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SYNTHESIS OF CARBAZOLES RELATED TO CARBAZOMYCIN, HYELLAZOLE AND ELLIPTICINE.

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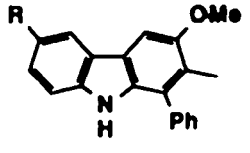
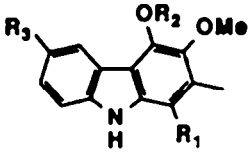
ABSTRACT: Two synthetic routes to 1,2-disubstituted carbazoles are described. The first involves condensation of 2-alkyl-substituted indoles with 2,3-unsaturated ketones in the presence of Pd/C and molecular sieves, the second is based on the reaction of a 2-vinylic indole with the Vilsmeier reagent. The vinylic indoles were prepared by a Fischer indole synthesis, or *via* 1-benzenesulphonyl-2-lithioindole.

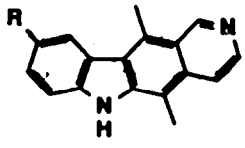
Carbazoles with carbon substituents in the 1- and 2-positions constitute the framework of the hyellazoles (1), isolated from the blue-green alga *Hyella caespitosa*,[1] and of the carbazomycins (2), produced by the actinomycete *Streptoverticillium ehimence*.[2] These structural features are also included in the pyrido[4,3-*b*]carbazole alkaloids ellipticine (3a), 9-methoxyellipticine (3b) and olivacine (4). The antibiotic activity of carbazomycin B (2b)[2] and the antitumoral action of (3)[3,4], have made this class of compounds interesting synthetic targets for several research groups.[5-16] We here present the full details[17,18] of our work in this area.



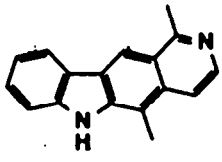
1a R=H hyellazole
b R=Cl chlorohyellazole



	R_1	R_2	R_3		
2a	Me	H	H	carbazomycin	A
b	Me	Me	H		B
c	Me	H	OMe		C
d	Me	Me	OMe		D
e	CHO	H	H		E (=carbazomycinal)
f	CHO	H	OMe		F (=6-methoxycarbazomycinal)



3a R = H ellipticine
b R = OMe 9-methoxyellipticine

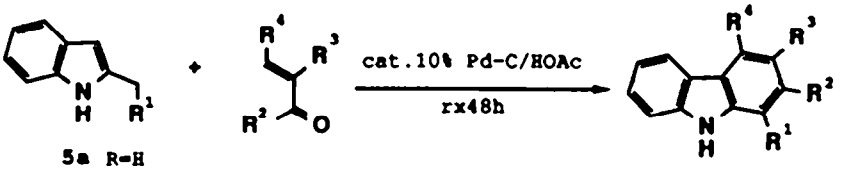


4 olivacine

2,3-Unsaturated carbonyl compounds[19-27,30] are known to alkylate indoles in the 3-position by an 1,4-addition process. The products formed have successfully been employed as intermediates in the synthesis of carbazoles.[28,29] Under suitable conditions (*e.g.* neat heating in the presence of hydroquinone[25] or reflux in acetic acid[24,30]) 2-methylindole (**5a**) undergoes condensation with 2,3-unsaturated ketones to produce carbazoles directly. However, with the exception of some 2-hydroxymethylene-ketones (= 2-formylketones)[24,30] the yields are low.

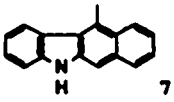
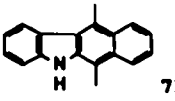
Considerable improvements of the yields were obtained if the 2,3-unsaturated ketones and the 2-alkylsubstituted indoles were refluxed in acetic acid for an extended time in the presence of Pd-C (Table 1).[17] In contrast with the reported[24] failure of 2-ethylindole (**5b**) to give any crystalline products with 2-hydroxymethyl-eneketones, it was found that (**6b**) was formed in the reaction of (**5b**) and 2-ethyli-denecyclohexanone[31] (Entry 10; Table 1). In the reactions with 2-ethylidenecyclo-hexanone the yields were further improved upon by addition of 3Å molecular sieves to the reaction mixture (Entries 9 and 10; Table 1). Substantial amounts of 5H-benz[*b*]-carbazoles **7a** and **7b**, probably formed by Pd-C catalyzed dehydrogenation of the

Table 1.



5a R=H
b Me
c Ph

6

Entry	R^1	R^2	R^3	R^4	Product	Yield (%)
1	H	Me	H	H	**6a**	28 (30*)
2	Me	Me	H	H	**6b**	81
3	Ph	Me	H	H	**6c**	80
4	Me	Et	H	H	**6d**	63
5	H	Me	H	Me	**6e**	35
6	Me	Me	H	Me	**6f**	36
7	H	Me	H	Ph	**6g**	23 (26*)
8	Me	Me	H	Ph	**6h**	32*
9	H	$-(CH_2)_4-$		Me	**6i**	38 (44*)
					 **7a**	0 (34*)
10	Me	$-(CH_2)_4-$		Me	**6j**	29 (38*)
					 **7b**	0 (22*)
11	Ph	$-(CH_2)_4-$		Me	**6k**	64 (76**)
12	H	Me	H	OMe	2-methylcarbazole (**6a**)	24
13	Me	Me	H	OMe	1,2-dimethylcarbazole (**6b**)	28 (31*)

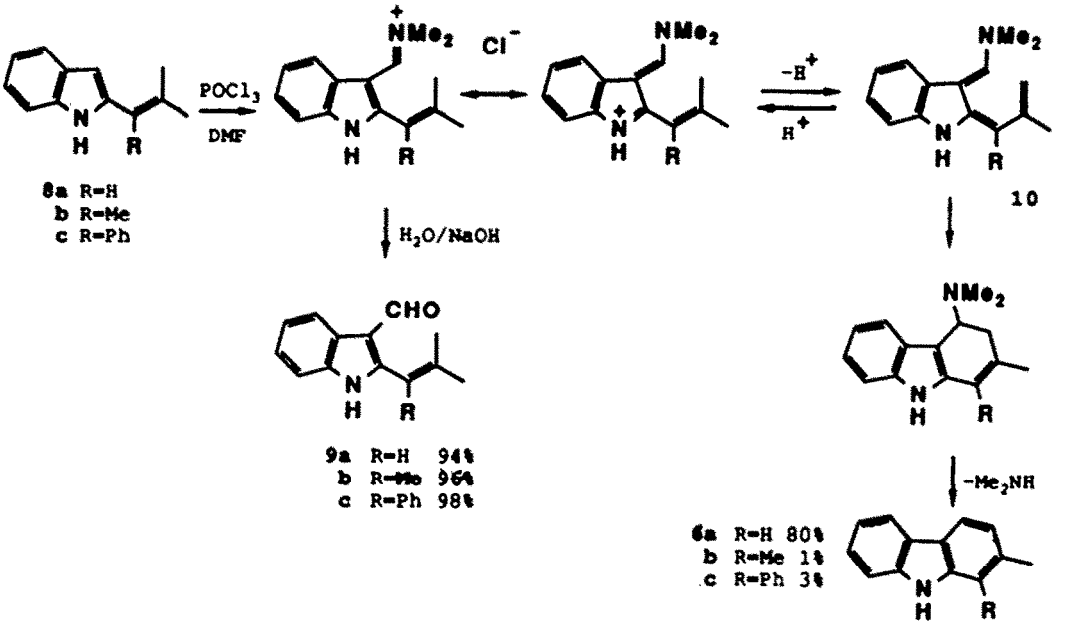
* The reaction performed in the presence of 3Å molecular sieves.
** Based on recovered 2-benzylindole.

tetrahydro compounds **6i** and **6j**, were also formed in these two cases. In the reaction with **5c** (Entry 11; Table 1) only the tetrahydro compound **6k** was formed, which however was readily dehydrogenated with Pd-C in refluxing diglyme to yield the fully aromatic 11-methyl-6-phenyl-5H-benz[*b*]carbazole (**7c**). 5H-Benz[*b*]carbazoles are of interest as being desaza analogues of ellipticine (**3**).

