Iminophosphorane-mediated Annelation of a Pyridine or Pyrimidine Ring into an Indole Ring: Synthesis of β-, γ-Carbolines and Pyrimido[4,5-*b*]indole Derivatives

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A number of pyrido[3,4-*b*]indole, pyrido[4,3-*b*]indole, and pyrimido[4,5-*b*]indole derivatives have been prepared. Ethyl 3-(1-methylindol-3-yl)-2-triphenylphosphoranylideneaminoprop-2-enoate (**2**) reacts with aromatic isothiocyanates to yield the corresponding 1-arylamino-3-ethoxycarbonyl-9-methylpyrido[3,4-*b*]indoles [(**3**)—(**6**)]. Similarly, the ethyl 3-(1-methylindol-2-yl)-2-triphenylphosphoranylideneaminoprop-2-enoate (**10**) under similar reaction conditions leads to 1-arylamino-3-ethoxycarbonyl-5-methylpyrido[4,3-*b*]indoles [(**11**)—(**14**)]. Also, iminophosphoranes (**2**) and (**10**) react with carbon disulphide to give the 1-thioxopyrido[3,4-*b*]indole (**8**) and 1-thioxopyrido[4,3-*b*]indole (**15**) respectively. The reaction of the 3-formyl-1-phenyl-2-triphenylphosphoranylideneaminoindole (**17**) with isothiocyanates at room temperature leads directly to 3-aryl-2,3-dihydro-2-oxo-9-phenylpyrimido[4,5-*b*]indoles [(**20**)—(**22**)].

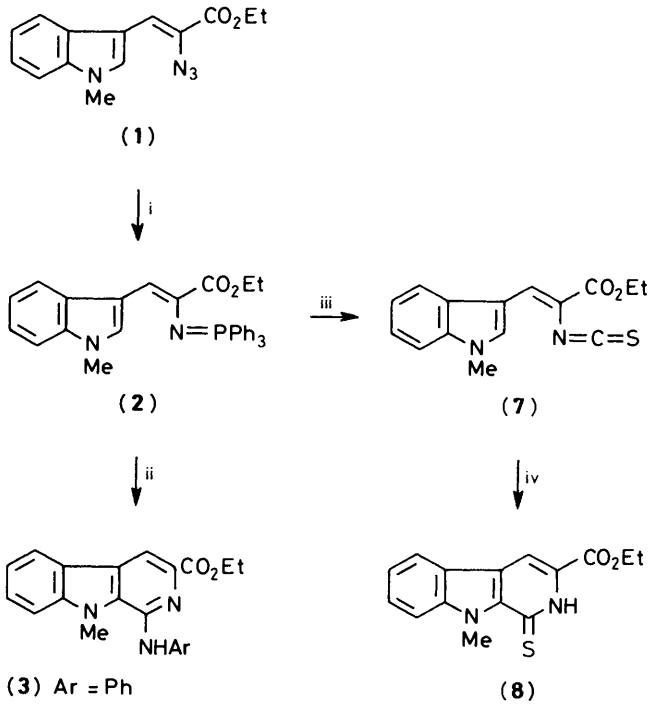
Indoles containing an additional ring fused across the 2,3-positions are widely distributed in Nature. Examples in which the fused ring contains six members include β-carboline alkaloids and lavendamycin, an antitumor antibiotic;[1] the recent isolation of ethyl β-carboline-3-carboxylate (β-CCE) from human urine and brain tissue and the demonstration that it possesses a high affinity for benzodiazepine-binding brain proteins[2] has prompted a renewed interest in the synthesis and biological activity evaluation of new β-carboline derivatives.[3] Extensive research on environmental mutagens and carcinogens over the last decade has led to the identification of many of these substances in food, water, and air. The first isolated and highly potent mutagens among these compounds are the γ-carboline derivatives 3-amino-1,4-dimethyl-5*H*-pyrido[4,3-*b*]indole (Trp-P-1) and 3-amino-1-methyl-5*H*-pyrido[4,3-*b*]indole (Trp-P-2) isolated from tryptophan pyrolysates.[4]

We now report a simple general procedure for the preparation of β-, γ-carbolines and pyrimido[4,5-*b*]indoles under completely neutral conditions, based on the ready synthesis and subsequent aza-Wittig reaction of iminophosphoranes derived from azidoacrylates bearing β-indolyl substituents. Pyrido-annulation occurs *via* a 1,3,5-hexatriene entity containing a cumulated double bond at one end, derived from the iminophosphorane and heterocumulenes, which undergoes electrocyclic ring-closure to give the cyclic valence tautomeric pyridine ring.

