₄; ii, Ph₂C=CHCHO

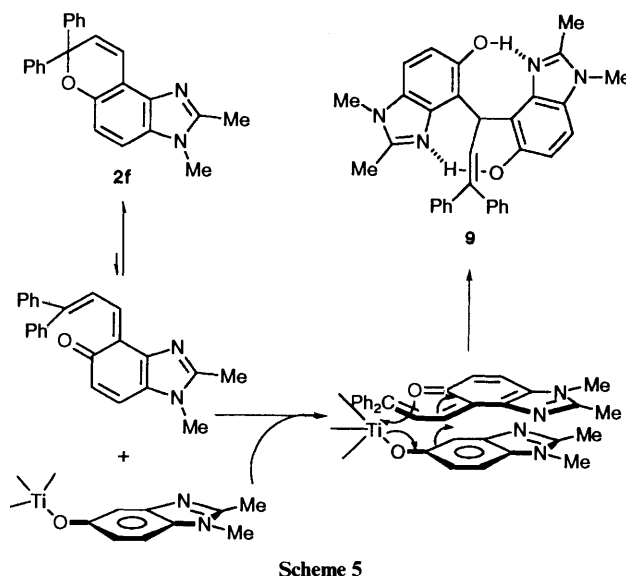
the Type III azolo-fused 2*H*-[1]benzopyrans is possible although in lower yield (see Table 1).

The crude reaction product from suitable titanium(IV) phenolates and β -phenylcinnamaldehyde were analysed using liquid chromatography coupled with mass spectrometry techniques. This revealed that the formation of different chromenes was accompanied by variable amounts of a by-product having a high molecular weight.

This product arises from a side reaction and has been isolated and fully characterized in the case of the benzimidazole derivative. It results from the condensation of two phenol moieties and one α,β -unsaturated carbonyl compound unit. Indeed, the high resolution mass spectra FAB⁺ gives C₃₃H₃₁N₄O₂ as the elemental composition ($m/z = 515.2447$ for MH⁺). Interestingly, the electron impact mass spectrum gives m/z 515.3 (30%), m/z 353.4 (65%) and then multiple fragmentation having $m/z = 58$ (100%). The second peak presumably corresponds to the related chromene formed through a loss of a phenol unit and subsequent cyclisation. The IR spectrum displays an intense and broad band centred at 3200–

2500 cm⁻¹ belonging to the OH function and characteristic for the stretching of chelated hydroxy groups. The ¹H NMR spectrum displays four methyl groups at δ 2.42, 2.56, 3.46 and 3.50 which substantiates the presence of two 1,2-dimethylbenzimidazole moieties. Two doublets of 6.22 and 7.93 integrating each for one proton and having a coupling constant of 8.6 and a complex in the aromatic region are also observed. The proton at δ 6.22 was assigned to 3-H since the HETCOR experiment shows a correlation with a carbon atom having 35.94 as chemical shift which is characteristic for an sp³ one.

These data support the proposal of structure **9** (Scheme 5). The ability of such a compound to form hydrogen bonds between hydroxy groups and sp² nitrogen atoms of both benzimidazole moieties, has been verified using molecular mechanics program GenMol.¹⁶ The molecular model indicates the N–O bond to be <2.7 Å.



Its formation should involve the *o*-quinone allide which should either come from the equilibrium with the pyran form or could be directly trapped from the earlier mentioned synthetic pathway (see Scheme 1). The electronic deficiency of the central carbon of the delocalised chain on *o*-quinone allide intermediate allows the nucleophilic attack of a second organometallic complex. The formation of this product of bicondensation is mainly favoured by an excess of phenol. Indeed, the yield of the so-called 'bisubstitution product' arises from 18 to 31% (based on β -phenylcinnamaldehyde) when double quantities of phenol were used with corresponding reduced yield of chromenes (from 45 to 30%). Two hydrogen bonds involving the hydroxy groups and the nitrogen atoms could also, *via* stabilization, contribute to its outcome.

Such bisubstitution products have been reported¹⁷ in the chromenic series arising from the reaction of salicylaldehyde derivatives and 1,1-diphenylethylene, leading to the formation of 2,2-diphenyl-4-(2,2-diphenylvinyl)chroman. This shows the reactivity of *o*-quinone allides towards nucleophilic reagents and substantiates the proposed mechanism, although in this case *via* acidic catalysis.