In an attempt to synthesize 4-methoxy substituted carbazoles using the same protocol, 4-methoxy-3-buten-2-one was condensed with 2-alkylindoles (Entries 12 and 13; Table 1). Unfortunately, the methoxy group was lost during the reaction. This result is however not very surprising as 4-methoxy-3-buten-2-one is reported to give 2-methyl-3(2-oxo-3-buten-4-oyl)indole on reaction with 2-methylindole (**5a**).[21]

A different approach in the synthesis of carbazoles[6,7,32-43] is the inter- or intramolecular cycloaddition of a dienophile to a 2-vinylindole[44]. We have however also found[17] that the carbazoles **6a-c** are formed in the reaction of an appropriate 2-vinylic indole (**8**) and an electrophilic C_1-unit such as the Vilsmeier reagent (Scheme 1).

Scheme 1.

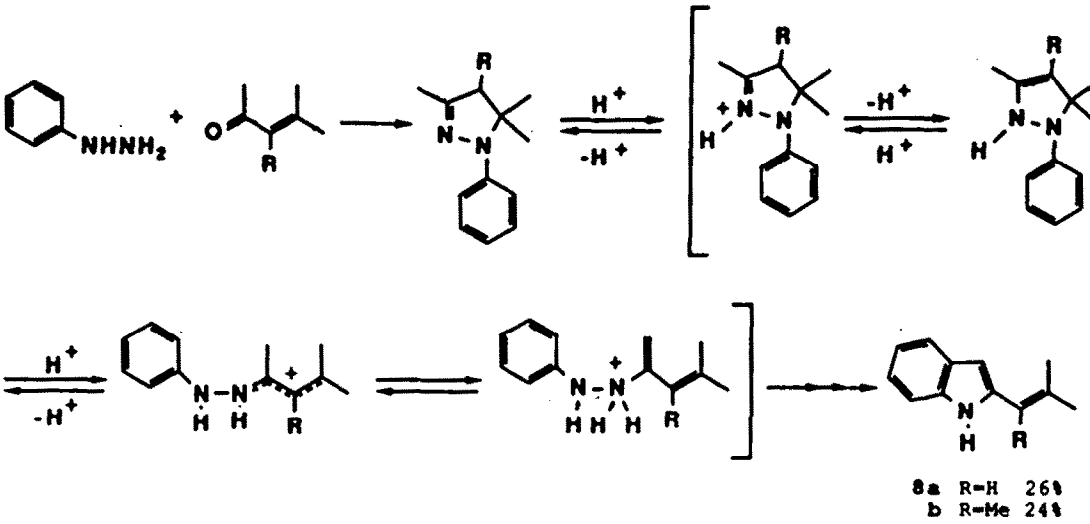


Although **8a-c** gave good yields of the corresponding 3-carboxaldehydes (**9**), only **8a** could be converted to a carbazole (**6a**) in an acceptable yield. An explanation of this result is suggested by inspection of the postulated intermediates (Scheme 1); steric congestion making it more difficult for **10** (R ≠ H) to form or to attain the proper conformation required for ring closure. Compound **6a** was also formed, albeit in a much lower yield (<20%) when $HC(OEt)_3/TsOH$[45] or $HC(OEt)_3/BF_3{\cdot}OEt_2$[46] were employed as the C_1-unit.

The 2-vinylic indoles **8a** and **8b** were synthesized by Fischer indolization[47] using polyphosphoric acid (PPA).[17] This is of interest as several unsuccessful attempts to synthesize 2-vinylindoles *via* the Fischer indole synthesis have been reported.[48] We believe that the indoles are formed *via* the pyrazolines as depicted in Scheme 2. The

reported[49] conversion of 1,5-diphenyl-3-methylpyrazoline to 2-styrylindole strengthens this hypothesis. In the syntheses of **8a** and **8b** it was however not necessary, nor of any advantage, to isolate or purify the pyrazolines. Although the yields of **8a** and **8b** are modest they are well compensated for by the expeditious synthetic procedure.

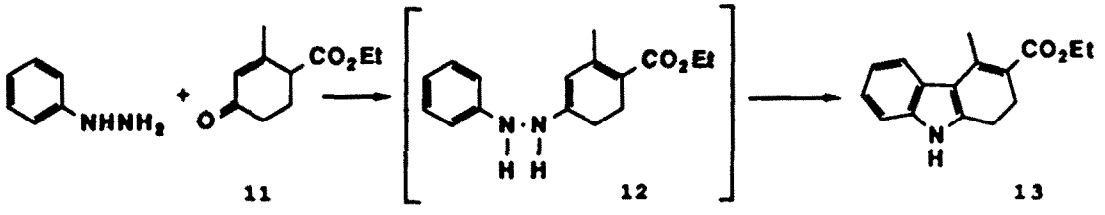
Scheme 2.



8a R=H 26%
b R=Me 24%

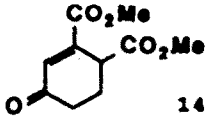
In this context the synthesis of **13** from 2-methyl-4-oxo-2-cyclohexene-1-carboxylate (**11**, Hagemann's ester)[50] is of interest (Scheme 3)[17]. Compound **13** has previously been prepared[51] by a multistep sequence involving alkylation of ethyl acetoacetate with 2-(2-tosyloxyethyl)indole **17**. A few unsuccessful attempts were also made to reproduce this synthesis. In this connection a new synthesis of **16**, based on alkylation of 1-benzenesulphonyl-2-lithioindole with ethylene oxide was developed (Scheme 4).

Scheme 3.



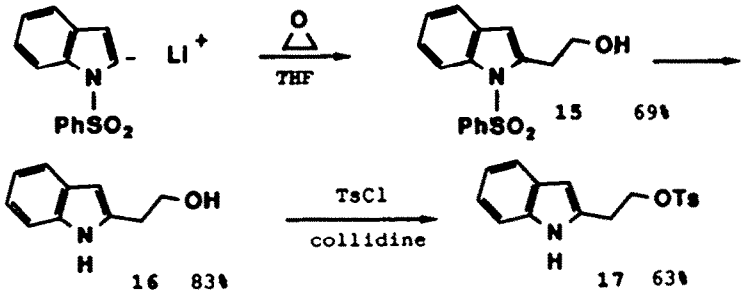
11 **12** **13**

The regioselectivity observed in the synthesis of **13** (Scheme 3) is a consequence of conjugation with the ester groups in the crucial intermediate **12**. In the indolization of the phenylhydrazone of **14**, which gives a 1:1 mixture of 2,3-dicarbomethoxy-3,4-dihydrocarbazole and 3,4-dicarbomethoxy-1,2-dihydrocarbazole the lack of regioselectivity[33] is similarly explained by conjugation in the intermediates on both reaction pathways.



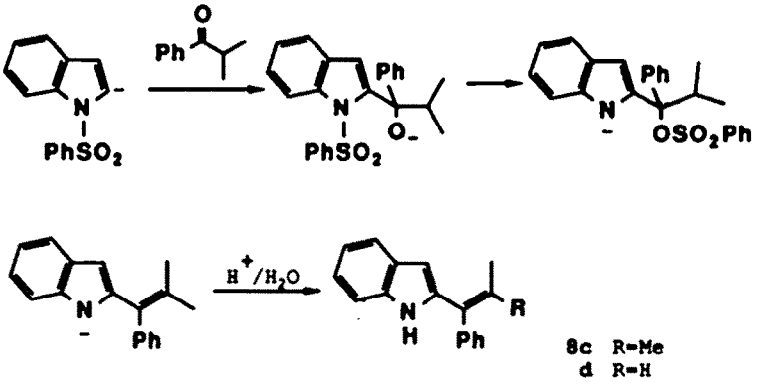
14

Scheme 4.



The vinylindole **8c** was obtained directly when isobutyrophenone was allowed to react with 1-benzenesulphonyl-2-lithioindole. An explanation of this *in situ* deprotection[52]/dehydration is given in Scheme 5. This behavior is in contrast to the analogous reaction of propiophenone with 1-benzenesulphonyl-2-lithioindole which required a separate deprotection/dehydration step[7,8].