Results and Discussion

The starting ethyl 2-azido-3-(1-methylindol-3-yl)prop-2-enoate (**1**), available from 3-formyl-1-methylindole and ethyl azidoacetate,[5] reacts with triphenylphosphine in dry dichloromethane at 0 °C to give the iminophosphorane (**2**) in near quantitative yield. Compound (**2**) reacts with aromatic isothiocyanates in dry toluene at reflux temperature for 12 h to give triphenylphosphine sulphide and the corresponding 1-arylamino-3-ethoxycarbonyl-9-methylpyrido[3,4-*b*]indole (**3**)—(**6**) in high yields (70—94%) (Scheme 1, Table). In addition, iminophosphorane (**2**) reacts with carbon disulphide in toluene at reflux temperature to give the isothiocyanate (**7**) as a crystalline solid in 89% yield, which on heating at 170 °C undergoes cyclization to give 3-ethoxycarbonyl-1,2-dihydro-9-methyl-1-thioxopyrido[3,4-*b*]indole (**8**) in 90% yield.

This approach has also shown to be useful in the preparation of γ-carbolines. Thus, iminophosphorane (**10**), available from ethyl 2-azido-2-(1-methylindol-2-yl)prop-2-enoate[6] (**9**) and triphenylphosphine, reacts with isothiocyanates under similar reaction conditions to give 1-arylamino-3-ethoxycarbonyl-5-methylpyrido[4,3-*b*]indoles (**11**)—(**14**) in excellent yields (81—94%) (Scheme 2, Table). However, reaction between iminophosphorane (**10**) and carbon disulphide in toluene at reflux temperature leads directly to 3-ethoxycarbonyl-1,2-dihydro-5-methyl-1-thioxopyrido[4,3-*b*]indole (**15**) in excellent yield (96%).

