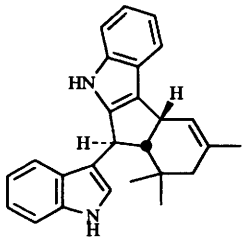
Cyclopenta[*b*]indoles. Part 1. Synthesis of cyclopenta[*b*]indoles by formal [3 + 2] addition of indolylmethyl cations to alkenes

Carrie-Ann Harrison, Ralf Leineweber, Christopher J. Moody* and Jonathan M. J. Williams
Department of Chemistry, Loughborough University of Technology, Loughborough, Leicestershire LE11 3TU, UK

Treatment of indole-2- or 3-methanols with tin(IV) chloride as Lewis acid in the presence of styrenes or indene results in formal [3 + 2] addition of the indole stabilised cation to the alkene to give cyclopenta[*b*]indoles with a high degree of stereoselectivity; use of methylcyclohexene as the alkene component gave the *cis*-fused cyclopenta[*b*]indole **17**, which was independently synthesised as its (−)-enantiomer from the diketone **18**.

The cyclopenta[*b*]indole ring system occurs in a number of indole alkaloids, notably the structurally complex tremorgenic mycotoxins such as paxilline, paspaline, the lolitrems, penitrems and janthitrems,[1] and the monoterpenoid yuehchukene **1**.[2] We now report the details of a new approach[3] to



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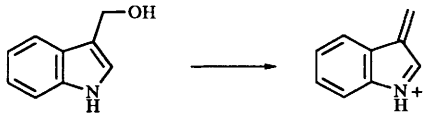
cyclopenta[*b*]indoles based on the formal [3 + 2] cycloaddition of the stabilised cation derived from indole-2- or 3-methanols to alkenes.[4]

Results and discussion

It is well known that on treatment with acids, 1*H*-indole-3-methanol **2** is readily converted into a stabilised cation which



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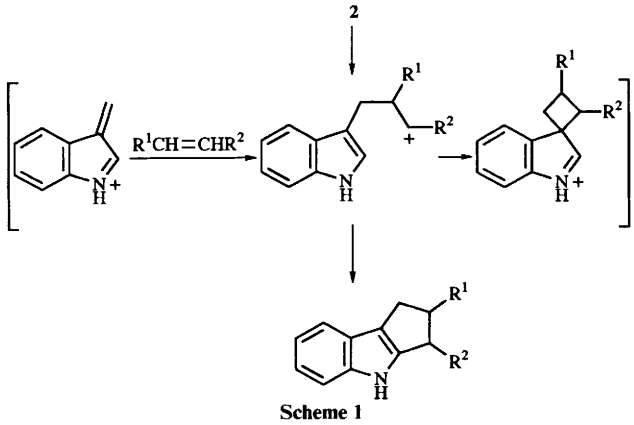
subsequently reacts further to give diindol-3-ylmethane.[5] The same product is obtained by reaction of indole itself with formaldehyde,[5] and further examples of 'dimerisation' reactions involving indole stabilised cations (derived from indolemethanols as above or by protonation of vinylindoles) are known.[2a,2d,6]

By analogy with the recently reported preparation of dihydroindenes by reaction of benzylic cations with styrenes,[7] it seemed possible that, in the presence of a sufficiently reactive alkene, the 'dimerisation' of indole stabilised cations might be suppressed in favour of a formal [3 + 2] addition to the alkene to give cyclopenta[*b*]indoles as shown in Scheme 1. This indeed proved to be the case and the reaction provides a simple route to a range of cyclopenta[*b*]indoles.