Scheme 5.



We were intrigued by the possibility of obtaining 4-heterosubstituted carbazoles by using an electrophilic C_1-unit with a higher oxidation state than the Vilsmeier reagent in the reaction with the 2-vinylic indoles. However, when Viehe's reagent (dichloromethylene dimethylimmonium chloride, phosgene immonium chloride, **18**)[61-63], was allowed to react with **8a** followed by thermolysis of the immonium salt **19** (Scheme 6), the only isolated product was the nitrile **20**. Despite numerous changes in the reaction conditions we were unable to isolate any carbazolic products.

The inability of **19** to give any carbazole can again be attributed to steric congestion; the dimethylamino/imino group and the chlorine preventing the necessary intermediate for ring closure to be formed (Scheme 6).

To explore the scope and limitations of the electrophilic cyanation, a few other substrates were investigated (Table 2). The low yield in the case of 1,3-dimethoxybenzene is a result of slow conversion to the immoniumsalt **22**[62,64], as indicated by the isolation of large amounts of recovered starting material. Increased reaction temperature or extended reaction time resulted in a decreased yield, probably as a result of decomposition[63] of **18**. Also the addition of a Lewis acid, ($AlCl_3$[64], $EtAlCl_3$) which is known to increase the reactivity of **18** toward 1,3-dimethoxybenzene, proved unfruitful.

Scheme 6.

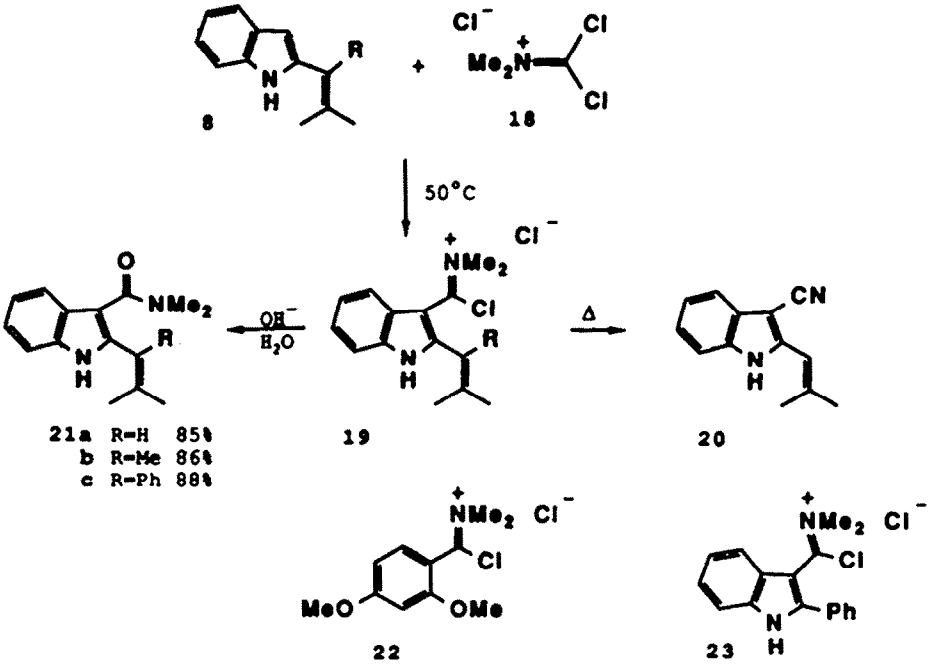
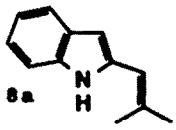
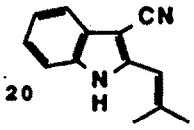
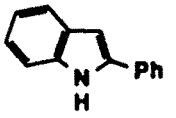
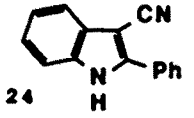
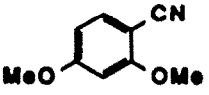


Table 2.

Substrate	Product	Yield	Method
 8a	 20	54 20 0	a b c
	 24	54 33 0	a b c
	 25	28 19	c d

a: reflux in 1,2-dichlorobenzene
b: thermolysis of immonium salt
c: reflux in acetonitrile
d: reflux in chlorobenzene

The indoles being more nucleophilic, readily reacted with **19** giving good yields of the dimethyl amides **21** after hydrolysis of the immonium salts **19**. Whereas **22** is completely converted to the nitrile in refluxing acetonitrile, **19** and **23** are inert at that temperature, reflecting the larger resonance stabilization of **19** and **23** as compared with **22**.

EXPERIMENTAL

Light petroleum refers to the fraction with a boiling range of 40-60 °C unless otherwise stated. Hexanes and EtOAc used for chromatography were distilled. Solvents were dried by distillation from CaH_2 (collidine, 1,2-dichlorobenzene) or from P_2O_5 (DMF, MeCN) and stored over 4Å molecular sieves. Diisopropylamine (DIPA) and THF were distilled immediately before use from CaH_2 and from sodium benzophenone ketyl, respectively. Methylvinylketone (MVK) and other unsaturated ketones were purified by distillation if necessary. Melting points were determined on a Reichert WME Kofler hot stage and are uncorrected. ^{1}H-NMR were recorded on a Bruker VP-200 (200 MHz) or on a Varian EM360 (60 MHz) instrument. IR (KBr discs) were obtained using a Perkin-Elmer 257 instrument. MS (70 eV) were obtained with a LKB-9000 spectrometer.

2-Benzylindole (5c)[65]. - Phenylacetone phenylhydrazone[66] (2.24 g, 10 mmol) was mixed with PPA (50 ml) at rt. The mixture was heated at 120 °C for 20 min whereafter the light brown solution was decomposed with NH_3 (aq., 25%)/ice (1:1, 500 ml) and extracted twice with ether. The combined etheral extracts were washed with water and brine, dried ($MgSO_4$) and concentrated. Flash-chromatography (hexanes /EtOAc, 9:1) gave 2-benzylindole (0.90 g, 43%) as a white solid, m.p. 85-86 °C (from light petroleum /cyclohexane) (lit. 84-85 °C [68], 86 °C [69], 85-86 °C [70]). IR: 3400, 1490, 1455, 1340, 790, 745 and 710 cm^{-1} (lit.[70].3420 cm^{-1}); ^{1}H-NMR (60 MHz, CCl_4): 7.4-6.7 (10H, m), 6.05 (1H, s) and 3.85 (2H, s). (lit.[70], 7.55, 7.40, 7.20-6.80, 6.20 and 3.95).

2-Methylcarbazole (6a) from 2-methylindole (5a). - A mixture of (**5a**) (1.31 g, 10 mmol), MVK (0.70 g, 10 mmol), 3Å molecular sieves (2.5 g), Pd-C (~0.1 g, 10%) and AcOH (25 ml) was stirred and refluxed under N_2 for 48 h, allowed to cool, diluted with EtOAc, filtered through Celite and concentrated. Flash-chromatography (hexanes/EtOAc, 9:1) gave **6a** (0.55 g, 30%) as a white solid, m.p. 264-266 °C (lit.[71],264-266 °C); IR: 3400, 1610, 1465, 1440, 1330, 1250, 810, 770, 750 and 730 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$): 8.05-7.93 (3H, m), 7.38 (2H, m), 7.23 (2H, m), 7.06 (1H, d) and 2.53 (3H, s) (lit.[71], 2.45); MS: 181 (M$^+$).

Repetition of the above procedure with omission of the molecular sieves gave 2-methylcarbazole in a yield of 28%, as did replacement of MVK for 4-methoxy-3-buten-2-one (24%).