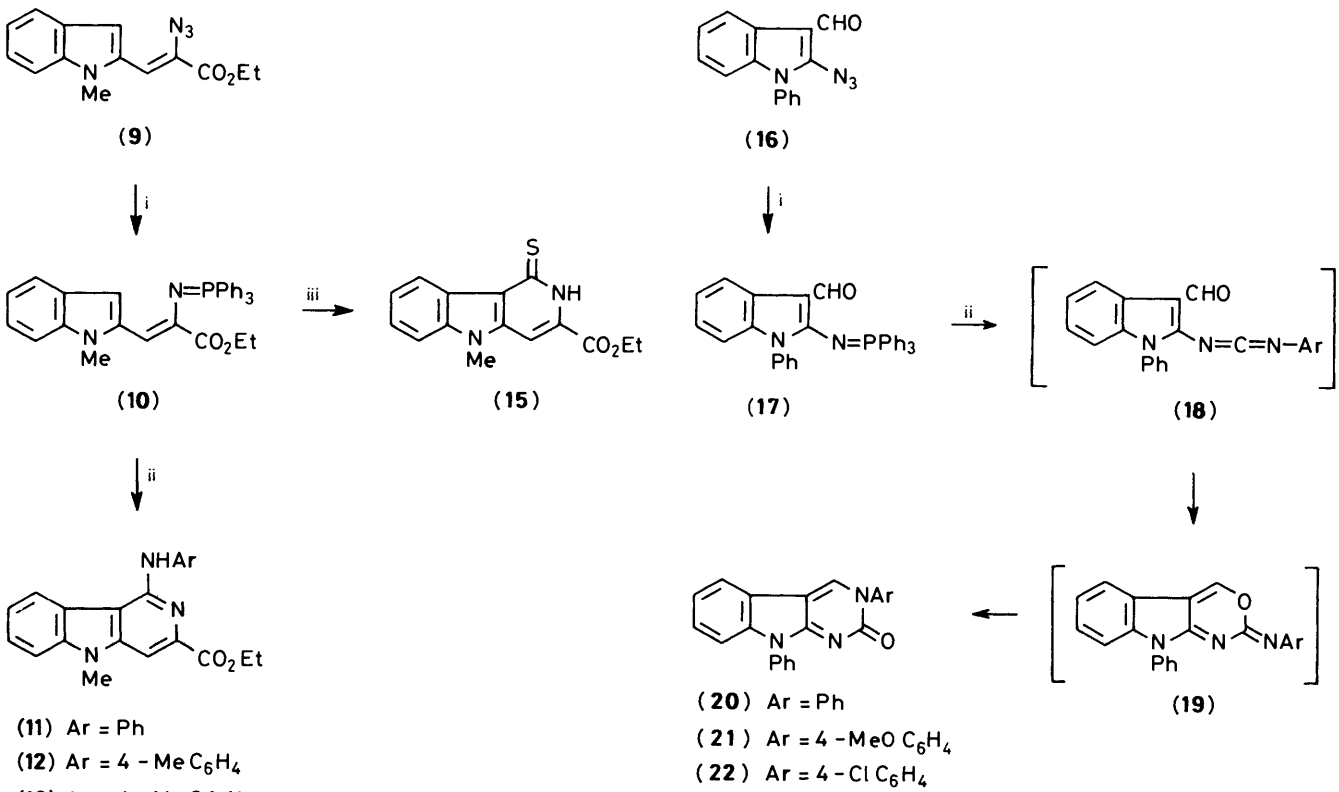


(**3**) Ar = Ph
(**4**) Ar = 4-MeC$_6$H$_4$
(**5**) Ar = 4-MeOC$_6$H$_4$
(**6**) Ar = 4-ClC$_6$H$_4$

Scheme 1. *Reagents:* i, $Ph_3P{=}CH_2Cl_2$, r.t.; ii, ArN=C=S–toluene, reflux; iii, CS_2–toluene, reflux; iv, 170 °C

Table. Pyrido[3,4-*b*]indoles [(**3**)—(**6**)] and pyrido[4,3-*b*]indoles [(**11**)—(**14**)]

Compd.	Crystal form	Yield (%)	M.p. (°C)	Found (%) C	H	N	Formula	Required (%) C	H	N
(**3**)	Yellow prisms	79	194—196	72.9	5.6	12.1	$C_{21}H_{19}N_3O_2$	73.03	5.54	12.17
(**4**)	Pale yellow prisms	70	169—170	73.4	5.7	11.5	$C_{22}H_{21}N_3O_2$	73.52	5.89	11.69
(**5**)	Yellow prisms	82	179—180	70.5	5.5	11.3	$C_{22}H_{21}N_3O_3$	70.38	5.64	11.19
(**6**)	Yellow prisms	84	186—188	66.5	4.8	11.2	$C_{21}H_{18}ClN_3O_2$	66.40	4.78	11.06
(**11**)	White prisms	94	127—128	73.1	5.5	12.2	$C_{21}H_{19}N_3O_2$	73.03	5.54	12.17
(**12**)	Colourless prisms	81	193—194	73.6	5.9	11.6	$C_{22}H_{21}N_3O_2$	73.52	5.89	11.69
(**13**)	Pale yellow prisms	89	172—174	70.4	5.5	11.2	$C_{22}H_{21}N_3O_3$	70.38	5.64	11.19
(**14**)	Colourless needles	93	212—214	66.6	4.9	10.9	$C_{21}H_{18}ClN_3O_2$	66.40	4.78	11.06



Scheme 2. *Reagents:* i, Ph_3P–CH_2Cl_2'r.t.; ii, ArN=C=S–toluene, reflux; iii, CS_2–toluene, reflux

Scheme 3. *Reagents:* i, Ph_3P–CH_2Cl_2, r.t.; ii, ArN=C=S–CH_2Cl_2, r.t.

