Tetrahedron Vol. 48, No. 36, pp. 7601-7608, 1992
Printed in Great Britain

0040-4020/92 $5.00+.00

Palladium-Catalysed Intramolecular Cyclisation of 7-Halo-N-Allyl-Indoles+

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(*Received in USA* 27 *April* 1992)

Keywords: Indoles, palladium catalysts, pyrroloquinolines

Abstract: The N-allyl substituted-7-bromo-indoles (4-9) and the N-propargyl-7-bromo-indole(10) were prepared from the 7-bromo-indole (3). Compounds (4) and (7) undergo palladium-catalysed cyclisation to the pyrroloquinolines (11) and (13). Similar reactions of compounds (5), (6), (8) and (10) led to unstable cyclisation products, whilst compound (9) did not react. An attempt to prepare the 7-iodo analog of compound (3) resulted in formation of the 7,7'-bi-indolyl (2).

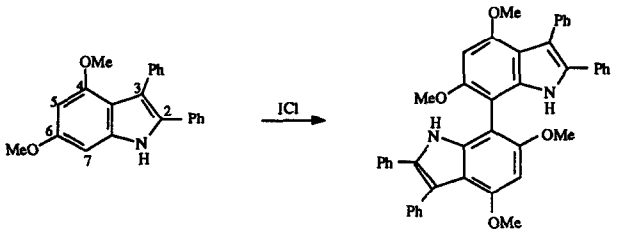
4,6-Dimethoxyindoles show a capacity for electrophilic substitution at C7[1,-3] and consequently provide the possibility of cyclisation between N1 and C7 to afford tricyclic systems of the pyrroloquinoline[4] or pyrrolo-indole type. We have previously reported the synthesis of 4-oxo-4H-pyrrolo[3,2,1-ij]quinolines by the reaction of indole-7-carboxaldehydes with ethyl acetate[5]. Furthermore, related dihydro-pyrroloquinolines can be formed by the intramolecular 1,3-dipolar cycloaddition of a 7-nitrone substituent on to an N-allyl double bond[3,6]. We now report the extension of this synthetic strategy to include a Heck-type cyclisation[7] of an N-allyl-7-bromo-indole. This reaction between an organic halide and an alkene is catalysed by a palladium triarylphosphine complex, often generated *in situ* from palladium acetate and a triarylphosphine.

Hegedus and co-workers have investigated the palladium-catalysed cyclisation of 2-bromo-N-allylaniline to yield 3-methylindole[8]. Preference is observed for the formation of a five-membered ring rather than a six-membered one, possibly because of the development of the aromatic indole system. This cyclisation reaction was extended to include crotyl and dimethylallyl substituents on nitrogen, but β-methallyl and cyclohexenyl groups failed to participate in cyclisation.

The preparation of our desired 7-bromo-N-allylindoles required the allylation of 7-bromo-indoles as the correct sequence of steps. Existing literature examples of 7-bromo-indoles often require the construction of the indole ring with the halogen already present. For example, treatment of 2-bromoaniline with chloracetonitrile followed by cyclisation yields 7-bromo-indole in 32% yield[9]. Another approach involves the addition of ethyl oxalate to 3-bromo-2-nitrotoluene, followed by a reductive cyclisation and decarboxylation to give an overall yield of 19% for the 7-bromo-indole[10]. An alternative more direct approach involves the halogenation of 2,3-dihydro-indole via selective thallation at C7 of the related N-acetyl derivative[11]. After exchange of halogen for thallium, the nitrogen protecting group is removed. The overall yield for 7-bromo-indole is 43% by this route. Direct thallation of N-acetyl indoles did not succeed.