Experimental

M.p.s were determined in capillary tubes on a Buchi 510 apparatus and are uncorrected. Fourier Transform IR spectra were recorded on a Matson Polaris spectrophotometer. ¹H and ¹³C NMR spectra were recorded in CDCl₃ solution on a Bruker BM 250 or AMX 400 instrument. *J* Values are given in

Hz. UV-visible spectra were recorded on a Beckman DU 7500 instrument for solutions in spectrophotometric grade EtOH. Flash chromatographic separations were performed on Merck 60H Silica Gel (5–40 μm).

The starting heterocyclic phenols were purchased from Lancaster Chemicals Ltd or were prepared by demethylation of corresponding commercially available compounds (benzothiazole, benzoselenazole, indole). The benzoxazoles were prepared according to the literature procedure.¹⁸

General Procedure for Azolo-fused 2,2-Diphenyl-2H-[1]benzopyrans 2a–f, 4a–d, 6 and 8.—Under an atmosphere of nitrogen, titanium tetraethoxide (2.4 g, 10.4 mmol) in dry toluene (10 cm^3) was added over 10 min to the heterocyclic phenol (10.4 mmol) in dry toluene (40 cm^3). When the addition was complete the reaction mixture was boiled (15 min) and then slowly distilled to remove ethanol; solvent (20 cm^3) was collected. The reaction mixture was allowed to cool to room temperature and β -phenylcinnamaldehyde (2.17 g, 10.4 mmol) in dry toluene (50 cm^3) was added dropwise to it. When the addition was complete, the reaction mixture was refluxed (2–5 h), allowed to cool and poured onto 2 mol dm^{-3} aqueous ammonium chloride (100 cm^3). The organic layer was separated, dried (MgSO_4) and evaporated under reduced pressure. Subsequent elution from silica with pentane–diethyl ether as the eluent [percentage Et_2O , solvent system A:5%; B:15%; C:40%; D:100%] gave the desired product. The crystalline residue was recrystallised twice from the appropriate solvent (the first time with decolourisation by charcoal). The following compounds were obtained by this protocol.

2-Methyl-7,7-diphenyl-7H-pyrano[3,2-e]benzoxazole 2a [solvent system B] (56%); m.p. 163 °C (from hexane–benzene) (Found: C, 81.6; H, 5.0; N, 4.1. $\text{C}_{23}\text{H}_{17}\text{NO}_2$ requires C, 81.4; H, 5.05; N, 4.15%); δ_{H} (400 MHz) 2.56 (3 H, s, 2-Me), 6.29 (1 H, d, J 9.9, 8-H), 6.88 (1 H, d, J 8.65, 5-H), 7.16 (1 H, d, J 8.70, 4-H), 7.17 (1 H, d, J 9.9, 9-H), 7.24 (2 H, m, 4'-H), 7.31 (4 H, m, 3'-H) and 7.45 (4 H, m, 2'-H); δ_{C} (100 MHz) 14.70 (2-Me), 82.51 (7-C), 109.67 (4-C), 113.37 (5-C), 118.87 (9-C), 127.18 (4 \times C, 2'-C), 127.61 (2 \times C, 4'-C), 128.19 (4 \times C, 3'-C), 129.92 (8-C), 144.72 (2 \times C, 1'-C), 164.86 (2-C); λ_{max} (EtOH)/nm 213 (ϵ/dm^{-3} mol $^{-1}$ cm^{-1} 46 000), 250 (12 200), 264 (14 140), 289 (16 450), 325 (4320) and 340sh (3180).

2-Ethyl-7,7-diphenyl-7H-pyrano[3,2-e]benzoxazole 2b [solvent system A] (49%); m.p. 132 °C (from cyclohexane) (Found: C, 81.7; H, 5.5; N, 3.9. $\text{C}_{24}\text{H}_{19}\text{NO}_2$ requires C, 81.55; H, 5.4; N, 4.0%); δ_{H} (250 MHz) 1.40 (3 H, t, J 7.6, CH_2CH_3), 2.91 (2 H, q, J 7.6, CH_2CH_3), 6.28 (1 H, d, J 9.85, 8-H), 6.88 (1 H, dd, J 8.8, 5-H), 7.17 (1 H, d, J 8.7, 4-H), 7.20 (1 H, dd, J 9.8 and 0.45, 9-H), 7.25 (2 H, m, 4'-H), 7.31 (4 H, m, 3'-H) and 7.46 (4 H, m, 3'-H); δ_{C} (62.5 MHz) 11.37 (CH_2CH_3), 22.59 (CH_2CH_3), 82.63 (7-C), 109.84 (4-C), 113.46 (5-C), 119.14 (9-C), 127.32 (4 \times C, 2'-C), 127.74 (2 \times C, 4'-C), 128.31 (4 \times C, 3'-C), 129.97 (8-C), 143.63 (2 \times C, 1'-C) and 164.76 (2-C); λ_{max} (EtOH)/nm 208 (ϵ/dm^{-3} mol $^{-1}$ cm^{-1} 45 000), 269sh (14 600), 284 (18 450), 325 (3480) and 345sh (2950).