1,2-Dimethylcarbazole (6b) from 2-ethylindole (5b). - A mixture of (**5b**) (14.5 g, 100 mmol), MVK (7.0 g, 100 mmol), Pd-C (~0.5 g, 10%) and AcOH (300 ml) was stirred and refluxed under N_2 for 48 h, allowed to cool, filtered through Celite and poured into water. The ppt was collected by filtration and dried to give **6b** (15.8 g, 81%) as a pale yellow solid, m.p. 140-143 °C (lit.[71], 151.3-151.8 °C). IR: 3440, 1610, 1460, 1420, 1325, 1185, 820, 765, 750 and 735 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$): 8.02 (1H, d), 7.88 (1H, broad s), 7.81 (1H, d), 7.45-7.33 (2H, m), 7.25-7.16 (1H, m), 7.06 (1H, d), 2.46 (3H, s) and 2.45 (3H, s), (lit.[71] 2.45 (6H)); MS: 195 (M$^+$).

Repetition of the above procedure on a 10 mmol scale with replacement of MVK for 4-methoxy-3-buten-2-one likewise gave **6b** (31%). Replacement of MVK for 4-methoxy-3-buten-2-one and addition of 3Å molecular sieves gave **6b** in a yield of 28 %.

2-Methyl-1-phenylcarbazole (6c) from 2-benzylindole (5c). - A mixture of **5c** (0.39 g, 1.9 mmol), MVK (0.13 g, 1.9 mmol), Pd-C (~0.05 g, 10%) and AcOH (5 ml) was stirred and refluxed under N_2 for 48 h, allowed to cool, filtered through Celite, poured into water and extracted twice with EtOAc. The combined organic extracts were washed with water and Na_2CO_3 (aq. 10%), dried ($MgSO_4$) and concentrated. Flash-chromatography (hexanes/EtOAc, 9:1) gave the title compound (0.39 g, 80%) as a colourless oil that slowly solidified, m.p. 109-111 °C. IR: 3400, 1615, 1465, 1425, 1185, 810, 780, 760, 745 and 710 cm^{-1}; MS: 257 (M$^+$).

2-Ethyl-1-methylcarbazole (6d). - A mixture of **5b** (1.45 g, 10 mmol), 1-penten-3-one (1.0 ml, 10 mmol), Pd-C (~0.1 g, 10%) and AcOH (25 ml) was stirred and refluxed under N_2 for 48 h, allowed to cool, filtered through Celite and poured into water. Saturation with NaCl gave a sticky reddish solid which was purified by flash-chromatography (CH_2Cl_2) to give the title compound (1.31 g, 63%) as a pale yellow solid, m.p. 93-95 °C, (lit.[72],97.5-98 °C). IR: 3410, 2960, 1605, 1455, 1415, 1325, 1310, 1235, 1180, 815, 745 and 730 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$): 8.02 (1H, d), 7.91 (1H, broad s), 7.85 (1H, d), 7.47-7.33 (2H, m), 7.24-7.16 (1H, m), 7.08 (1H, d), 2.83 (2H, q), 2.50 (3H, s) and 1.27 (3H, t), (lit.[72] 8.15-6.92, 2.78, 2.37 and 1.24).

2,4-Dimethylcarbazole (6e) - A mixture of **5a** (1.31 g, 10 mmol), 3-penten-2-one (0.84 g, 10 mmol), Pd-C (~0.1 g, 10%) and AcOH (25 ml) was stirred and refluxed under N_2 for 48 h, allowed to cool, filtered through Celite and concentrated. Flash-chromatography (hexanes/EtOAc, 8:2) gave a yellowish solid which on trituration with light petroleum gave 2,4-dimethylcarbazole (0.67 g, 35 %) as white needles, m.p. 133-135 °C (lit.[71],137-138.5 °C). IR: 3400, 1610, 1455, 1330, 1285, 1255, 835, 745 and 730 cm^{-1}; MS: 195 (M^+).

1,2,4-Trimethylcarbazole (6f) - A mixture of **5b** (1.45 g, 10 mmol), 3-penten-2-one (0.84 g, 10 mmol), Pd-C (~0.1 g, 10%) and AcOH (25 ml) was stirred and refluxed under N_2 for 48 h, allowed to cool, filtered through Celite and concentrated. Flash-chromatography (hexanes/EtOAc, 8:2) gave a yellow oil which on trituration with light petroleum gave **6f** (0.75 g, 36%) as white needles, m.p. 104-105 °C. (lit.[73] 101.5-102 °C) IR: 3520, 1615, 1580, 1455, 1390, 1325, 1295, 845, 750 and 735 cm^{-1} (lit.[73] [in Nujol] 3410, 1615, 1515, 1505, 1320, 1290, 750 and 730 cm^{-1}); ^{1}H-NMR (200 MHz, $CDCl_3$): 8.13 (1H, d),.7.92 (1H, broad s), 7.5-7.2 (3H, m), 6.86 (1H, s), 2.81 (3H, s) and 2.44 (6H, s). (lit.[73] [CCl_4-$CDCl_3$] 8.3-6.7, 2,8 and 2.2); MS: 209 (M^+).

2-Methyl-4-phenylcarbazole (6g) - A mixture of **5a** (1.31 g, 10 mmol), benzylideneacetone (1.47 g, 10 mmol), Pd-C (~0.1 g, 10%),3Å molecular sieves (2.5 g) and AcOH (25 ml) was stirred and refluxed under N_2 for 48 h, allowed to cool, filtered through Celite and concentrated. Flash-chromatography (hexanes/EtOAc, 8:2) gave a yellow oil which on trituration with light petroleum /cyclohexane (1:1) gave **6g** (0.68 g, 27%) as colourless crystals, m.p. 129-130 °C. IR: 3400, 3370, 1605, 1450, 1320, 845, 760, 745, 730 and 700 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$): 8.02 (1H, broad s), 7.65-7.21 (9H, m), 6.95 (2H, m) and 2.54 (3H, s); MS: 257 (M^+).

1,2-Dimethyl-4-phenylcarbazole (6h) - The same procedure as for **6g** but with **5b** instead of **5a** gave the title compound (0.87 g, 32%) as pale yellow crystals, m.p. 141-143 °C. IR: 3430, 1610, 1570, 1460, 1445, 1375, 1320, 860, 770, 755, 740 and 710 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$): 7.98 (1H, broad s), 7.6-7.2 (8H, m), 6.95 (2H, t) and 2.48 (6H, s); MS: 271 (M^+).

11-Methyl-7,8,9,10-tetrahydro-5H-benz[*b*]carbazole (6i) and 11-Methyl-5H-benz[*b*]-carbazole (7a). - A mixture of **5a** (1.31 g, 10 mmol), 2-ethylidenecyclohexanone[31] (1.24 g, 10 mmol), 3Å molecular sieves (2.5 g), Pd-C (~0.1 g, 10 %) and AcOH (25 ml) was stirred and refluxed under N_2 for 48 h. On cooling a solid was formed. The mixture was dissolved/diluted with EtOAc, filtered through Celite and concentrated. Flash-chromatography (hexanes /EtOAc, 9:1) gave I: **6i** (1.00 g, 44%) as a yellowish solid, m.p. 212-213 °C (from light petroleum, 60-80 °C) (lit.[27], 216-218 °C). IR: 3390, 2910, 1605, 1450, 1270, 850, 745 and 725 cm^{-1} (lit.[27], (in Nujol) 3440, 1630 and 1614 cm^{-1}); ^{1}H-NMR (200 MHz, $CDCl_3$): 8.20 (1H, d), 7.76 (1H, broad s), 7.36 (2H, d), 7.24-7.17 (1H, m), 6.97 (1H, s), 2.98-2.84 (4H, m), 2.75 (3H, s) and 1.94-1.78 (4H, m); MS: 235 (M^+); II: **7a** (0.78 g, 34%) as a yellowish solid. Recrystallization from

cyclohexane gave a white solid, m.p. 236 °C (lit.[22], 243-244 °C).IR: 3380, 1635, 1610, 1470, 1460, 1340, 1270, 870, 830 and 740 cm^{-1} (lit.[22],(in Nujol): 3380 cm^{-1}); ^1H-NMR (200 MHz, $CDCl_3$): 8.42-8.29 (2H, m), 7.96-7.91 (2H, m), 7.66 (1H, s), 7.50-7.41 (4H, m), 7.28-7.25 (1H, m) and 3.26 (3H, s); MS: 231 (M^+).