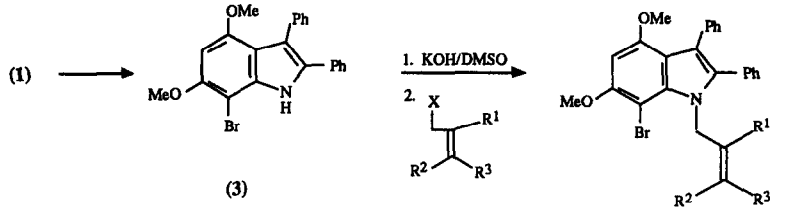
One objective of our work was to utilise the activation at C7 of 4,6-dimethoxyindoles to achieve a direct route from an indole to a 7-halo-indole. Initially, iodination was attempted, so as to produce a more reactive 7-iodo-indole. However, treatment of the indole (1) with iodine monochloride gave numerous products. When repeated in the absence of light, the reaction gave a 65% yield of the 7,7'-bi-indolyl (2), previously prepared by quinone oxidation of the indole (1)[12].

+ Dedicated to Professor Charles Rees on the occasion of his 65th birthday.



(1) (2) 65%

In contrast, bromination of the indole (1) was accomplished in high yield using bromine in dimethylformamide or trimethylammonium bromide in tetrahydrofuran. Some care needs to be taken during isolation of the 7-bromo-indole (3), which is moderately sensitive to heat. This readily-available bromo-indole was converted into a range of N-allyl derivatives (4-9) by alkylation in basic conditions.



(3) 92%

	R^1	R^2	R^3	Yield %
(4)	H	H	H	98
(5)	Me	H	H	61
(6)	H	H	Me	64
(7)	H	Me	Me	86
(8)	H	H	Ph	75

(9) 86% (10) 78%

The related N-propargyl derivative (10) was also prepared. These compounds thus provide the precursors for a variety of substituted cyclic products.

The allyl derivative (4), when heated with palladium (II) acetate in the presence of tri-*o*-tolylphosphine and triethylamine in acetonitrile, gave the pyrroloquinoline derivative (11) in 96% yield. This product undergoes oxidative decomposition on standing and consequently its elemental composition was verified by exact mass measurement. The precise structure was confirmed by ^{1}H n.m.r. spectroscopy. In particular, a triplet resonance corresponding to two protons appears at 4.84 ppm and is indicative of a methylene group adjacent to nitrogen.

The formation of a six-membered ring in preference to a five-membered one, as in the case of 2-bromo-N-allylaniline is not surprising. However, the complete specificity of six-membered ring formation is noteworthy. Replacement of the aniline with an indole results in the bromo and allyl substituents being peri

rather than *ortho* to each other. Consequently, the reactive allylic carbon atoms are further away from the organopalladium halide site, and this results in bond formation involving the terminal allyl carbon atom. Since this work was completed, Hegedus and his co-workers have published a similar cyclisation of a 3-allyl-4-bromo-indole to form a new six-membered ring as part of a naphthalene compound[13].

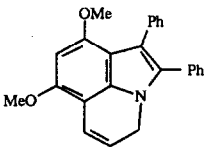
Palladium-catalysed cyclisation of the N-crotyl derivative (6) gave the pyrroloquinoline (12), in which the double bond is adjacent to the nitrogen atom. This was confirmed by the presence of a doublet at 1.46 ppm in the ^{1}H n.m.r. spectrum, indicating the environment of the methyl group. This product also underwent oxidation on standing. The position of the double bond probably minimises the steric interaction between the methyl and methoxy groups, in comparison with the isomeric structure in which the double bond is in conjugation with the benzene ring. The dimethylallyl derivative (7) underwent cyclisation to the expected *gem*- dimethyl product (13), which was stable to further oxidative decomposition, presumably because of a lack of allylic protons.

The β-methallyl derivative (5) and the cinnamyl derivative (8) both reacted under the palladium catalysis conditions to give mixtures of products. In each case, there was a spectroscopic indication of the expected cyclisation products (14) and (15) respectively, but these contain acidic allylic and/or benzylic protons, which could provide sites for decomposition.

Reaction of the cyclohexenyl compound (9) did not proceed at all. This is not surprising, as the only possible bond formation leading to cyclisation would give a relatively-strained five-membered ring.