2-Methyl-7,7-diphenyl-7H-pyrano[3,2-e]benzoselenazole 2c [solvent system C] (33%); m.p. 221 °C (from EtOH) (Found: C, 68.8; H, 4.05; N, 3.2; Se 19.4. $\text{C}_{23}\text{H}_{17}\text{NOSe}$ requires C, 68.65; H, 4.25; N, 3.45; Se 19.6%); δ_{H} (250 MHz) 2.85 (3 H, s, 2-Me), 6.32 (1 H, d, J 9.9, 8-H), 6.94 (1 H, d, J 8.50, 5-H), 7.05 (1 H, d, J 9.9, 9-H), 7.14 (1 H, d, J 8.4, 4-H), 7.23 (2 H, m, 4'-H), 7.30 (4 H, m, 3'-H) and 7.44 (4 H, m, 2'-H); δ_{C} (62.5 MHz) 24.38 (2-Me), 83.10 (7-C), 116.46 (4-C), 118.62 (5-C), 123.17 (9-C), 127.31 (4 \times C, 2'-C), 127.74 (2 \times C, 4'-C), 128.30 (4 \times C, 3'-C), 130.43 (8-C) and 144.27 (2 \times C, 1'-C); λ_{max} (EtOH)/nm 213 (ϵ/dm^{-3} mol $^{-1}$ cm^{-1} 25 650), 251 (31 550), 273 (7250) and 356 (3930).

7,7-Diphenyl-7H-pyrano[3,2-e]indole 2d [solvent system C] (46%); m.p. 143 °C (from pentane) (Found: C, 84.25; H, 5.6; N,

4.55. $\text{C}_{23}\text{H}_{17}\text{NO}$ requires C, 84.25; H, 5.7; N, 4.65%); δ_{H} (400 MHz) 6.20 (1 H, d, J 9.75, 8-H), 6.50 (1 H, ddd, J 3.3, 2.1 and 0.8, 1-H), 6.86 (1 H, d, J 8.6, 5-H), 6.99 (1 H, dd, J 9.65 and 0.5, 9-H), 7.11 (1 H, dd, J 8.6 and 0.8, 4-H), 7.13 (1 H, m, 2-H), 7.21 (2 H, m, 4'-H), 7.29 (4 H, m, 3'-H), 7.48 (4 H, m, 2'-H) and 7.96 (1 H, br, N-H); δ_{C} (100 MHz) 81.70 (7-C), 99.70 (1-C), 111.41 (6-C), 112.54 (5-C), 121.27 (9-C), 125.14 (2-C), 127.10 (4 \times C, 2'-C), 127.26 (2 \times C, 4'-C), 127.80 (8-C), 127.97 (4 \times C, 3'-C) and 145.87 (2 \times C, 1'-C); λ_{max} (EtOH)/nm 219 (ϵ/dm^{-3} mol $^{-1}$ cm^{-1} 30 650), 256sh (10 420), 314 (13 560), 335sh (9040) and 354 (5220).

3-Methyl-7,7-diphenyl-7H-pyrano[3,2-e]indole 2e [solvent system C] (41%); m.p. 184 °C (from MeOH) (Found: C, 85.6; H, 5.5; N, 4.05. $\text{C}_{24}\text{H}_{19}\text{NO}$ requires C, 85.45; H, 5.65; N, 4.15%); δ_{H} (250 MHz) 2.34 (3 H, s, 3-Me), 6.17 (1 H, d, J 9.7, 8-H), 6.38 (1 H, d, J 2.95, 1-H), 6.84 (1 H, d, J 8.65, 5-H), 6.96 (1 H, d, J 9.65, 9-H), 6.97 (1 H, d, J 3, 2-H), 7.03 (1 H, d, J 8.7, 6-H), 7.23 (2 H, m, 4'-H), 7.30 (4 H, m, 4'-H) and 7.44 (4 H, m, 2'-H); δ_{C} (62.5 MHz) 32.51 (3-Me), 97.67 (1-C), 109.66 (6-C), 112.07 (5-C), 121.36 (9-C), 127.11 (4 \times C, 2'-C), 127.25 (2 \times C, 4'-C), 127.86 (4 \times C, 3'-C), 127.98 (8-C) and 129.62 (2-C); λ_{max} (EtOH)/nm 213 (ϵ/dm^{-3} mol $^{-1}$ cm^{-1} 34 900), 249 (9950), 267 (9200), 318 (10 950), 341 (8160) and 360sh (6250).