6,11-Dimethyl-7,8,9,10-tetrahydro-5H-benz[*b*]carbazole (6j) and 6,11-Dimethyl-5H-benz[*b*]carbazole (7b).- The same conditions as above with **5b** instead of **5a** gave I: **7b** (0.96 g, 38%) as a yellowish solid. Recrystallization from cyclohexane gave a white solid, m.p. 160-161 °C. IR: 3410, 2920, 1605, 1445, 1385, 1335, 1310, 1290, 750, 735 and 730 cm^{-1}; ^1H-NMR (200 MHz, $CDCl_3$): 8.21 (1H, d), 7.82 (1H, broad s) 7.45-7.31 (2H, m), 7.25-7.15 (1H, m), 2.87 (4H, m), 2.76 (3H, s), 2.39 (3H, s) and 1.87 (4H, m); MS: 249 (M^+); II: **7b** as a pale yellow solid (0.55 g, 22%), m.p. 211-213 °C. Recrystallization from light petroleum (b.p. 60-80 °C) gave almost colourless fine needles, m.p. 215-216 °C (lit., 208-209 °C [74], 211-213 °C [59]. IR: 3415, 1625, 1610, 1470, 1385, 1240, 760, 745 and 710 cm^{-1} (lit.[59], 3480 cm^{-1} (in $CHCl_3$)); ^1H-NMR (200 MHz, DMSO-d_6): 11.07 (1H, s), 8.38-8.32) (2H, m), 8.13 (1H. d), 7.58-7.40 (4H, m), 7.24-7.16 (1H, m), 3.17 (3H, s) and 2.84 (3H, s) (lit.[59], 11.05, 3.18 and 2.82); MS: 245 (M^+).

11-Methyl-6-phenyl-7,8,9,10-tetrahydro-5H-benz[*b*]carbazole (6k). - A mixture of **5c** (0.41 g, 2 mmol), 2-ethylidenecyclohexanone[31] (0.25 g, 2 mmol), 3Å molecular sieves (0.5 g), Pd-C (~0.05 g, 10%) and AcOH (5 ml) was stirred and refluxed under N_2 for 48 h, allowed to cool, diluted with EtOAc, filtered through Celite and concentrated. Flash-chromatography (hexanes/EtOAc, 95:5) gave **8c** (0.40 g, 64%) as a white solid, m.p. 117-120 °C. IR: 3380, 2910, 1600, 1450, 1390, 1315, 795, 750, 740 and 705 cm^{-1}; ^1H-NMR (200 MHz, $CDCl_3$): 8.25 (1H, d), 7.59-7.20 (9H, m), 2.96 (2H, t), 2.83 (3H, s) 2.69 (2H, t), 1.88 (2H, m) and 1.74 (2H, m); Further eluation gave recovered **5c** (0.06 g, 15%).

6,11-Dimethyl-5H-benz[*b*]carbazole (7b) from (6j). - A mixture of **8b** (0.25 g, 1 mmol), Pd-C (~ 0.05 g, 10%) and diglyme (10 ml) was refluxed under N_2 for 18 h, allowed to cool, filtered through Celite and poured into water. The ppt formed was collected by filtration and dried to give **7b** (0.21 g, 86%) as an off white solid, m.p. 218-220 °C. TLC, IR and ^1H-NMR were identical with those from the compound prepared from **5b** and 2-ethylidenecyclohexanone (*vide supra*).

11-Methyl-6-phenyl-5H-benz[*b*]carbazole (7c). - A mixture of **6k** (0.18 g, 0.58 mmol), Pd-C (~ 0.05 g, 10%) and diglyme (5 ml) was refluxed under N_2 for 20 h, allowed to cool, filtered through Celite and poured into water. After saturation with NaCl, a ppt eventually formed which was collected by filtration and dried to give **7c** (0.18 g, 99%) as a grey solid, m.p. 176-178 °C. IR 3420, 1610, 1390, 1380, 1240, 770, 745 and 700 cm^{-1}; ^1H-NMR (200 MHz, $CDCl_3$): 8.41 (2H, t), 7.82-7.79 (2H, m), 7.64-7.26 (10H, m) and 3.31 (3H, s).

2-(2-Methyl-1-propenyl)indole (8a). - A mixture of mesityl oxide (39.3 g, 0.4 mol), phenylhydrazine (43.3 g, 0.4 mol) and AcOH (25 drops) was heated on a steam-bath for 1 h. The reaction mixture was decanted from the water formed into PPA (150 ml) at rt. After mixing the mixture was carefully (exothermic) heated to 125 °C, and kept at that temperature for 20 min with occasional stirring whereafter it was poured into NH_3 (aq., 25%)/ice (1500 ml, 1:1) and extracted twice with ether. The etheral extracts were washed with water and brine, dried ($MgSO_4$) and concentrated. Trituration of the residue with light petroleum induced crystallization. The crystals were collected and washed with cyclohexane to give **8a** (18.2 g, 26%), m.p. 104-105 °C (lit. 103-105 °C [75], 102-103 °C [76]). IR: 3390, 1450, 1340, 1315, 1290, 840, 795, 750 and 665 cm^{-1} (lit.[75].,($CHCl_3$): 3490, 3000, 1455, 1340, 1325, 1280 and 640 cm^{-1}); ^1H-NMR (200 MHz, $CDCl_3$): 7.90 (1H, broad s), 7.57 (1H, d), 7.29 (1H, t), 7.2-7.0 (2H, m), 6.43 (1H, s), 6.18 (1H, s), 2.05 (3H, s) and 1.96 (3H, s), (lit.[75] ($CDCl_3$): 7.90, 7.6-7.0, 6.43, 6.16, 2.04 and 1.96); MS: 171 (M^+).

2-(1,2-Dimethyl-1-propenyl)indole (8b) - Prepared as **8a** on a 100 mmol scale from 3,4-dimethyl-3-penten-2-one[77] giving **8b** (4.5 g, 24%), m.p. 111-112. IR: 3400, 1455, 1405, 1350, 1305, 800, 750 and 695 cm^{-1}; ^1H-NMR (60 MHz, CCl_4): 7.6-7.2 (2H, m), 7.1-6.8 (3H, m), 6.15 (1H, s), 1.95 (3H, s) and 1.80 (6H, s); MS: 185 (M^+).

3-Carboxymethyl-1,2-dihydro-4-methylcarbazole (13).

Method A : A mixture of **11** (9.11 g, 50 mmol), phenylhydrazine (5.41 g, 50 mmol) and AcOH (3 drops) was heated on a steam-bath for 45 min, allowed to cool and added to PPA (25 ml) at rt. The mixture was heated at 125 °C for 20 min, decomposed with NH_3 (aq., 25%)/ice (250ml, 1:1) and extracted twice with CH_2Cl_2. The combined organic extracts were washed with water, dried ($MgSO_4$) and concentrated. Trituration of the residue with MeOH gave **13** (1.23 g) as a tan solid, collected by filtration. The filtrate was concentrated and the residue was extracted with hot cyclohexane/PhH (5×50 ml) Concentration of the extracts and trituration with MeOH gave another crop (0.37 g) of **13** .Total yield 13 %. M.p. 163-165 °C (lit[51]., 162-163 °C). IR: 3270, 1660, 1590, 1530, 1485, 1455, 1430, 1365, 1325, 1280, 1245, 1200, 1060, 1020, 770, 735, 705 and 675 cm^{-1} .(lit[51]., 3248 and 1662 cm^{-1}); ^1H-NMR (200 MHz, $CDCl_3$): 8.22 (1H, broad s), 7.86-7.81 (1H, m), 7.35-7.30 (1H, m), 7.18-7.12 (2H, m), 4.25 (2H, q); 2.81 (4H, s), 2.79 (3H, s) and 1.35 (3H, t), (lit[51]., 8.35, 4.29, 2.76 and 1.32).