The N-propargyl indole (10) requires a slightly different approach. The expected intermediate hydridopalladium complex would contain no β-hydrogen atom for elimination because of the degree of unsaturation. This would prevent elimination of the palladium catalyst from the complex and thus the reaction would stop. It has been reported recently[14] that a modified Heck reaction involving an exchange would overcome such a problem. The modification involves an exchange of the halide in the intermediate complex, and this would then allow for the reductive elimination of Pd(O). However, reaction of the N-propargyl indole (10) with palladium acetate and tri-*o*-tolylphosphine in acetonitrile, together with piperidine as a base and formic acid as a hydride source, resulted in a complex mixture of products.

In summary, the palladium-catalysed cyclisation of an N-allyl-7-bromo-indole can provide a useful route to pyrroloquinoline derivatives, provided care is taken in the selection of examples. The reaction is not general, owing to the instability of at least some of the products. It is significant that the related 4-oxo-pyrroloquinolines[5] are very stable and present no problem in isolation or purification. These compounds lack the allylic protons which appear to be the source of instability in the products of palladium-catalysed cyclisation.



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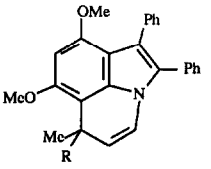
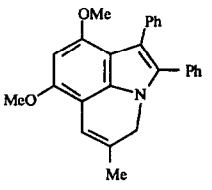


	R
(12)	H
(13)	Me



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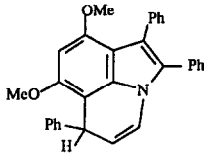

(15)

Experimental

General information Kieselgel 60H (Merck, Art 7736) was used for flash chromatography and thin layer chromatography (t.l.c.) was performed on DC Aluminium Foil Kieselgel F254 (Merck, Art 5554). Radical chromatography was carried out under nitrogen on a chromatotron model 7924T using Kieselgel $60PF_{254}$ (Merck, Art 7749). ^1H n.m.r. spectra were recorded at 300 MHz with a Bruker CXP-300 or at 500 MHz with a Bruker AM-500 spectrometer, and refer to deuterochloroform solutions with chloroform as internal standard (7.26 ppm) or to d^6-dimethylsulfoxide solutions with dimethylsulfoxide (2.50 ppm) or benzene (7.16 ppm) as internal standard. Signals refer to deuterochloroform unless otherwise stated. Signals due to exchangeable protons (OH and NH) were identified by exchange with deuterium oxide. The usual notational conventions are used. ^{13}C n.m.r. spectra were recorded at 125.77 MHz with a Bruker AM-500 spectrometer. They refer to deuterochloroform solutions with chloroform as internal standard (77.0 ppm). Low resolution mass spectra were obtained on an A.E.I. MS12 spectrometer at 70eV and 8000V accelerating potential at 210° ion source temperature. High resolution exact mass spectra were recorded on a V.G. Autospec spectrometer with an accelerating potential of 8000V at 70eV. Infrared spectra were recorded with a Perkin Elmer 580B and refer to thin films of liquids or paraffin mulls of solids unless otherwise stated. Ultraviolet spectra refer to solutions in spectroscopic methanol. Microanalyses were performed by Dr. H.P. Pham of the UNSW Microanalytical Unit.

7,7'-Bi(4,6-dimethoxy-2,3-diphenyl)indolyl (2)

To a solution of 4,6-dimethoxy-2,3-diphenylindole (1) (0.504g, 1.53 mmol) in dry DMF (30 mL) and glacial acetic acid (30 mL) was added iodine monochloride (0.08 mL, 1.57 mmol) and the reaction was stirred in the absence of light for 24 h. Water (100 mL) was added and the resulting precipitate filtered and washed with 5% sodium thiosulphate solution. The residue was flash chromatographed and the fraction eluted with dichloromethane/light petroleum (1:1) was concentrated and was radially chromatographed. The fraction eluted with dichloromethane/light petroleum (1:1) was concentrated and recrystallized from dichloromethane/light petroleum to yield the bi-indolyl (2) (0.325g, 65%) as a white solid, m.p. 287-288° (lit.[12]m.p. 290°).