2,3-Dimethyl-7,7-diphenyl-7H-pyrano[3,2-e]benzimidazole 2f [solvent system D] (45%); m.p. 161 °C (from cyclohexane–benzene) (Found: C, 81.7; H, 5.65; N, 7.9. $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}$ requires C, 81.8; H, 5.7; N, 7.95%); δ_{H} (400 MHz) 2.50 (3 H, s, 2-Me), 3.53 (3 H, s, 3-Me), 6.25 (1 H, d, J 10, 8-H), 6.86 (1 H, d, J 8.65, 5-H), 6.94 (1 H, d, J 8.6, 4-H), 7.21 (2 H, m, 4'-H), 7.28 (4 H, m, 3'-H), 7.33 (1 H, dd, J 10 and 0.8, 9-H) and 7.46 (4 H, m, 2'-H); δ_{C} (100 MHz) 13.65 (2-Me), 29.75 (3-Me), 82.79 (7-C), 109.54 (4-C), 113.78 (5-C), 118.54 (9-C), 127.58 (4 \times C, 2'-C), 127.97 (2 \times C, 4'-C), 128.33 (4 \times C, 3'-C), 130.11 (8-C), 144.42 (2 \times C, 1'-C), 165.27 (2-C); λ_{max} (EtOH)/nm 209 (ϵ/dm^{-3} mol $^{-1}$ cm^{-1} 39 500), 224 (34 350), 250 (28 750), 320 (8450) and 347sh (4550).

3,3-Diphenyl-3H-pyrano[3,2-a]carbazole 4a [solvent system C] (31%); m.p. 182 °C (from heptane–benzene) (Found: C, 86.6; H, 5.1; N, 3.7. $\text{C}_{27}\text{H}_{19}\text{NO}$ requires C, 86.8; H, 5.15; N, 3.75%); δ_{H} (400 MHz) 6.25 (1 H, d, J 9.95, 2-H), 6.88 (1 H, d, J 8.2, 5-H), 6.89 (1 H, d, J 10, 1-H), 7.17 (1 H, ddd, J 7.7, 6.9 and 1.3, 9-H), 7.23 (2 H, m, 4'-H), 7.28 (1 H, m, 8-H), 7.31 (4 H, m, 3'-H), 7.32 (1 H, m, 7-H), 7.48 (4 H, m, 2'-H), 7.77 (1 H, d, J 8.5, 6-H), 7.89 (1 H, d, J 7.8, 10-H) and 7.93 (1 H, br, N-H); δ_{C} (62.5 MHz) 82.56 (3-C), 109.79 (5-C), 110.47 (7-C), 118.21 (1-C), 119.48 (10-C), 119.82 (9-C), 121.02 (6-C), 124.68 (8-C), 127.06 (4 \times C, 2'-C), 127.53 (2 \times C, 4'-C), 127.99 (2-C), 128.11 (4 \times C, 3'-C) and 144.84 (2 \times C, 1'-C); λ_{max} (EtOH)/nm 217 (ϵ/dm^{-3} mol $^{-1}$ cm^{-1} 26 000), 236 (38 750), 289 (25 650), 339 (5150) and 5200).

2-Methyl-7,7-diphenyl-7H-pyrano[2,3-g]benzothiazole 4b [solvent system C] (44%); m.p. 215 °C (from heptane–benzene) (Found: C, 77.5; H, 5.0; N, 3.9; S, 9.2. $\text{C}_{23}\text{H}_{17}\text{NOS}$ requires C, 77.7; H, 4.8; N, 3.95; S 9.05%); δ_{H} (400 MHz) 2.75 (3 H, s, 2-Me), 6.27 (1 H, d, J 9.75, 8-H), 6.67 (1 H, J 9.75, 9-H), 7.04 (1 H, d, J 8.7, 5-H), 7.22 (2 H, m, 4'-H), 7.30 (4 H, m, 3'-H), 7.45 (4 H, m, 2'-H) and 7.66 (1 H, d, J 8.7, 4-H); δ_{C} (100 MHz) 20.17 (2-Me), 83.06 (7-C), 116.17 (5-C), 121.63 (9-C), 122.65 (4-C), 127.9 (4 \times C, 2'-C), 127.78 (2 \times C, 4'-C), 128.27 (4 \times C, C2'), 129.76 (8-C), 144.52 (2 \times C, 1'-C) and 164.12 (2-C); λ_{max} (EtOH)/nm 212 (ϵ/dm^{-3} mol $^{-1}$ cm^{-1} 24 800), 221 (26 500), 250 (33 250), 284sh (5500) and 372 (4310).