Thus, treatment of a mixture of 1*H*-indole-3-methanol **2**, or its *N*-methyl derivative **3**, and prop-1-enylbenzene **4** with tin(IV) chloride at −78 °C gave, after aqueous work-up and chromatography, the desired cyclopenta[*b*]indoles **5** (55%) and



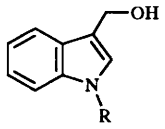
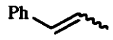
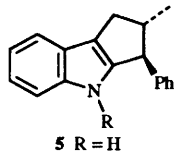
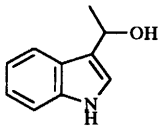
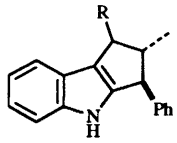
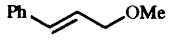
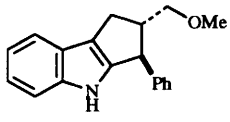
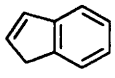
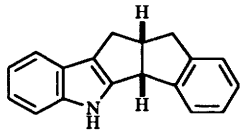
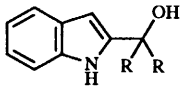
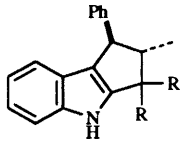
Scheme 1

6 (55%), the *trans*-stereochemistry being proved by NOE difference spectroscopy. The use of alternative Lewis acids such as boron trifluoride–diethyl ether proved unsatisfactory. The substituted indole-3-methanol **7** reacts similarly with the styrene **4** to give the cyclopenta[*b*]indoles **8** and **9** (63% combined) as a 1:10 mixture of diastereoisomers (Table 1). Thus, in common with the related reactions involving benzylic cations,[7] the formal [3 + 2] additions of indole stabilised cations with alkenes are highly stereoselective; not only is the original alkene stereochemistry preserved, but the new stereocentre at C-1 is also formed stereoselectively. Angle has speculated about the origin of the stereocentre in his related cationic cyclisations,[7] but the exact mechanism remains unknown, although in the case of our indoles we assume that a spiro[cyclobutane-1,3′-indolium] cation must be an intermediate (Scheme 1).[8]

The method was extended to other styrenes (the allylic ether **10** and indene), and to the indole-2-methanols **13** and **14** to give the corresponding cyclopenta[*b*]indoles **11**, **12**, **15** and **16**, stereospecifically albeit in poorer yield (Table 1). Finally, the use of alkenes other than styrenes was investigated. Although no cyclopentaindoles could be isolated from reactions involving dihydropyran, 1-diethylaminocyclohexene or allyltriisopropylsilane,[7c,9] the use of 1-methylcyclohexene gave the octahydroindenoindole **17** in 18% yield (Scheme 2).

The structure and *cis*-stereochemistry of **17** was confirmed by an independent synthesis of the (−)-enantiomer (−)-**17**, starting from the known *cis*-fused ketone **21**,[10] prepared by reduction[11] of the enantiomerically pure (*R*)-diketone **18** (Scheme 2). Thus, the (*R*)-diketone **18**, prepared by the (D)-proline catalysed Robinson annelation of 2-methylcyclopentane-1,3-dione with methyl vinyl ketone,[12] was treated with sodium boranuide ($NaBH_4$) under acidic conditions.[11,13] This resulted in complete reduction of the enone carbonyl, with

Table 1 Synthesis of cyclopenta[*b*]indoles by reaction of indolemethanols with alkenes

Indole	Alkene	Product	Yield (%)
 **2** R = H **3** R = Me	 **4** [*E* : *Z* = 9 : 1]	 **5** R = H **6** R = Me	**5** 55 **6** 55
 **7**	**4**	 **8** R = —Me **9** R = ---Me	**8** + **9** 63 [**8** : **9** = 1 : 10]
2	 **10**	 **11**	22
2		 **12**	19
 **13** R = H **14** R = Me	**4**	 **15** R = H **16** R = Me	**15** 27 **16** 17

concomitant reduction of the 5-membered ring ketone to give the corresponding alcohol **19**. Catalytic hydrogenation of the double bond resulted in formation of the *cis*-fused hexahydroindane **20**, accompanied by *ca.* 4% of the *trans*-isomer; this was followed by pyridinium chlorochromate (PCC) oxidation to give the ketone **21**. Finally, a Fischer indole reaction with phenylhydrazine gave the desired cyclopenta[*b*]indole **17** in 40% yield.