Method B : A mixture of **11** (9.11 g, 50 mmol), phenylhydrazine (5.41 g, 50 mmol) and AcOH (50 ml) was refluxed for 2h. The mixture was allowed to cool and poured into water to give a brown viscous oil which was triturated with MeOH to give **13** (1.14 g) as a tan solid. The filtrate was concentrated and the residue was extracted with hot cyclohexane/PhH as in method A to give a second crop (0.49 g) of **13**. Total yield 13 %.

1-Benzenesulphonylindole. - The method of Illy *et al*[78]. was adopted. Thus, indole (37.4 g, 320 mmol) was added in one portion to a vigorously stirred ice-cooled mixture of tetrabutylammonium hydrogen sulphate (2.8 g, 8.2 mmol), crushed NaOH pellets (40 g, 1 mol) and CH_2Cl_2 (500 ml) followed by a solution of benzenesulphonyl chloride (70.6 g, 400 mmol) in CH_2Cl_2 (300 ml) which was added in portions, keeping the temperature below 25 °C. The mixture was stirred at rt for 2 h and filtered. The filter cake was washed with CH_2Cl_2, the combined organic phases were concentrated and triturated with hot MeOH. On standing colourless crystals precipitated. The mixture was put into the freezer and the crystals were collected the following day. Yield 76.3 g (93%), m.p. 78-79 °C (lit.[79] 78-79 °C).

1-Benzenesulphonyl-2-(2-hydroxyethyl)indole (15). - To a solution of LDA [prepared from DIPA (8.4 ml, 60 mmol), *n*-BuLi (1.6 M, 34 ml, 55 mmol) and THF (100 ml)] was added 1-benzenesulphonylindole (12.86 g, 50 mmol) in THF (100 ml) over 2 h keeping the temperature below -70 °C. After 90 min at -75 °C the solution was allowed to come to -15 °C whereafter ethylene oxide (7.5 ml, 150 mmol) in THF (25 ml) was added dropwise over 20 min keeping the temperature below -10 °C. The mixture was allowed to come to rt overnight and poured into NH_4Cl (aq., sat.). After separation, the aqueous phase was extracted with ether, and the combined organic phases were washed with 2M HCl and brine, dried ($MgSO_4$) and concentrated to give a red oil which was purified by chromatography (hexanes with increasing proportions of EtOAc). The pale brown oil (10.36 g, 69%) was used without further purification. ^1H-NMR (60 MHz, $CDCl_3$): 8.3-7.1 (9H, m), 6.45 (1H, s), 3.95 (3H, m) and 3.20 (2H, t).

2-(2-Hydroxyethyl)indole (16). - Compound **15** (3.73 g, 12.3 mmol), 2M NaOH (65 ml) and EtOH (65 ml) was refluxed for 20 h. The mixture was cooled, concentrated and partitionated between water and ether. After separation, the aqueous phase was extracted with ether, and the combined organic phases were washed with water and brine, dried ($MgSO_4$) and concentrated. Flash-chromatography (CH_2Cl_2) yielded **16** (1.65 g, 83%) as a light tan oil that solidified, m.p. 55-56 °C.[80] IR: 3390, 3250 (broad), 1545, 1455, 1415, 1345, 1290, 1050, 790 and 755 cm^{-1}.

2-(2-Tosyloxyethyl)indole (17). - A solution of **16** (0.79 g, 4.9 mmol) in dry collidine (10 ml) was added over 45 min to a stirred solution of TsCl (0.93 g, 4.9 mmol) in collidine (10 ml) at 0 °C. After 5 h at 0 °C the mixture was poured into 2M HCl/ice (150 ml) and extracted twice with EtOAc. The combined organic extracts were washed with 1M HCl and brine, dried ($MgSO_4$) and concentrated. Trituration with MeOH gave **17** (0.76 g) as a white solid. A second crop (0.22 g) was obtained after concentration and trituration of the filtrate. Total yield 63%, m.p. 113-115 °C (lit.[51], 114-116 °C) IR: 3385, 1345, 1165, 1155, 1095, 985, 915, 815, 800, 780, 765 and 665 cm^{-1} (lit.[51], 3480, 1340, 1170 and 1160 cm^{-1}); MS: 315 (M^+).

2-(2-Methyl-1-phenyl-1-propenyl)indole (8c). - To a solution of LDA [prepared from DIPA (7.7 ml, 55 mmol), *n*-BuLi (1.6M, 34 ml, 55 mmol) and THF (40 ml)] was added 1-benzenesulphonylindole (12.86 g, 50 mmol) in THF (80 ml) over 2 h keeping the temperature below -70 °C. After 90 min at -75 °C, isobutyrophenone (8.3 ml, 55 mmol) in THF (40 ml) was added over 2h at -70 °C. The mixture was allowed to come to rt overnight and poured into NH_4Cl (aq., sat.). After separation the aqueous layer was extracted with EtOAc, and the combined organic phases were washed with water and brine, dried ($MgSO_4$) and concentrated to give an orange oil which was dissolved in a small volume of light petroleum (b.p. 60-80 °C). On standing a solid formed which was collected to give **8c** (8.34 g, 68%) as an off white solid, m.p. 99-100 °C. IR: 3390, 1450, 1300, 790, 755, 705 and 695 cm^{-1}; ^1H-NMR (200 MHz, $CDCl_3$): 7.64-7.60 (2H, m), 7.41-7.09 (8H, m), 6.53 (1H, d), 2.19 (3H, s) and 1.84 (3H, s); MS: 247 (M^+).

3-Formyl-2-(2-methyl-1-propenyl)indole (9a). - $POCl_3$ (1 ml, 10.5 mmol) was carefully added to DMF (5 ml) at 0 °C. The solution was stirred at 0 °C for 15 min whereafter **8a** (1.71 g, 10 mmol) in DMF was added dropwise. The mixture was stirred at rt for 16 h, poured into ice-water and made alkaline with 2M NaOH. The ppt formed was collected by filtration and dried to give **9a** (1.88 g, 94%) as an off-white solid, m.p. 164-166 °C. IR: 3200 (broad), 1620, 1580, 1440, 1340, 1230, 975, 830, 750 and 645 cm^{-1}.

3-Formyl-2-(1,2-dimethyl-1-propenyl)indole (9b). - Prepared as above from **8b** (0.37 g, 2 mmol) and $POCl_3$ (0.2 ml, 2.1 mmol) to give **9b** (0.41 g, 96%) as a yellowish solid, m.p. 170-176 °C. IR: 3160 (broad), 1620, 1580, 1440, 1370, 1345, 1240, 930, 870, 785, 745 and 670 cm^{-1}.

3-Formyl-2-(2-methyl-1-phenyl-1-propenyl)indole (9c). - Prepared as above from **8c** (0.49 g, 2 mmol) and $POCl_3$ (0.2 ml, 2.1 mmol) to give **9c** (0.54 g, 98%) as a yellowish solid, m.p. 195-198 °C. IR: 3200 (broad), 1625, 1580, 1450, 1370, 1240, 805, 770, 750 and 705 cm^{-1}.

2-Methylcarbazole (6a), from 2-(2-methyl-1-propenyl)indole (8a). - $POCl_3$ (1 ml, 10.5 mmol) was carefully added to DMF (10 ml) at 0 °C. The solution was stirred at 0 °C for 15 min whereafter **8a** (1.71 g, 10 mmol) was added in one portion. The mixture was stirred at rt for 90 min, refluxed for 4 h, cooled and poured into water. The solid formed was collected by filtration and dried to give **6a** (1.45 g, 80%) as grey solid. TLC, IR, NMR and MS were identical to **6a** prepared from **5a** and MVK.

1,2-Dimethylcarbazole (6b) from 2-(1,2-dimethyl-1-propenyl)indole (8b). - Prepared as above from **8b** (0.92 g, 5 mmol) to give a solid which was purified by chromatography (hexanes/EtOAc, 9:1) to give **6b** (20 mg, 1%). TLC, IR and MS were identical to **6b** prepared from **5b** and MVK.