2-Methyl-7,7-diphenyl-7H-pyrano[2,3-g]benzoxazole 4c [solvent system B] (42%); m.p. 195 °C (from benzene) (Found: C, 81.55; H, 5.0; N, 4.1. $\text{C}_{23}\text{H}_{17}\text{NO}_2$ requires C, 81.40; H, 5.05; N, 4.15%); δ_{H} (400 MHz) 2.57 (3 H, s, 2-Me), 6.29 (1 H, d, J 9.8, 8-H), 6.91 (1 H, d, J 8.6, 5-H), 6.97 (1 H, d, J 9.8, 9-H), 7.26 (2 H, m, 4'-H), 7.32 (4 H, m, 3'-H), 7.35 (1 H, d, J 8.55, 4-H) and 7.44 (4 H, m, 2'-H); δ_{C} (100 MHz) 14.44 (2-Me), 82.89 (7-C), 113.37 (5-C), 117.10 (9-C), 118.91 (4-C), 127.03 (4 \times C, 2'-C) 127.67

(2 × C, 4'-C), 128.16 (4 × C, 2'-C), 129.75 (8-C), 144.43 (2 × 1'-C) and 163.26 (2-C); $\lambda_{\max}(\text{EtOH})/\text{nm}$ 213 ($\epsilon/\text{dm}^{-3} \text{mol}^{-1} \text{cm}^{-1}$ 44 800), 222 (42 550), 254 (45 860), 286 (8070), 315 (4100) and 333 (2800).

5-Hexyl-2-methyl-7,7-diphenyl-7H-pyrano[2,3-g]benzoxazole 4d [solvent system A] (23%); m.p. 127 °C (from heptane) (Found: C, 82.35; H, 6.7; N, 3.2. $\text{C}_{29}\text{H}_{29}\text{NO}_2$ requires C, 82.25; H, 6.9; N, 3.3%); $\delta_{\text{H}}(250 \text{ MHz})$ 0.90 (3 H, $(\text{CH}_2)_5\text{CH}_3$), 1.25 (8 H, m, $\text{CH}_2(\text{CH}_2)_4\text{CH}_3$), 2.57 (3 H, s, 2-Me), 2.69 (2 H, m, $\text{CH}_2(\text{CH}_2)_4\text{CH}_3$), 6.28 (1 H, d, J 9.8, 8-H), 6.93 (1 H, d, J 9.8, 9-H) 7.27 (2 H, m, 4'-H), 7.31 (1 H, s, 4-H), 7.33 (4 H, m, 3'-H) and 7.44 (4 H, m, 2'-H); $\lambda_{\max}(\text{EtOH})/\text{nm}$ 214 ($\epsilon/\text{dm}^{-3} \text{mol}^{-1} \text{cm}^{-1}$ 44 100), 222 (41 050), 253 (42 650), 283 (7870), 320 (4090) and 332 (3150).

2,9-Dimethyl-7,7-diphenyl-7H-pyrano[3,2-f]benzoxazole 6 [solvent system C] (19%); m.p. 118 °C (from hexane) (Found: C, 81.7; H, 5.3; N, 3.9. $\text{C}_{24}\text{H}_{19}\text{NO}_2$ requires C, 81.55; H, 5.4; N, 3.95%); $\delta_{\text{H}}(400 \text{ MHz})$ 2.42 (3 H, s, 9-Me), 2.55 (3 H, s, 2-Me), 6.16 (1 H, d, J 9.85, 6-H), 6.71 (1 H, d, J 9.9, 5-H), 7.10 (1 H, s, 4-H), 7.24 (2 H, m, 4'-H), 7.31 (4 H, m, 3'-H) and 7.45 (4 H, m, 2'-H); $\delta_{\text{C}}(100 \text{ MHz})$ 9.12 (9-Me), 14.47 (2-Me), 113.49 (4-C), 124.52 (5-C), 126.86 (4 × C, 2'-C), 127.44 (2 × C, 4'-C), 128.10 (4 × C, 3'-C) and 129.75 (6-C); $\lambda_{\max}(\text{EtOH})/\text{nm}$ 218 ($\epsilon/\text{dm}^{-3} \text{mol}^{-1} \text{cm}^{-1}$ 35 100), 239 (23 860), 287 (17 450), 318 (5100) and 339sh (3860).