The 2-azido-3-formyl-1-phenylindole (**16**), readily available from 2-chloro-3-formyl-1-phenylindole[7] and sodium azide, reacts with triphenylphosphine in dry dichloromethane at 0 °C to give the corresponding iminophosphorane (**17**) in good yield, (85%). Iminophosphorane (**17**) reacts with isothiocyanates in dry dichloromethane at room temperature to give the corresponding 3-aryl-2,3-dihydro-9-phenyl-2-oxopyrimido[4,5-*b*]-indoles (**20**)—(**22**) in good yields (82—76%). Presumably, the conversion of (**17**) into (**20**)—(**22**) involves initial aza-Wittig reaction between iminophosphorane (**17**) and isothiocyanates to give the carbodi-imide (**18**), which undergoes electrocyclic ring-closure to give an unstable 1,3-oxazine-2-imine which by a typical Dimroth rearrangement undergoes ring-opening and closure to furnish the 2-oxopyrimido[4,5-*b*]indoles (**20**)—(**22**) (Scheme 3). The i.r. of (**20**)—(**22**) show a strong absorption at 1 678—1 666 cm^{-1} due to the carbonyl group. In the ^1H n.m.r. spectra the chemical shift of 4-H is characteristic at δ 8.55—8.25. Electron-impact mass spectra show the expected molecular ion peak in high intensity, peaks are also found at *m/z* ($M^+ - 1$) and ($M^+ - NCO$).

Experimental

M.p.s. were recorded on a Kofler hot-stage apparatus and are uncorrected. I.r. spectra were recorded on a Nicolet FT-5DX spectrometer and ^1H n.m.r. spectra on a Varian FT-80 (80 MHz) spectrometer with Me_4Si as internal standard. Electron-impact mass spectra were carried out on a Hewlett-Packard 5993C spectrometer at an ionization potential of 70 eV. Elemental analyses were performed with a Perkin-Elmer 240C instrument.

Reagents. All solvents were dried according to standard procedures, distilled and stored over activated molecular sieves 4A.

The ethyl 2-azido-3-(1-methylindol-3-yl)prop-2-enoate[5] (**1**) and ethyl 2-azido-3-(1-methylindol-2-yl)prop-2-enoate[6] (**9**) were prepared following literature methods.

General Procedure for the Preparation of Iminophosphoranes (**2**) *and* (**10**).—Triphenylphosphine (2.62 g, 10 mmol) was added to a solution of the appropriate ethyl 2-azidoprop-2-enoate (**1**) or (**9**) (2.58 g, 10 mmol) in dry dichloromethane (50 ml), and the reaction mixture stirred at room temperature for 12 h. The solvent was evaporated off under reduced pressure and the residual material treated with hexane (10 ml); the solid was separated by filtration and recrystallized from benzene–hexane (1:1, v/v).

The following compounds were obtained. *Ethyl* 3-(1-*methylindol-3-yl*)-2-*triphenylphosphoranylideneaminoprop-2-enoate* (**2**) 97% as yellow plates, m.p. 199—201 °C (Found: C, 76.1; H, 5.6; N, 5.45. $C_{32}H_{29}N_2O_2P$ requires C, 76.17; H, 5.79; N, 5.55); $\nu_{max.}$(Nujol) 1 685, 1 591, 1 546, 1 475, 1 462, 1 436, 1 407, 1 379, 1 319, 1 247, 1 208, 1 109, 1 068, 1 039, 853, 822, 788, 770, 747, 726, and 715 cm^{-1}; $\delta_H(CDCl_3)$ 8.40 (1 H, s), 8.1—7.2 (20 H, m), 3.95 (2 H, q), 2.65 (3 H, s), and 1.0 (3 H, t); *m/z* (%) 504 (M^+, 23), 254 (16), 221 (15), 220 (100), 183 (29), 170 (14), 169 (96), 115 (11), and 108 (21).

Ethyl 3-(1-*methylindol-2-yl*)-2-*triphenylphosphoranylideneaminoprop-2-enoate* (**10**) (91%) as yellow plates, m.p. 150 °C (Found: C, 75.95; H, 5.6; N, 5.65); $\nu_{max.}$(Nujol) 1 679, 1 584, 1 467, 1 427, 1 329, 1 240, 793, 754, 731, 712, and 697 cm^{-1}; $\delta_H(CDCl_3)$ 8.1—6.7 (21 H, m), 3.9 (2 H, q), 3.8 (3 H, s), and 1.0 (3 H, t); *m/z* (%) 504 (M^+, 27), 263 (17), 262 (30), 220 (60), 183 (64), 169 (100), 129 (17), 115 (21), 108 (43), 107 (15), 97 (10), 83 (11), and 81 (11).