2-Methyl-1-phenylcarbazole (6c), from 2-(2-methyl-1-phenyl-1-propenyl)indole (8c). - $POCl_3$ (0.2 ml, 2.1 mmol) was carefully added to DMF (2 ml) at 0 °C. The solution was stirred at 0 °C for 15 min whereafter **8c** (0.49 g, 2 mmol) was added in one portion. The mixture was stirred at rt for 1 h, refluxed for 27 h, cooled and poured into water. The solid formed was purified by chromatography (hexanes/EtOAc, 9:1) to give **6c** (14 mg, 3%). TLC, IR, and MS were identical to **6c** prepared from **5c** and MVK.

3-Cyano-2(2-methyl-1-propenyl)indole (20).

Method A :Compound **18** (0.40 g, 2.5 mmol) was added to a stirred mixture of **8a** (0.34 g, 2 mmol) and 1,2-dichlorobenzene (10 ml) at 0 °C. After 5 h at 50 °C and reflux for 14 h, the mixture was allowed to cool, poured into water and extracted twice with CH_2Cl_2. The combined extracts were washed with water and $NaHCO_3$ (aq., sat.) dried ($MgSO_4$) and concentrated. Flash-chromatography (hexanes/ EtOAc; 8:2) gave **20** (0.21 g, 54%) as a yellowish solid, m.p. 134-135 °C (from cyclohexane/MeOH). IR: 3300 (broad), 2215, 1655, 1585, 1445, 1380, 1320, 1235, 840 and 740 cm^{-1}; MS: 196 (M⁺).

Method B :Compound **18** (0.81 g, 5 mmol) was added in one portion to a solution of **8a** (0.86 g, 5 mmol) in MeCN (10 ml) at 0 °C. The mixture was stirred at 50 °C for 18 h, concentrated and the residue sublimed (200 °C, 0.02 mbar) to give **20** (0.20 g, 20%) as an off-white solid, m.p. 132-135 °C. TLC and IR as above.

3-Cyano-2-phenylindole (24).

Method A :Compound **18** (0.80 g, 5 mmol) was added to a stirred mixture of 2-phenylindole (0.77 g, 4 mmol) and 1,2-dichlorobenzene (10 ml) at 0 °C. After 5 h at 50 °C and reflux for 14 h, the mixture was allowed to cool, poured into water and extracted twice with CH_2Cl_2. The combined extracts were washed with water and $NaHCO_3$ (aq., sat.) dried ($MgSO_4$) and concentrated.Trituration with hot MeOH gave the title compound (0.47 g, 54%) as a tan solid, m.p. 244-245 °C (from MeOH, lit.[79], 246-248 °C) IR; 3210 (broad), 2220, 1585, 1490, 1450, 1425, 1245, 770, 740 and 685 cm^{-1} (lit.[81], 3200 and 2210 cm^{-1}); MS: 218 (M⁺).

Method B : Compound **18** (0.9 g, 5.5 mmol) was added in one portion to a solution of 2-phenylindole (0.96 g, 5 mmol) in MeCN (20 ml) at 0 °C. The mixture was stirred at 50 °C for 18 h, refluxed for 6 h, cooled and concentrated. The residue was sublimed (200 °C, 0.02 mbar) to give the title compound (0.36 g, 33%) as a tan solid, m.p. 234-242 °C. TLC and IR as above.

2,4-Dimethoxybenzonitrile (25). - Compound **18** (0.9 g, 5.5 mmol) was added in one portion to a solution of 1,3-dimethoxybenzene (0.69 g, 5mmol) in dry MeCN at rt. The mixture was refluxed for 20 h, cooled, poured into water, made alkaline with 2M NaOH and extracted twice with EtOAc. The combined organic extracts were washed with water and brine, dried ($MgSO_4$) and concentrated. Flash-chromatography (hexanes/EtOAc, 8:2) gave the title compound (0.23 g, 28%) as a white solid, m.p. 83-84 °C (lit.[82], 89 °C). IR: 2220, 1605, 1580, 1480, 1330, 1290, 1275, 1215, 1110, 1020, 845 and 810 cm^{-1}; MS: 163 (M⁺).

Employing the same method as above, exchanging MeCN for PhCl likewise gave the title compound (0.10 g, 12%).

3-(N,N-Dimethylformamido)-2-(2-methyl-1-propenyl)indole (21a). - Compound **18** (0.4 g, 2.5 mmol) was added in one portion to a solution of **8a** (0.34 g, 2 mmol) in MeCN (10 ml) at 0 °C. The solution was stirred at 50 °C for 5 h, allowed to cool and poured into water. The clear solution was made alkaline with 2M NaOH and the ppt formed was collected by filtration and dried to give **21a** (0.41 g, 85%) as a light tan solid, m.p. 159-161 °C. IR: 3170, 2910, 1580, 1500, 1450, 1395, 1050 and 745 cm^{-1}.

3-(N,N-Dimethylformamido)-2-(1,2-dimethyl-1-propenyl)indole (21b). - Prepared as above from **8b** (0.37 g, 2 mmol) to give **21b** (0.44 g, 86%) as a light tan solid, m.p. 222-223 °C. IR: 3130, 2910, 1575, 1500, 1450, 1390, 1105 and 755 cm^{-1}.

3-(N,N-Dimethylformamido)-2-(2-methyl-1-phenylpropenyl)indole (21c). - Prepared as above from **8c** (0.49 g, 2 mmol) to give **21c** (0.56 g, 88%) as a light tan solid, m.p. 205-207 °C. IR: 3160, 2910, 1595, 1530, 1490, 1445, 1390, 1045, 740 and 755 cm^{-1}.