8,8-Diphenyl-8H-pyrano[2,3-e]indole 8 [solvent system C] (21%); m.p. 113 °C (from MeOH) (Found: C, 84.4; H, 5.6; N, 4.6. $\text{C}_{23}\text{H}_{17}\text{NO}$ requires C, 84.25; H, 5.7; N, 4.65%); $\delta_{\text{H}}(250 \text{ MHz})$ 6.03 (1 H, d, J 8.75, 7-H), 6.69 (1 H, d, J 9.8, 6-H), 6.73 (1 H, m, 1-H), 7.09 (1 H, dd, J 3.3 and 2.25, 2-H), 7.21 (1 H, m, 5-H), 7.25 (2 H, m, 4'-H), 7.32 (4 H, m, 3'-H), 7.36 (1 H, m, 4-H), 7.51 (4 H, m, 2'-H) and 8.08 (1 H, br, NH); $\delta_{\text{C}}(62.5 \text{ MHz})$ 100.28 (4-C), 104.25 (5-C), 121.67 (6-C), 123.71 (2-C), 124.55 (1-C), 124.68 (7-C), 127.18 (4 × C, 2'-C), 127.51 (2 × C, 4'-C) and 128.26 (4 × C, 3'-C); $\lambda_{\max}(\text{EtOH})/\text{nm}$ 215 ($\epsilon/\text{dm}^{-3} \text{mol}^{-1} \text{cm}^{-1}$ 47 000), 259 (45 850), 269sh (36 950), 294 (5250), 314 (4950) and 320sh (1860).

3,3-Bis(5-hydroxy-1,2-dimethylbenzimidazol-4-yl)-1,1-diphenylpropene 9.—Under an atmosphere of nitrogen, titanium tetraethoxide (3.51 g, 15.4 mmol) in dry xylene (20 cm^3) was added over 10 min to 5-hydroxy-1,2-dimethylbenzimidazole (2.5 g, 15.4 mmol) in dry xylene (60 cm^3). When the addition was complete the reaction mixture was boiled (10 min) and then slowly distilled to remove ethanol; solvent (30 cm^3) was collected. The reaction mixture was allowed to cool to room temperature and β -phenylcinnamaldehyde (1.6 g, 15.4 mmol) in dry xylene (50 cm^3) was added dropwise. When the addition was complete, the reaction mixture was refluxed (4 h), allowed to cool and poured onto 2 mol dm^{-3} aqueous ammonium chloride (120 cm^3). The organic layer was separated, dried (MgSO_4) and evaporated under reduced pressure. The product, isolated by flash chromatography using 98% Et_2O –2% CH_2Cl_2 as the

eluent, was crystallized from heptane–benzene to afford the title compound (2.46 g, 31%), m.p. 154 °C (Found: MH^+ , 515.244; C, 76.9; H, 5.95; N, 10.85. $\text{C}_{33}\text{H}_{30}\text{N}_4\text{O}_2$ requires MH^+ , 515.244; C, 77; H, 5.9; N, 10.9%); $\delta_{\text{H}}(400 \text{ MHz})$ 2.42, 2.56 (2 × 3 H, s, CMe), 3.46, 3.51 (2 × 3 H, s, NMe), 6.22 (1 H, d, J 8.6, 3-H), 6.83–7.33 (14 H, m, Ar-H) and 7.93 (1 H, J 8.6, 2-H); $\delta_{\text{C}}(100 \text{ MHz})$ 13.56, 13.75 (2 × C, CqMe), 29.72, 29.76 (2 × C, NMe), 35.94 (3-C), 106.99, 107.10, 115.37, 126.43, 127.62 (4 × C), 127.84 (2 × C), 128.74 (2-C) and 129.82 (4 × C); $\lambda_{\max}(\text{EtOH})/\text{nm}$ 215 ($\epsilon/\text{dm}^{-3} \text{mol}^{-1} \text{cm}^{-1}$ 64 400), 251sh (36 450), 262 (52 630), 292 (13 400) and 304sh (10 850); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ (OH chelated) 3200–2400.

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