General Procedure for the Preparation of Pyrido[3,4-b]*indoles* (**3**)—(**6**) *and Pyrido*[4,3-b]*indoles* (**11**)—(**14**).—The appropriate isothiocyanate (2 mmol) was added dropwise to a stirred solution of iminophosphorane (**2**) or (**10**) (2 mmol) in dry toluene (20 ml) at 0 °C under nitrogen. After 30 min the mixture was heated under reflux for 12 h, cooled, the solvent evaporated off under reduced pressure, and the residual material was recrystallized from toluene–hexane (1:1, v/v). The following compounds were obtained (yields, m.p.s, and analyses are given the Table). 3-*Ethoxycarbonyl*-9-*methyl*-3-*phenylaminopyrido*[3,4-b]*indole* (**3**), $\nu_{max.}$(Nujol) 3 432, 1 689, 1 561, 1 464, 1 269, 1 252, 1 029, 783, 746, 734, and 691 cm^{-1}; $\delta_H[(CD_3)_2SO]$ 8.9 (1 H, s), 8.75 (1 H, s), 8.5 (1 H, d), 7.9—6.9 (8 H, m), 4.45 (2 H, q), 4.2 (3 H, s), and 1.4 (3 H, t); *m/z* (%) 345 (M^+, 47), 316 (10), 272 (21), 271 (100), 270 (53), 268 (14), 256 (15), 194 (30), 168 (13), 153 (10), 140 (20), 136 (18), 127 (30), 101 (10), 91 (10), and 74 (42). 3-*Ethoxycarbonyl*-9-*methyl*-1-(p-*tolylamino*)*pyrido*[3,4-b]*indole* (**4**), $\nu_{max.}$(Nujol) 3 431, 1 692, 1 600, 1 559, 1 527, 1 512, 1 265, 1 246, 819, 747, and 734 cm^{-1}; $\delta_H[(CD_3)_2SO]$ 8.7 (1 H, s), 8.5 (1 H, d), 7.9—7.1 (8 H, m), 4.5 (2 H, q), 4.2 (3 H, s), 2.3 (3 H, s), and 1.4 (3 H, t); *m/z* (%) 359 (M^+, 66), 330 (10), 286 (23), 285 (100), 284 (53), 271 (18), 270 (62), 268 (20), 168 (11), 140 (17), 135 (14), 127 (25), 115 (10), 105 (12), 91 (24), and 77 (10). 3-*Ethoxycarbonyl*-1-(p-*methoxyphenylamino*-9-*methylpyrido*[3,4-b]*indole* (**5**), $\nu_{max.}$(Nujol) 3 480, 1 706, 1 599, 1 559, 1 508, 1 262, 1 236, 1 041, 1 028, 831, 787, 783, 752, and 734 cm^{-1}; $\delta_H[(CD_3)_2SO]$ 8.7 (1 H, s), 8.6 (1 H, s), 8.55 (1 H, d), 7.9—7.1 (7 H, m), 4.5 (2 H, q), 4.3 (3 H, s), 3.9 (3 H, s), and 1.4 (3 H, t); *m/z* (%) 375 (M^+, 43), 314 (10), 302 (20), 301 (80), 300 (32), 286 (50), 270 (51), 258 (18), 194 (98), 169 (15), 168 (28), 151 (17), 140 (37), 127 (54), 121 (100), 92 (17), and 77 (31). 1-(p-*Chlorophenylamino*)-3-*ethoxycarbonyl*-9-*methylpyrido*[3,4-b]-*indole* (**6**), $\nu_{max.}$(Nujol) 3 420, 1 691, 1 600, 1558, 1 526, 1 492, 1 268, 1 085, 835, 746, and 734 cm^{-1}; $\delta_H(CDCl_3)$ 8.75 (1 H, s), 8.3 (1 H, d), 7.75—6.90 (8 H, m), 4.55 (2 H, q), 4.0 (3 H, s), and 1.55 (3 H, t); *m/z* (%) 381 (M + 2, 16), 379 (M^+, 46), 350 (10), 307 (34), 306 (30), 305 (76), 304 (42), 290 (11), 271 (23), 270 (100), 268 (21), 194 (27), 168 (15), 101 (10), and 77 (7). 3-*Ethoxycarbonyl*-5-*methyl*-1-*phenylaminopyrido*[4,3-b]*indole* (**11**), $\nu_{max.}$(Nujol) 3 443, 1 710, 1 646, 1 621, 1 601, 1 462, 1 415, 1 271, 1 183, 1 033, 743, 734, and 693 cm^{-1}; $\delta_H(CDCl_3)$ 8.0—7.15 (11 H, m), 4.55 (2 H, q), 3.85 (3 H, s), and 1.55 (3 H, t); *m/z* (%) 345 (M^+, 100), 344 (33), 316 (21), 273 (45), 272 (35), 271 (72), 270 (27), 257 (16), 256 (14), 231 (10), 168 (10), and 77 (17). 3-*Ethoxycarbonyl*-5-*methyl*-1-(p-*tolylamino*)*pyrido*[4,3-b]-*indole* (**12**), $\nu_{max.}$(Nujol) 3 472, 1 709, 1 617, 1 599, 1 565, 1 527, 1 326, 1 279, 1 267, 1 287, 1 120, 1 036, 876, 831, 777, 741, and 729 cm^{-1}; $\delta_H(CDCl_3)$ 7.9—7.1 (10 H, m), 4.55 (2 H, q), 3.85 (3 H, s), 2.4 (3 H, s), and 1.55 (3 H, t); *m/z* (%) 359 (M^+, 100), 358 (23), 330 (21), 287 (41), 286 (31), 285 (78), 284 (26), 271 (18), 270 (16), 245 (10), 194 (15), 168 (18), 140 (17), 115 (10), 91 (21), and 77 (6). 3-*Ethoxycarbonyl*-1-(p-*methoxyphenylamino*)-5-*methylpyrido*[4,3-b]*indole* (**13**), $\nu_{max.}$(Nujol) 3 436, 1 697, 1 620, 1 602, 1 570, 1 524, 1 511, 1 267, 1 247, 1 230, 1 185, 1 112, 1 031, 837, 775, 742 and 730 cm^{-1}; $\delta_H(CDCl_3)$ 7.95—6.95 (10 H, m), 5.0 (2 H, q), 3.9 (3 H, s), 3.85 (3 H, s), and 1.55 (3 H, t); *m/z* (%) 375 (M^+, 94), 360 (37), 346 (15), 303 (17), 302 (16), 301 (39), 287 (24), 286 (100), 271 (11), 243 (15), 194 (25), 180 (22), 179 (11), 168 (16), 140 (16), 129 (16), 97 (17), 82 (13), and 77 (14). 1-(p-*Chlorophenylamino*-3-*ethoxycarbonyl*-5-*methylpyrido*[4,3-b]*indole* (**14**), $\nu_{max.}$(Nujol) 3 457, 1 701, 1 621, 1 602, 1 568, 1 524, 1 494, 1 401, 1 330, 1 281, 1 265, 1 180, 1 094, 831, 776, 746, and 730 cm^{-1}; $\delta_H(CDCl_3)$ 7.9—7.3 (9 H, m), 7.0 (1 H, s), 4.5 (2 H, q), 3.75 (3 H, s), and 1.5 (3 H, t); *m/z* (%) 381 (M + 2, 35), 379 (M^+, 100), 350 (18), 308 (12), 307 (48), 306 (24), 305 (60), 194 (13), 168 (15), 140 (17), 136 (10), 111 (15), 77 (7), and 75 (21).