REFERENCES AND NOTES

1. J.H.Cardelina II, M.P. Kirkup, R.E. Moore, J.S. Mynderse, K. Seff, C.J. Simmons, *Tetrahedron Letters*, 4915 (1979).
2. T. Naid, T. Kitahara, M. Kaneda, S. Nakamura, *J. Antibiotics.*, **40**, 157, (1987),and refs. cited therein.
3. V.K. Kansal, P. Potier, *Tetrahedron*, **42**, 2389 (1986).
4. S. Archer, B.S. Ross, L. Pica-Mattocia, D. Cioli, *J. Med. Chem.*, **30**, 1204 (1987).
5. For the synthesis of **1** see refs. 6-8 and for a synthesis of analogues to **2**, ref.9. The syntheses of **3** and **4** have been extensively reviewed.[3,10] Some more recent examples are given in refs. 11-16.
6. S. Kano, E. Sugino, S. Hibino, *J. Chem. Soc., Chem. Commun.*, 1241 (1980).
7. S. Kano, E. Sugino, S. Shibuya, S. Hibino, *J. Org. Chem.*, **46**, 3856 (1981).
8. S. Takano, Y. Suzuki, K. Ogasawara, *Heterocycles*, **16**, 1479 (1981).
9. U. Pindur, L. Pfeuffer, *Heterocycles*, **26**, 325 (1987).
10. G.W. Gribble, M.G. Saulnier, *Heterocycles*, **23**, 1277 (1985).
11. C. Kashima, S. Hibi, T. Maruyama, K. Harada, Y. Omote, *J. Heterocyclic Chem.*, **24**, 913 (1987).
12. M.J.E. Hewlins, A.H. Jackson, A. Long, A. Oliveira-Campos, P.V.R. Shannon, *J. Chem. Res. (M)*, 2645 (1986).
13. D.W.M. Benzies, P.M. Fresneda, R.A. Jones, H. McNab, *J. Chem. Soc., Perkin Trans. I*, 1651 (1986).
14. G.R. Stephenson, *J. Organomet. Chem.*, **286**, C41 (1985).
15. E. Differding, L. Ghosez, *Tetrahedron Letters* **26**, 1647 (1985).
16. N.S. Narasimhan, S.M. Gokhale, *J. Chem. Soc., Chem. Commun.*, 86 (1985).
17. J. Bergman, B. Pelcman, *Tetrahedron Letters*, **26**, 6389 (1985).
18. J. Bergman, B. Pelcman, *Tetrahedron Letters*, **27**, 1939 (1986).
19. H.E. Johnson, D.G. Crosby, *J. Org. Chem.* **28**, 2030 (1963).
20. R.L. Garnick, Ph.W. Le Quesne, *J. Am. Chem. Soc.*,**100**, 4213 (1978).
21. H.J. Teuber, G. Schmitt, *Tetrahedron Letters*, 4911 (1971).
22. D.C. Johnson, Diss., Univ. Minnesota, (1961).
23. H.E. Johnson, D.G. Crosby, *J. Org. Chem.*, **25**, 569 (1960).
24. J.E. Johnson, M. S. Thesis, Univ. Minnesota, (1959).
25. J. Szmuszkovicz, *J. Am. Chem. Soc.*,**79**, 2819 (1957).
26. W.E. Noland, D.N. Robinson, *J. Org. Chem.*, **22**, 1134 (1957).
27. D.N. Robinson, Diss., Univ. Minnesota, (1959), and refs. cited therein.
28. Y. Oikawa, O. Yonemitsu, *Heterocycles*, **5**, 233 (1976).
29. J. Bergman, R. Carlsson, *Tetrahedron Letters*, 4051 (1978).
30. W.E. Noland, J.E. Johnson, *Tetrahedron Letters*, 589 (1962).
31. G. Vavon, V.M. Mitchovitch, *Bull. Soc. Chim. Fr.*, **45**, 961 (1929).
32. B. Weinstein, L.-C. Lin, F.W. Fowler, *J. Org. Chem.*, **45**, 1657 (1980).
33. G.W.B. Reed, P.T.W. Cheng, S. McLean, *Can. J. Chem.* **60**, 419 (1982).
34. R.A. Jones, P.M. Fresneda, T.A. Saliente, J.S. Arques, *Tetrahedron*, **40**, 4837 (1984).
35. N.S. Narasimhan, R.S. Kusurkar, D.D. Dhvale, *Indian J. Chem.*,**22b**, 1004 (1983).
36. F.E. Ziegler, E.B. Spitzner, *J. Am. Chem. Soc.*,**95**, 7146 (1973); *ibid.*,**92**, 3492 (1970).
37. G.A. Cordell, G.F. Smith, G.N. Smith, *Chem. Commun.*, 191 (1970).
38. D. Beck, K. Schenker, *Helv. Chim. Acta*, **51**, 264 (1968).
39. 2-Vinylic indoles have been proposed as transient intermediates in the synthesis of Aspidosperma-alkaloids.[40-43]
40. M.E. Kuehne, W.G. Bornmann, W.G. Earley, I. Marko, *J. Org. Chem.*, **51**, 2913 (1986), and previous papers in this series.
41. J.P. Brennan, J.E. Saxton, *Tetrahedron*, **42**, 6719 (1986).
42. G. Kalaus, M. Kiss, M. Kajtár-Peredy, J. Brlik, L. Szabó, C. Szántay, *Heterocycles*, **23**, 2783 (1985).

43. M.-C. Barsi, B.C. Das, J.-L. Fourrey, R. Sundaramoorthi, *J. Chem. Soc., Chem. Commun.*, 88 (1985), and refs. cited therein.
44. For a recent review on 2-vinylindoles see: E. Akgün, U. Pindur, *Chimia*, **39**, 264 (1985).
45. E. Akgün, U. Pindur, J. Müller, *J. Het. Chem.*, **20**, 1303 (1983).
46. U. Pindur, C. Flo, E. Akgün, M. Tunali, *Liebigs Ann. Chem.*, 1621 (1986).
47. B. Robinson, "The Fischer Indole Synthesis", Wiley-Interscience (1982).
48. Ref. 47, p. 764.
49. F. Sannicolò, *Tetrahedron Letters*, **25**, 3101 (1984).
50. M.V. Baker, C. Ghitgas, R.K. Haynes, A.E. Hilliker, G.J. Lynch, G.V. Sherwood, H.-L. Yeo, *Aust. J. Chem.*, **37**, 2037 (1984).
51. T. Sakan, S. Matsabura, H. Takagi, *Tetrahedron Letters*, 4925 (1968).
52. Several examples of migration[53] or *in situ* debenzenesulphonylation from pyrroles[54] and indoles[55-60] are known.
53. D. Nagarathnam, P.C. Srinivasan, *Indian J. Chem.*, **22B**, 1050 (1983).
54. R. Greenhouse, C. Ramirez, J.M. Muchowski, *J. Org. Chem.*, **50**, 2961 (1985).
55. S. Hibino, E. Sugino, T. Yamochi, M. Kuwata, H. Hashimoto, K. Sato, F. Amanuma, Y. Karasawa, *Chem. Pharm. Bull.*,**35**, 2261 (1987).
56. D.M. Ketcha, G.W. Gribble, *J. Org. Chem.*, **50**, 5451 (1985).
57. M.G. Saulnier, G.W. Gribble, *J. Org. Chem.*, **48**, 2690 (1983).
58. S. Kano, E. Sugino, S. Hibino, *Heterocycles*,**19**, 1673 (1982).
59. D.A. Taylor, M.M. Baradarani, S.J. Martinez, J.A. Joule, *J. Chem. Res. (M)*, 4801 (1979).
60. R. Besselièvre, C. Thal, H.-P. Husson, P. Potier, *J. Chem. Soc., Chem. Commun.*, 90 (1975).
61. H.G. Viehe, *Chem. Ind.*, 386 (1977).
62. Z. Janousek, H.G. Viehe, *Adv. Org. Chem.*, **9**(1), 343 (1976).
63. Z. Janousek, *Diss*, Univ. Louvain-la-Neuve (1972).
64. G. Duchêne, *Diss*, Univ. Louvain-la-Neuve (1977).
65. Fischer indolization of phenylacetone phenylhydrazone has been reported to give mixtures of 2- and 3-benzylindole.[66-67]2-Benzylindole has also been prepared directly from phenylacetone, phenylhydrazine and PPA[68] the method described here was however found to be more practical.
66. N.P. Buu-Hoi, P. Jacquignon, O. Périn-Roussel, *Bull. Soc. Chim. Fr.* 2849 (1965).
67. M.H. Palmer, P.S. McIntyre, *J. Chem. Soc.*(B), 446 (1969).
68. H. Yamamoto, A. Misaki, T. Izumi, M. Koshiba, *Jap. Pat.* 71 01,408. [*Chem. Abstr.* **74**, 87819y (1971).
69. P.L. Julian, J. Pikl, *J. Am. Chem. Soc.*, **55**, 2105 (1933).
70. G. Adam, J. Andrieux, M. Plat, *Tetrahedron*, **41**, 399 (1985).
71. M. Kuroki, Y. Tsunashima, *J. Het. Chem.*, **18**, 709 (1981).
72. B. Miller, E.R. Matjeka, *J. Am. Chem. Soc.*,**102**, 4772 (1980).
73. H. Takeuchi, K. Takano, *J. Chem. Soc., Perkin I*, 611 (1986).
74. G.W. Gribble, M.G. Saulnier, M.P. Sibi, J.A. Obaza-Nutaitis, *J. Org. Chem.*, **49**, 4518 (1984).
75. A.B. Smith, III, M. Visnick, J.N. Haseltine, P.A. Sprengler, *Tetrahedron*, **42**, 2957 (1986).
76. N.N. Komzolova, N.F. Kucherova, V.A. Zagorevski, *Zh. Org. Khim.*, **1**, 1139 (1965).
77. H.O. House, C.-Y. Chu, J.M. Wilkins, M.J. Umen, *J Org. Chem.*, **40**, 1460 (1975).
78. V.O. Illy, *Synthesis*, 387 (1979).
79. R.J. Sundberg, J.D. Bloom, *J Org. Chem.*, **45**, 3382 (1980).
80. This melting point is not in accordance of that reported: A.N. Kost, S.M. Gorbunova, L.P. Basova, V.K. Kiselev, V.I. Gorbunov, *Khim.-Farm. Zh.*, **8**, 74 (1974).
81. Y. Tamura, M. Adachi, T. Kawasaki, H. Yasuda, Y. Kita, *J. Chem. Soc., Perkin I*, 1132 (1980).
82. G. Lohaus, *Chem. Ber.*, **100**, 2719 (1967).