7-Bromo-4,6-dimethoxy-2,3-diphenylindole (3)

Method A. To a solution of 4,6-dimethoxy-2,3-diphenylindole (1) (0.993g, 3.01 mmol) in dimethylformamide (1mL) was added bromine (0.249g, 3.11mmol) and the reaction mixture was stirred at room temperature for 0.5 h. Water (50mL) was added followed by 10% sodium metabisulphite solution (50mL) and the resulting precipitate was filtered, washed with water and dried to yield the 7-bromoindole (3)(1.13g, 92%) as a white *solid*, m.p. 155-156°. υ_{max} 1627, 1604, 1341, 1289, 1222, 1205, 1150, 1142, 779, 698 cm^{-1}. ^1H n.m.r. δ 3.71, 3.97, 2s, OMe; 6.34, s, H5; 7.32, m, aryl; 8.42, s, NH. ^{13}C n.m.r. δ 55.6, 57.5, OMe; 84.6, C7; 90.6, C5; 113.9, 115.7, 132.3, 133.0, 135.4, 136.2, 152.7, 154.3, aryl; 126.1,127.3, 127.4, 128.0, 128.4, 131.3, aryl CH. *m/z* 409 (M ^{81}Br 100%), 407 (M ^{79}Br 99), 394 (50), 393 (49), 313 (24).

Method B. To a solution of 4,6-dimethoxy-2,3-diphenylindole (1)(0.489g, 1.48 mmol) in dry THF (100mL) was added phenyltrimethylammonium tribromide (0.560g, 1.49mmol). After stirring for 5 min., the solution was filtered and the solvent carefully removed to leave the 7-bromoindole (3) (0.533g, 88%) as a white solid, which was spectroscopically identical to that produced by method A.

7-Bromo-4,6-dimethoxy-2,3-diphenyl-1-(prop-2'-en-1'-yl)indole (4).

To a solution of the bromo indole (3) (0.37g, 0.91 mmol) in DMSO (1 mL) was added crushed potassium hydroxide (0.2g, 3.57 mmol) and the mixture stirred at room temperature for 15 min. Allyl bromide (0.17 mL, 1.96 mmol) was added dropwise and stirring continued for a further 0.5 h. Water (100mL) was added and the resulting precipitate collected and dried to yield the bromo indole (4) (0.40g, 98%) as a white solid. Recrystallization from ethanol resulted in white *crystals*, m.p. 143-144° (Found: C, 67.0; H, 5.3; N, 3.1. $C_{25}H_{22}BrNO_2$ requires C, 67.0; H, 5.0; N, 3.1%). υ_{max} 1606, 1558, 1345, 1329s, 1263, 1212, 1169, 1134, 733cm^{-1}. λ_{max} 222 (ε8,600), 234nm (8,200). ^1H n.m.r. δ 3.66, 3.90, 2s, OMe; 4.40, bd, *J* 16.1 Hz, H3'; 4.97, m, H1' and H3'; 5.82, m, H2'; 6.57, s, H5; 7.21, m, aryl. ^{13}C n.m.r. δ 47.3, C1'; 55.5, 57.9, OMe; 86.0, C5; 91.1, C7; 114.9, 116.1, 131.8, 134.7, 135.5, 138.9, 153.1, 154.0, aryl C; 115.5, C3'; 125.4, 126.7, 127.9, 128.0, 131.4, 131.5, 135.5, aryl CH and C2'. *m/z* 449, (M ^{81}Br, 8%),447 (M ^{79}Br, 8%), 370 (32), 369 (100), 308 (48).

7-Bromo-1-(2'-methyl-prop-2'-en-1'-yl)-4,6-dimethoxy-2,3-diphenylindole (5).