3-*Ethoxycarbonyl*-1,2-*dihydro*-9-*methyl*-1-*thioxopyrido*[3,4-b]*indole* (**8**).—Carbon disulphide (0.6 ml, 10 mmol) was added slowly with stirring at room temperature to a solution of ethyl 3-(1-methylindol-3-yl)-2-triphenylphosphoranylideneaminoprop-2-enoate (**2**) (1.01 g, 2 mmol) in dry toluene (20 ml) and the mixture was stirred under reflux temperature for 12 h. After cooling, the solvent was removed under reduced pressure to give a residual oil, which when recrystallized from toluene–hexane gave the isothiocyanate (**7**) (0.51 g, 89%) as yellow crystals, m.p. 110 °C (Found: C, 62.9; H, 4.7; N, 9.8. $C_{15}H_{14}N_2O_2S$ requires C, 69.92; H, 4.93; N, 9.78); $\nu_{max.}$(Nujol) 2 107, 2027, 1 701, 1 618, 1 522, 1 477, 1 256, 750, 715, 693, and 638 cm^{-1}; $\delta_H(CDCl_3)$ 8.2 (1 H, s), 7.9—7.2 (5 H, m), 3.9 (2 H, q), 2.6 (3 H, s), and 1.1 (3 H, t); *m/z* (%) 286 (M^+, 27), 183 (65), 170 (57), 169 (100), 155 (43), 144 (15), 140 (20), 139 (38), 127 (26), 101 (18), and 77 (52). The isothiocyanate (**7**) (0.29 g, 1 mmol) was treated at 170 °C for 3 h under reduced pressure. After being cooled, the residual material was recrystallized from ethanol to give (**8**) (0.26 g, 90 %) as yellow prisms, m.p. 213—215 °C (Found: C, 62.8; H, 4.8; N, 9.9. $C_{15}H_{14}N_2O_2S$ requires C, 62.92; H, 4.93; N, 9.78); $\nu_{max.}$(Nujol) 3 233, 1 724, 1 549, 1 465, 1 264, 1 121, 1 103, 881, 757, 747, 724, 716, and 692 cm^{-1}; $\delta_H(CDCl_3)$ 7.93—7.23 (5 H, m), 4.61 (3 H, s), 4.50 (2 H, q), and 1.45 (3 H, t); *m/z* (%) 286 (M^+, 16), 214 (8), 213 (17), 212 (100), 211 (67), 153 (16), 140 (40), 127 (15), 115 (12), 106 (13), and 77 (10).