Experimental

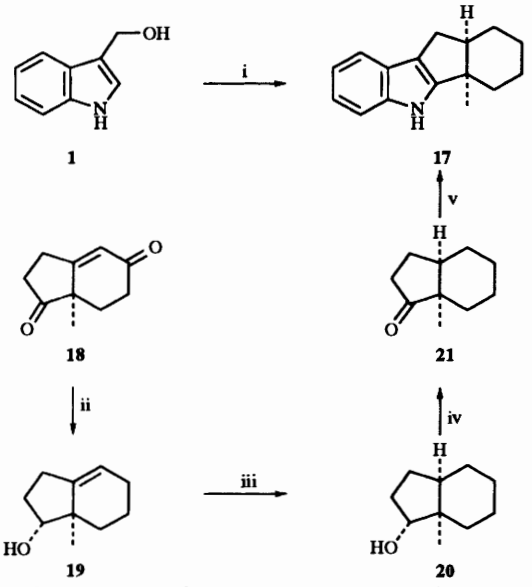
For general experimental details, see ref. 14. Compounds characterised by high resolution mass spectrometry were chromatographically homogeneous.

General procedure for cationic cyclisation

Tin(IV) chloride (4 equiv.) was added slowly to a stirred solution of the indolemethanol (1 equiv.) and the alkene (2 equiv.; 5 equiv. in the case of methylcyclohexene) in dry dichloromethane under nitrogen at −78 °C. After the addition was complete, the mixture was stirred for 10 min at −78 °C, allowed to warm to room temperature, and stirred for a further 40 min (15 h for indolemethanol **13**) when the solution was poured into saturated aqueous sodium hydrogen carbonate, and extracted with dichloromethane. The extracts were washed with water, dried ($MgSO_4$) and evaporated. The residue was purified by flash chromatography on silica gel to give the cyclopenta-[*b*]-indole. The following compounds were made by this method:

2-Methyl-3-phenyl-1,2,3,4-tetrahydrocyclopenta[*b*]indole 5. 55%, mp 155 °C (Found: M^+, 247.1360; $C_{18}H_{17}N$ requires *M*, 247.1360); $\nu_{max}(CHCl_3)/cm^{-1}$ 3065, 920, 800 and 725; δ_H(400 MHz; $CDCl_3$) 1.34 (3 H, d, *J* 7, CH_3), 2.55 (1 H, dd, *J* 14 and 7, CH_2), 2.85 (1 H, m, C*H*CH_3), 3.19 (1 H, dd, *J* 14 and 7, CH_2), 3.92 (1 H, d, *J* 7, C*H*Ph), 7.10–7.14 (2 H, m), 7.20–7.35 (5 H, m), 7.50–7.53 (2 H, m) and 7.63 (1 H, br s, NH); δ_C(100.6 MHz; $CDCl_3$) 19.91 (CH_3), 32.74 (*C*HCH_3), 50.91 (CH_2), 53.88 (*C*HPh), 111.46, 118.65, 119.49, 120.77, 124.61, 126.66, 127.70, 128.55, 129.40, 140.62, 143.55 and 144.11; *m*/*z* 247 (M^+, 100%), 232 (45) and 218 (65).

2,4-Dimethyl-3-phenyl-1,2,3,4-tetrahydrocyclopenta[*b*]indole 6. 55%, mp 79 °C (Found: M^+, 261.1501; $C_{19}H_{19}N$ requires *M*, 261.1517); $\nu_{max}(CHCl_3)/cm^{-1}$ 3019, 1466, 1368, 792, 735 and 705; δ_H(250 MHz; $CDCl_3$) 1.36 (3 H, d, *J* 7, CHC*H*$_3$), 2.55 (1 H, dd, *J* 14 and 7, CH_2), 2.88 (1 H, m, C*H*CH_3), 3.20 (1 H, m, CH_2), 3.33 (3 H, s, NCH_3), 3.95 (1 H, d, *J* 7, C*H*Ph), 7.16–7.35 (8 H, m) and 7.54 (1 H, d, *J* 7); *m*/*z* 261 (M^+, 100%), 246 (38), 232 (35), 170 (28), 115 (27) and 69 (53).