This was prepared as described for the bromoallyl indole (4) from the bromoindole (3) (0.75g, 1.84 mmol) in DMSO (1 ml), crushed potassium hydroxide (0.02g, 3.6 mmol) and 3-chloro-2-methyl propene (0.30 mL, 3.0 mmol). The resulting precipitate was collected and dried to yield the crude bromo allyl indole (5) (0.80g, 93%). Recrystallization from ethanol yielded (5) (0.52g, 61%) as white *crystals*, m.p. 145-146° (Found: C, 67.6; H, 5.5, N, 3.2. $C_{26}H_{24}BrNO_2$ requires C, 67.5; H, 5.2; N, 3.0%). υ_{max} 1608, 1572, 1561, 1354, 1349, 1217, 1170, 1134, 1059 cm^{-1}. λ_{max} 222 (ε19,900), 236 (19,500), 300nm (7,700). ^1H n.m.r. δ 1.64, s, 2'-Me; 3.70, 3.96, 2s, OMe, 4.17, bs, H3'; 4.80, t, *J* 1.5 Hz, H3'; 4.90, bs, H1', 6.39, s, H5; 7.19, m, aryl. ^{13}C n.m.r. δ 20.0, 2'-Me; 50.5, C1'; 55.5, 57.9, OMe; 86.3, C5; 91.0, C7; 110.2, C3'; 114.8, 115.7, 131.6, 134.6, 135.6, 138.9, 143.5, 153.1, 154.0, aryl C and C2'; 125.4, 126.7, 127.9, 131.3, 131.5, aryl CH. *m/z* 463 (M ^{81}Br, 100%), 461 (M ^{79}Br, 100%), 408 (47), 406 (47), 383 (36), 382 (40), 381 (53), 380 (40), 367 (28), 366 (55).

7-Bromo-1-(but-2'-en-1'-yl)-4,6-dimethoxy-2,3-diphenylindole (6).

This was prepared as described for the bromo allyl indole (4) from the bromo indole (3) (0.70g, 1.72 mmol) in DMSO (1 mL), crushed potassium hydroxide (0.20g, 3.57 mmol) and 1-bromo-2-butene (85%, 0.42 mL, 3.47 mmol). The resulting precipitate was collected and dried to give a crude product (0.64g, 81%).

Recrystallization from ethanol gave the bromo crotyl indole (6) (0.51g, 64%) as white *crystals*, m.p. 125-126° (Found: C, 67.8; H, 5.2; N, 3.1. $C_{26}H_{24}BrNO_2$ requires C, 67.5; H, 5.2; N, 3.0%). υ_{max} 1604, 1573, 1560, 1354, 1329, 1216, 1167, 1058 cm^{-1}. λ_{max} 222 (ε21,600), 239 (21,700), 300nm (8,100). ^1H n.m.r. δ 1.68, d, *J* 5.2, H4'; 3.21, 3.97, 2s, OMe; 4.54, m, H1'; 5.53, m, H2' and H3'; 6.71, s, H5; 7.23, m, aryl. *m/z* 463 (M.^{81}Br, 96%), 461 (M ^{79}Br, 96%), 408 (98), 406 (100), 383 (65), 328 (68), 312 (25), 241 (26).

7-Bromo-1-(3'-methylbut-2'-en-1'-yl)-4,6-dimethoxy-2,3-diphenylindole (7).