3-*Ethoxycarbonyl*-1,2-*dihydro*-5-*methyl*-1-*thioxopyrido*[4,3-b]*indole* (**15**).—Carbon disulphide (0.6 ml, 10 mmol) was added slowly with stirring at room temperature to a solution of ethyl 3-(1-methylindol-2-yl)-2-triphenylphosphoranylideneaminoprop-2-enoate (**10**) (1.05 g, 2 mmol) in dry toluene (20 ml). The reaction mixture was heated under reflux for 12 h then cooled; the yellow solid which separated from the solution was collected by filtration, dried, and recrystallized from toluene to give (**15**)

(0.54 g, 96%) as yellow crystals, m.p. 248—249 °C (Found: C, 63.0; H, 4.8; N, 9.6. $C_{15}H_{14}N_2O_2S$ requires C, 62.92; H, 4.93; N, 9.78); $\nu_{max.}$(Nujol) 3 299, 1 704, 1 621, 1 600, 1 562, 1 517, 1 401, 1 273, 1 227, 1 194, 1 156, 1 080, 1 007, 918, 857, 842, 767, 752, and 725 cm^{-1}; *m/z* (%) 286 (M^+, 64), 214 (37), 213 (30), 212 (100), 198 (14), 172 (29), 153 (10), 140 (10), 128 (10), and 69 (15).