Scheme 2 *Reagents and conditions:* i, 1-methylcyclohexene, $SnCl_4$, CH_2Cl_2, −78 °C; ii, $NaBH_4$, CF_3CO_2H; iii, H_2, Pd–C, EtOH; iv, PCC, CH_2Cl_2; v, $PhNHNH_2$, H^+

1,2-Dimethyl-3-phenyl-1,2,3,4-tetrahydrocyclopenta[*b*]indole 9. 63% (with **8**), mp 118 °C (Found: M^+, 261.1495; $C_{19}H_{19}N$ requires *M*, 261.1517); $\nu_{max}(CHCl_3)/cm^{-1}$ 3019, 793 and 674; NMR data for major isomer: δ_H(400 MHz; $CDCl_3$) 1.18 (3 H, d, *J* 7, CH_3), 1.22 (3 H, d, *J* 7, CH_3), 2.87 (1 H, m, C*H*CH_3), 3.42 (1 H, m, C*H*CH_3), 3.94 (1 H, d, *J* 7, C*H*Ph), 7.10–7.14 (2 H, m), 7.21–7.36 (6 H, m), 7.53–7.56 (1 H, m) and 7.59 (1 H, br s, NH); δ_C(100.6 MHz; $CDCl_3$) 14.08 (CH_3), 15.54 (CH_3), 35.67 (*C*HCH$_3$), 52.02 (*C*HCH$_3$), 53.86 (*C*HPh), 111.52, 118.37, 119.44, 120.71, 125.43, 126.66, 127.84, 127.92, 128.50, 140.40, 142.90 and 143.20; *m/z* 261 (M^+, 86%), 246 (100), 217 (29), 170 (30) and 129 (28).

2-Methoxymethyl-3-phenyl-1,2,3,4-tetrahydrocyclopenta[*b*]-indole 11. 22%, mp 56 °C (Found: M^+, 277.1452; $C_{19}H_{19}NO$ requires *M*, 277.1466); $\nu_{max}(CHCl_3)/cm^{-1}$ 3065, 794, 703 and 675; δ_H(250 MHz; $CDCl_3$) 2.69 (1 H, dd, *J* 12 and 6, CH_2), 3.06–3.21 (2 H, m, CH_2 and C*H*CH_2O), 3.39 (3 H, s, OCH_3), 3.60 (2 H, d, *J* 6, CH_2O), 4.25 (1 H, d, *J* 6, C*H*Ph), 7.10–7.31 (8 H, m), 7.49 (1 H, m) and 7.69 (1 H, br s, NH); *m/z* 277 (M^+, 59%), 244 (28), 232 (100) and 115 (33).

5a,6,7,11c-Tetrahydro-5*H*-indeno[2′,1′;4,5]cyclopenta-[1,2-*b*]indole 12. 19%, mp 54 °C (Found: M^+, 245.1206; $C_{18}H_{15}N$ requires *M*, 245.1204); $\nu_{max}(CHCl_3)/cm^{-1}$ 3067, 793, 723 and 665; δ_H(400 MHz; $CDCl_3$) 2.72 (1 H, dm, *J* 14.5, indole-CH_2), 2.91 (1 H, dd, *J* 16.5 and 6, CH_2Ph), 3.2 (1 H, dd, *J* 14.5 and 7.6, indole-CH_2), 3.40 (1 H, dd, *J* 16.5 and 9.5, CH_2Ph), 4.71 (1 H, d, *J* 7.6, CH_2PH), 3.85–3.90 (1 H, m, CH_2CHCH_2), 7.04–7.44 (8 H, m) and 7.90 (1 H, br s, NH); δ_C(100.6 MHz; $CDCl_3$) 31.81 (CH_2CHCH_2), 40.29, 48.17, 50.68 (indole-CHPh), 111.43, 118.64, 119.50, 120.71, 123.67, 124.93, 126.43, 126.46, 126.96, 142.29 and 143.49; *m/z* 245 (M^+, 100%), 230 (18), 217 (21) and 130 (92).