To a solution of bromo indole (3) (0.50g, 1.23 mmol) in dry THF (50 mL) was added sodium hydride (50%, 0.1g, 2.08 mmol) and the mixture stirred for 15 min. After the dropwise addition of 4-bromo-2-methyl-2-butene (0.20g, 1.34 mmol), stirring was continued for a further 1 h before excess hydride was destroyed with water and the solvent then removed. The residue was extracted with water (50 mL) and dichloromethane (3 x 50 mL), the combined organic layers dried ($MgSO_4$), concentrated and recrystallized from ethanol to yield the bromo prenyl indole (7) (0.50g, 86%) as white *crystals*, m.p. 123-124° (Found: C, 68.1; H, 5.8; N, 3.0. $C_{27}H_{26}BrNO_2$ requires C, 68.1; H, 5.5; N, 2.9%). υ_{max} 1607, 1569, 1356, 1328, 1267, 1216, 1167, 1127, 1056,cm^{-1}. λ_{max} 224 (ε7,400), 240nm (7,000). ^1H n.m.r. δ 1.60, 1.72, 2s, 3'-Me and H4; 3.20, 3.97, 2s, OMe; 4.40, d, *J* 6.5 Hz, H1'; 5.28, m, H2'; 6.70, s, H5; 7.23, m, aryl. ^{13}C n.m.r. δ 17.7, 25.5, C4' and 3'-Me; 43.7, C1'; 55.5, 58.0, OMe; 86.2, C5; 91.1, C7; 115.2, 116.0, 132.0, 132.7, 134.8, 135.6, 139.0, 153.0, 154.0, aryl C and C3'; 122.4, 125.4, 126.6, 127.7, 127.9, 131.5, 131.7, aryl CH and C2'. *m/z* 477 (M ^{81}Br, 2%), 475 (M ^{79}Br, 2%), 397 (100) 342, (18), 329 (63), 328 (75), 314 (22), 301 (21).

7-Bromo-1-(3'-phenylprop-2'-en-1'-yl)-4,6-dimethoxy-2,3-diphenylindole (8).

This was prepared as described for the bromo allyl indole (4) from the bromo indole (3) (0.82g, 2.01 mmol) in DMSO (2 mL), crushed potassium hydroxide (0.20g, 3.57 mmol) and 3-bromo-1-phenyl-1-propene (0.40g, 2.03 mmol). The resulting precipitate was extracted with water (50 mL) and dichloromethane (3 x 50 mL), the combined organic layers dried ($MgSO_4$) and concentrated. Recrystallization from ethanol yielded the N-cinnamyl indole (8) (0.79g, 75%) as white *crystals*, m.p. 124-125°, (Found: C, 71.3; H, 5.0; N, 2.6. $C_{31}H_{26}BrNO_2$ requires C, 71.0; H, 5.0; N, 2.7%). υ_{max} 1605, 1570, 1559, 1357, 1347, 1323, 1252, 1217, 1164, 1137, 1051, 973 cm^{-1}. λ_{max} 244 (ε27,800), 293nm (8,800). ^1H n.m.r. δ 3.71, 3.98, 2s, OMe; 5.25, dd, *J* 1.6, 5.1 Hz, H1'; 5.97, dt, *J* 1.7, 15.9 Hz, H3'; 6.26, dt, *J* 5.1,15.9 Hz, H2'; 6.41, s, H5; 7.21, m, aryl. ^{13}C n.m.r. δ 47.0, C1'; 55.5, 57.9, OMe; 86.0, C5; 91.1, C7; 115.0, 116.3, 131.6, 134.7, 135.4, 136.7, 138.9, 153.2, 154.0, aryl C; 125.5, 126.4, 126.7, 127.2, 127.4, 128.0, 128.4, 130.7, 131.4, 131.7, aryl CH, C2' and C3'. *m/z* 526 (M+1 ^{81}Br, 8%), 524 (M+1 ^{79}Br, 8%), 446 (60), 409 (13), 407 (13), 329 (100).

7-Bromo-1-(cyclohex-2-en-1-yl)-4,6-dimethoxy-2,3-diphenylindole (9)

This was prepared as described for the N-allylindole (4) from the bromo indole (3) (0.994g, 2.43 mmol) with crushed potassium hydroxide (0.146g, 2.60 mmol) and 3-bromocyclohexene (0.503g, 3.31 mmol). The mixture solidified after 5 min and water (100 ml) was added followed by extraction with dichloromethane (4 x 50 ml). The combined organic layers were dried ($MgSO_4$), concentrated and recrystallized from ethanol to yield the N-cyclohexylindole (9) (1.026g, 86%) as white *crystals*, m.p. 124-125° (Found: C, 68.8; H, 5.6; N, 2.9.$C_{28}H_{26}BrNO_2$ requires C, 68.9; H, 5.4; N, 2.9%). υ_{max} 1606, 1556, 1344, 1291, 1213, 1169 cm^{-1}. λ_{max} 226nm (ε 19,400). ^1H n.m.r. δ 1.93, m, H4', H5' and H6'; 3.66, 3.96, 2s, OMe; 5.26, m, H1'; 5.57, bd, *J* 10.3 Hz, H2'; 6.40, m, H5 and H3'; 7.16, m, aryl. ^{13}C n.m.r. δ 22.4, 24.2, 31.5, C4', C5' and C6'; 54.4, C1'; 55.6, 58.2,