3-Formyl-1-phenyl-2-triphenylphosphoranylideneaminoindole (**17**).—A solution of triphenylphosphine (2.62 g, 10 mmol) in dry dichloromethane (50 ml) was added dropwise to a stirred solution of 2-azido-3-formyl-1-phenylindole (2.63 g, 10 mmol) in the same solvent (25 ml) at 0 °C under nitrogen and the reaction mixture was stirred at room temperature for 12 h. The solvent was evaporated under reduced pressure and the crude product was recrystallized from benzene–hexane (1:1, v/v) to give (**17**) (4.21 g, 85 %) as yellow prisms, m.p. 182 °C (Found: C, 79.7; H, 5.1; N, 5.4. $C_{33}H_{25}N_2OP$ requires C, 79.82; H, 5.08; N, 5.64); $\nu_{max.}$(Nujol) 1 631, 1 530, 1 516, 1 376, 1 302, 1 204, 1 156, 1 113, 1 027, 1 016, 970, 920, 884, 765, 752, 743, and 720 cm^{-1}; $\delta_H(CDCl_3)$ 9.9 (1 H, s), 8.3 (1 H, m), and 7.9—7.1 (23 H, m); *m/z* (%) 496 (M^+, 10), 371 (12), 295 (10), 262 (40), 234 (16), 205 (24), 201 (23), 184 (22), 183 (100), 152 (16), 108 (66), 107 (16), and 77 (26).

General Procedure for the Preparation of 3-Aryl-2,3-dihydro-2-oxo- 9-phenylpyrimido[4,5-b]*indoles* (**20**)—(**22**).—The appropriate isothiocyanate (1 mmol) was added to a stirred solution of iminophosphorane (**17**) (0.496 g, 1 mmol) in dry dichloromethane (10 ml) at 0 °C under nitrogen. The resulting solution was stirred at room temperature for 5 h. The solution was concentrated to dryness and the residual material was recrystallized from dichloromethane–hexane (1:1, v/v). The following compounds were obtained. *2,3-Dihydro-2-oxo-3,9-diphenylpyrimido*[4,5-b]*indole* (**20**), 76% as red prisms, m.p. 147 °C (Found: C, 78.4; H, 4.3; N, 12.4. $C_{22}H_{15}N_3O$ requires C, 78.32; H, 4.48; N, 12.46); $\nu_{max.}$(Nujol) 1 672, 1 594, 1 501, 1 458, 1 377, 1 261, 769, and 696 cm^{-1}; $\delta_H(CDCl_3)$ 8.25 (1 H, s) and 7.5—6.8 (14 H, m); *m/z* (%) 337 (M^+, 64), 336 (44), 308 (5), 295 (20), 259 (11), 231 (12), 230 (11), 205 (34), 190 (16), 169 (15), 140 (10), 119 (15), and 77 (100). *2,3-Dihydro-3-(p-methoxyphenyl)-2-oxo-9-phenylpyrimido*[4,5-b]*indole* (**21**), (81%) as colourless needles, m.p. 142 °C (Found: C, 75.2; H, 4.7; N, 14.6. $C_{23}H_{17}N_3O_2$ requires C, 75.19; H, 4.66; N, 11.44); $\nu_{max.}$(Nujol) 1 666, 1 651, 1 548, 1 513, 1 461, 1 378, 1 238, 1 036, 781, 749, 729, and 697 cm^{-1}; $\delta_H(CDCl_3)$ 8.6 (1 H, s), 8.0—7.1 (13 H, m), and 4.0 (3 H, s); *m/z* (%) 367 (M^+, 100), 366 (11), 352 (51), 325 (19), 245 (13), 244 (61), 231 (5), 230 (6), 205 (15), 190 (10), 92 (12), and 77 (41). *3-(p-Chlorophenyl)-2,3-dihydro-2-oxo-9-phenylpyrimido*[4,5-b]*indole* (**22**), 82% as red prisms, m.p. 126 °C (Found: C, 71.1; H, 3.9; N, 11.4. $C_{22}H_{14}ClN_3O$ requires C, 71.07; H, 3.79; N, 11.30); $\nu_{max.}$(Nujol) 1 678, 1 657, 1 488, 1 380, 1 237, 780, 749, and 700 cm^{-1}; $\delta_H(CDCl_3)$ 8.6 (1 H, s) and 7.8—7.4 (13 H, m); *m/z* (%) 373 (M + 2, 27), 371 (M^+, 83), 336 (5), 329 (20), 319 (27), 260 (10), 231 (28), 230 (33), 205 (73), 190 (20), 178 (18), 176 (10), 168 (62), 140 (16), 113 (24), 111 (62), 102 (19), and 77 (100).

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