2-Methyl-1-phenyl-1,2,3,4-tetrahydrocyclopenta[*b*]indole 15. 27%, mp 89 °C (Found: M^+, 247.1375; $C_{18}H_{17}N$ requires *M*, 247.1360); $\nu_{max}(CHCl_3)/cm^{-1}$ 3020, 1220, 775, 725 and 669; δ_H(250 MHz; $CDCl_3$) 1.36 (3 H, d, *J* 7, CH_3), 2.62 (1 H, dd, *J* 15 and 7, CH_2), 2.80 (1 H, m, C*H*CH_3), 3.18 (1 H, dd, *J* 15 and 7, CH_2), 3.96 (1 H, d, *J* 6.6, C*H*Ph), 6.94–7.40 (9 H, m) and 7.90 (1 H, br s, NH); *m/z* 247 (M^+, 100%), 232 (35), 218 (30) and 170 (30).

2,3,3-Trimethyl-1-phenyl-1,2,3,4-tetrahydrocyclopenta[*b*]-indole 16. 17%, mp 166 °C (Found: M^+, 275.1677; requires *M*, $C_{20}H_{21}N$ 275.1674); $\nu_{max}(CHCl_3)/cm^{-1}$ 3019, 1220, 791, 724 and 665; δ_H(400 MHz; $CDCl_3$) 1.11 (3 H, d, *J* 6.7, CHC*H*$_3$), 1.16 (3 H, s, CCH_3), 1.38 (3 H, s, CCH_3), 2.33 (1 H, m, C*H*CH_3), 3.87 (1 H, d, *J* 8.8, C*H*Ph), 6.96 (1 H, t, *J* 6), 7.08, (1 H, d, *J* 6), 7.09 (1 H, dt, *J* 7 and 1.5), 7.27 (1 H, m), 7.32 (5 H, m) and 7.83 (1 H, br s, NH); δ_C(100.6 MHz, $CDCl_3$) 11.49, 22.41, 26.26, 41.48, 51.27, 61.10, 111.37, 117.59, 118.80, 119.41, 120.46, 124.37, 126.08, 127.93, 128.08, 140.02, 143.92 and 151.45; *m/z* 275 (M^+, 100%), 260 (68) and 167 (27).

4a-Methyl-1,2,3,4,4a,5,10,10a-octahydroindeno[1,2-*b*]indole 17. 18%, Identical (except for rotation) with the sample prepared by the alternative route; data given below.