OMe; 86.4, C7; 91.4, C5; 115.2, 117.4, 126.6, 133.5, 135.6, 135.8, 153.3, 153.9, aryl C; 125.3, 126.5, 127.0, 127.7, 130.1, 131.4, 132.7, aryl CH, C2' and C3'. *m/z* 489 (^{81}Br, M+1, 8%), 487 (^{79}Br, M+1, 8), 409(100), 405(58), 329(95), 328(61).

7-Bromo-4,6-dimethoxy-2,3-diphenyl-1-(prop-2'-yn-1-yl) indole (10).

This was prepared as described for the bromo allyl indole (4) from the 7-bromo indole (3) (0.703g, 1.72 mmol) in DMSO (0.5 mL), potassium hydroxide (0.103g, 1.84 mmol) and propargyl bromide (0.406g, 3.41 mmol). Recrystallization from ethanol resulted in the N-propargyl indole (10) (0.603, 78%) as white *crystals* m.p. 165-166° (Found: C, 66.9; H, 4.6; N, 2.9. $C_{29}H_{20}BrNO_2$ requires C, 67.3; H, 4.5; N, 3.1%). υ_{max} (KBr disk) 1608, 1571, 1467, 1352, 1327, 1264, 1216, 1168, 1133, 1054 cm^{-1}. λ_{max} 239 (ε23,400), 299nm (9,400). ^{1}H n.m.r. δ 2.33, bt, *J* 2.5 Hz; H3'; 3.68, 3.97, 2s, OMe; 5.17, d, *J* 2.4 Hz, H1'; 6.41, s, H5; 7.22, m, aryl. ^{13}C n.m.r. δ 36.1, C1'; 55.5, 57.9, OMe; 73.1, C3'; 80.6, C2'; 86.0, 115.3, 116.8, 131.2, 135.0, 135.2, 138.5, 153.4, 154.1, aryl C; 91.5, C5; 125.7, 126.8, 128.1, 128.2. 131.4, 131.6, aryl CH. *m/z* 447 (100), 455 (98), 408 (48), 406 (48), 367 (20), 366 (63), 351 (33).

7,9-Dimethoxy-1,2-diphenyl-4H-pyrrolo[3,2,1-ij]quinoline (11)

A mixture of the bromoallylindole (4) (0.230g, 0.51 mmol), palladium acetate (0.030g, 0.13 mmol) and tri-*o*-tolylphosphine (0.068g, 0.22 mmol) in acetonitrile (10mL) with triethylamine (0.8 mL) was sealed in a thick walled reaction tube after flushing with nitrogen. The reaction was heated at 100° for 15 h, cooled and then filtered. The solvent was removed, the residue flash chromatographed and the fraction eluted with dichloromethane/light petroleum recrystallized from dichloromethane/light petroleum to yield the quinoline (11) (0.181g, 96%) as a white *solid*, m.p. 156-157°C. Exact Mass 367.1562. $C_{25}H_{21}NO_2$ requires 367.1572. υ_{max} 1604, 1520, 1406, 1360, 1306, 1269, 1224, 1208, 1192, 1132, 1064 cm^{-1}. λ_{max} 221 (ε30,100), 246 (22,900), 340 (12,200), 355nm (9,800). ^{1}H n.m.r. δ 3.70, 3.84, 2s, OMe; 4.84, m, H4; 5.61, m, H5; 6.24, s, H8; 6.65, m, H6; 7.21, m, aryl. ^{13}C n.m.r. δ 45.8, C4; 55.5, 57.5, OMe; 89.8, C8; 109.6, 115.7, 126.7, 128.0, 131.6, 131.9, 135.3, 151.0, 155.2, aryl, 117.5, 118.9, 125.3, 127.0, 127.6, 128.3, 130.6, 131.3, aryl CH, C5 and C6. *m/z* 367 (M, 39%), 366 (33) 304 (48), 289 (85), 101 (100).