(−)-(1*R*,7a*R*)-7a-Methyl-5,6,7,7a-tetrahydroindan-1-ol 19

Dry trifluoroacetic acid (28 cm^3, 0.36 mol) was added dropwise with stirring to a suspension of sodium boranuide ($NaBH_4$) (4.4 g, 0.12 mol) in dry acetonitrile (36 cm^3) and dry dichloromethane (28 cm^3) at −40 °C under an atmosphere of nitrogen so that the temperature did not exceed −10 °C. The solution was then re-cooled to −40 °C and a solution of the diketone **18**,[12] (5 g, 0.03 mol) in dry dichloromethane (44 cm^3) was added dropwise to it with stirring. The mixture was stirred at −40 °C for 2 h, allowed to warm to ambient temperature, and the stirring was continued overnight. The mixture was then neutralised with aqueous sodium hydroxide (4 mol dm^{-3}; *ca.* 80 cm^3) and extracted with dichloromethane (3 × 50 cm^3). The combined dichloromethane extracts were washed with aqueous sodium hydroxide (2 mol dm^{-3}; 100 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure to give the *title compound* **19** (3.9 g, 82%) as a colourless solid, mp 84–86 °C (from diethyl ether–light petroleum) [lit.,[13] mp 86–88 °C for (1*S*,7a*S*)-isomer], $[\alpha]_D^{20}$ −65 (*c* 0.5, $CHCl_3$) {lit.,[13] $[\alpha]_D^{24}$ +75 (*c* 1.0, $CHCl_3$) for (1*S*,7a*S*)-isomer}; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3362, 2965, 2852 and 1676; δ_H(250 MHz; $CDCl_3$) 0.94 (3 H, s, CH_3), 1.15 (1 H, m), 1.68 (4 H, m), 1.77 (1 H, m), 1.97 (4 H, m), 2.43 (1 H, m), 3.65 [1 H, dd, *J* 7.8 and 1.9, C*H*(OH)] and 5.35 (1 H, d, *J* 2.9, C=C*H*); δ_C(62.5 MHz; $CDCl_3$) 16.76 (CH_3), 18.70 (CH_2), 25.08 (CH_2), 25.87 (CH_2), 29.39 (CH_2), 34.46 (CH_2), 42.91 (C), 82.23 [*C*H(OH)], 119.47 (C=CH) and 144.13 (C, *C*=CH); *m/z* 152 (M^+, 43%), 134 (28), 110 (25), 108 (52) and 93 (100).

(1*R*,3a*R*, 7a*R*)-7a-Methylhexahydroindan-1-ol 20

Palladium-on-carbon (10%; 0.2 g) and a catalytic amount of hydrochloric acid (2 mol dm^{-3}) were added to a solution of the alcohol **19** (2 g, 0.013 mol) in ethyl acetate (20 cm^3). The system was stirred at room temperature under an atmosphere of hydrogen (45 psi) overnight † after which it was filtered through Celite and washed with water. The ethyl acetate layer was dried ($MgSO_4$) and evaporated under reduced pressure. The residue was distilled at 80–85 °C at 0.5 mmHg to give the *title compound* (1.7 g, 72%) as a colourless semi-solid, $[\alpha]_D^{20}$ −14 (*c* 0.44, $CHCl_3$) {lit.,[10] $[\alpha]_D^{24}$ +20 (*c* 1.0, $CHCl_3$) for (1*S*,3a*S*,7a*S*)-isomer}; ν_{max}(film)/cm^{-1} 3395, 2926 and 2864; δ_H(250 MHz; $CDCl_3$) 0.98 (3 H, s, CH_3), 1.16 (1 H, m), 1.45 (10 H, m), 1.79 (2 H, m), 2.18 (1 H, m) and 3.83 [1 H, dd, *J* 3.7 and 3.2, C*H*(OH)]; δ_C(62.5 MHz; $CDCl_3$) 19.56 (CH_3), 21.71 (CH_2), 22.17 (CH_2), 25.90 (CH_2), 26.09 (CH_2), 31.33 (CH_2), 31.78 (CH_2), 41.85 (CH), 44.01 (C) and 79.93 [*C*H(OH)]; *m/z* 154 (M^+, 64%), 110 (80) and 95 (100). The product was contaminated with *ca.* 4% of the *trans*-(1*R*,3a*S*,7a*R*)-isomer; δ_H(250 MHz; $CDCl_3$) 0.74 (3 H, s, CH_3) and 3.65 [1 H, M, CH(OH)]; other peaks obscured.

(3a*R*,7a*R*)-7a-Methylhexahydroindan-1-one 21

A mixture of the alcohol **20** (1.3 g, 8.4 mmol) and pyridinium chlorochromate (2.7 g, 12.6 mmol) in dichloromethane (30 cm^3) was stirred at room temperature for 90 min. The mixture was

† 1 psi = 6.89 × 10^3 Pa.

filtered through Celite and washed with water. The dichloromethane layer was dried ($MgSO_4$) and the solvent removed under reduced pressure to give a brown residue, which was subjected to chromatography (silica, dichloromethane–light petroleum, 2:1) which gave the title compound **21** (1.2 g, 92%) as a pale yellow liquid, $[\alpha]_D^{20}$ −53 (*c* 0.6, $CHCl_3$) {lit.,[10] $[\alpha]_D^{24}$ −57 (*c* 1.0, $CHCl_3$)}; ν_{max}(film)/cm^{-1} 2957, 2859 and 1736; δ_H(250 MHz; $CDCl_3$) 1.04 (3 H, s, CH_3), 1.18 (1 H, m), 1.41 (5 H, m), 1.66 (3 H, m), 1.91 (2 H, m) and 2.37 (2 H, m); δ_C(62.5 MHz; $CDCl_3$) 20.92 (CH_3), 22.14 (CH_2), 22.35 (CH_2), 23.03 (CH_2), 26.72 (CH_2), 29.50 (CH_2), 34.95 (CH_2), 42.54 (CH), 48.30 (C) and 222.89 (CO); *m*/*z* 152 (M^+, 20%), 110 (35), 96 (43) and 81 (100). The product was contaminated with *ca.* 4% of the *trans*-(3a*S*,7a*R*)-isomer; δ_H(250 MHz; $CDCl_3$) 0.87 (3 H, s, CH_3); other peaks obscured.

(4a*R*,10a*R*)-4a-Methyl-1,2,3,4,4a,5,10,10a-octahydroindeno-[1,2-*b*]indole 17

A mixture of the ketone **21** (1.2 g, 8 mmol) and phenylhydrazine (0.8 cm^3, 8 mmol) was refluxed overnight in dry toluene (10 cm^3) using a Dean–Stark apparatus. After removal of the solvent, the resulting hydrazone was refluxed in ethane-1,2-diol (13 cm^3) for 5 h. The mixture was cooled, then diluted with water and extracted into diethyl ether. The combined diethyl ether extracts were washed with hydrochloric acid (2 mol dm^{-3}) and water, dried ($MgSO_4$) and evaporated under reduced pressure to give a brown residue, which was subjected to chromatography (silica, dichloromethane–light petroleum, 2:1) to give the *title compound* (0.71 g, 40%) as colourless crystals, mp 95–96 °C (from light petroleum), $[\alpha]_D^{20}$ −41 (*c* 0.46, $CHCl_3$) (Found: C, 85.4; H, 9.1; N, 6.4%; M^+, 225.1523; $C_{16}H_{19}N$ requires C, 84.8; H, 9.0; N, 6.2%; *M*, 225.1517); $\nu_{max}(CH_2Cl_2)$/cm^{-1} 3401, 3060, 2926 and 2851; δ_H(250 MHz; $CDCl_3$) 1.29 (3 H, s, CH_3), 1.42 (4 H, m), 1.58 (4 H, m), 2.49 (1 H, m, CH), 2.51 (1 H, m), 2.85 (1 H, m), 7.07 (2 H, m), 7.26 (1 H, m), 7.44 (1 H, m) and 7.63 (1 H, br s, NH); δ_C(62.5 MHz; $CDCl_3$) 21.67 (CH_2), 22.82 (CH_2), 24.54 (CH_3) 27.26 (CH_2), 28.89 (CH_2), 35.36 (CH_2), 41.28 (C), 50.60 (CH), 111.49 (CH), 115.55 (C), 118.51 (CH), 119.45 (CH), 120.14 (CH), 125.51 (C), 139.75 (C) and 151.89 (C); *m*/*z* 225 (M^+, 77%) and 210 (100). The product was contaminated with *ca.* 4% of the *trans*-(4a*R*,10a*S*)-isomer; δ_H(250 MHz; $CDCl_3$) 0.98 (3 H, s, CH_3); other peaks obscured.

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