7,9-Dimethoxy-6-methyl-1,2-diphenyl-6H-pyrrolo[3,2,1-ij]quinoline (12)

This was prepared as described for the quinoline (11) from the bromocrotylindole (6) (0.142g, 0.31 mmol), palladium acetate (0.031g, 0.14 mmol) in acetonitrile (10mL). Recrystallization from dichloromethane/light petroleum gave the quinoline (12) (0.11g, 94%) as a white *solid,* m.p. 178-179°. Exact Mass 381.1641. $C_{26}H_{23}NO_2$ requires 381.1729. υ_{max} 1605, 1517, 1400, 1349, 1319, 1278, 1222, 1207, 1180, 1124, 1064 cm^{-1}. λ_{max}265nm (ε8,200). ^{1}H n.m.r. δ 1.46, d,*J* 6.8 Hz, 6-Me; 3.75, 3.93, 2s, OMe; 4.00, m,H6; 5.14, dd, *J* 4.4, 8.1 Hz, H5; 6.39, s, H8, 6.68, dd, *J* 1.3, 8.1 Hz, H4; 7.25,m, aryl. ^{13}C n.m.r. δ 23.7, 6-Me; 28.1, C6; 55.8, 56.5, OMe; 92.2, C8; 110.4, 115.8, 127.0, 128.4, 130.7, 131.4, 132.6, 152.9, 153.7, aryl C; 113.6, 120.9, 125.6, 127.1, 127.6, 128.2, 131.0, 131.3, aryl CH, C5 and C6. *m/z* 381 (M, 23%), 366 (100).

7,9-Dimethoxy-6,6-dimethyl-1,2-diphenyl-6H-pyrrolo[3,2,1-ij]quinoline (13).

This was prepared as described for the quinoline (11) from the N-allyl indole (7) (0.276g, 0.58 mmol), palladium acetate (0.035g, 0.16 mmol), tri-*o*-tolylphosphine (0.089g, 0.29 mmol) and triethylamine (0.8 mL) in acetonitrile (10 mL). Recrystallization from dichloromethane/light petroleum gave the quinoline (13) (0.178g, 78%) as a white *solid*, m.p. 194-195° (Found: C, 81.9; H, 6.7; N, 3.7. $C_{29}H_{25}NO_2$ requires C, 82.0; H, 6.4; N,

3.5%). υ_{max} (KBr disk) 1665, 1604, 1518, 1465, 1451, 1438, 1407, 1351, 1322, 1311, 1283, 1224, 1208, 1141, 1066 cm^{-1}. λ_{max} 266 (ε84,900), 337nm (38,400). ^1H n.m.r. δ 1.58, s, CH_3; 3.73, 3.92, OMe; 4.86, d, *J* 8.1 Hz, H5; 6.38, s, H8; 6.58, d, *J* 8.1 Hz, H5; 7.24, m, aryl. ^{13}C n.m.r. δ 30.7, 34.5, CH_3; 55.7, 56.8, OMe; 93.1, C6; 109.1, 110.4, 115.7, 130.7, 132.5, 133.6, 135.1, 152,.7, 154.8, aryl C; 118.3, 120.1, 125.1, 127.0, 127.6, 128.2, 131.1, 131.3, aryl CH, C4 and C5. *m/z* 396 (M+1, 8%), 394 (16), 379 (100).

Acknowledgements

We thank the Australian Research Council for support and acknowledge the award of a Commonwealth Postgraduate Studentship (to P.A.K.)

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