Preparation of Tetrahydrobenz[*cd*]indoles from 1-Tetralones

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3,4-Bridged indoles (**5**) are prepared from readily available aromatic ketones (**1**) by conversion into the epoxides (**2**), ring opening with azide ion to give the azido alcohols (**3**), dehydration, and thermolysis of the resulting vinyl azides (**4**).

The tetrahydrobenz[*cd*]indole ring system is a key structural feature in a number of naturally occurring indoles, such as the well known ergot alkaloids,[1] α-cyclopiazonic acid,[2] and the more recently isolated hapalindoles.[3] Since many of these indoles possess important pharmacological properties, new routes to them are of interest,[4] and therefore we now report the full details of a novel approach to this, and related, ring systems which starts from readily available aromatic ketones.[5]

Results and Discussion

The route, which is shown in the Scheme, is based on cyclisation reactions of vinylnitrenes,[6] obtained by thermolysis of vinyl azides, and stems from our use of such reactions in the synthesis of the left-hand unit of the antitumour antibiotic CC-1065.[7] The required vinyl azides (**4**) were prepared from the commercially available aromatic ketones (**1**) by conversion into the corresponding epoxides (**2**), ring opening with azide ion, and dehydration of the resulting azido alcohols (**3**).

Preparation of Epoxides.—The epoxides were readily prepared from aromatic ketones by reaction with dimethylsulphoxonium methylide[8] in dimethyl sulphoxide (DMSO). Thus 1-tetralone (**1a**), and its 5- and 7-methoxy derivatives (**1b,c**) were converted into the corresponding epoxides in good yield. The epoxide derived from 6-methoxy-1-tetralone is known to be very unstable, rapidly rearranging into the corresponding acetaldehyde derivative,[9] and therefore was not investigated. Benzosuberone (**1d**) was also readily converted into its epoxide (**2d**), and the epoxides (**2e**), (**2f**), and (**2g**) were prepared from 4,4-dimethyl-1-tetralone,[10] dibenzosuberone, and benzocyclo-octanone[11] respectively, although in the case of dibenzosuberone, the more reactive dimethylsulphonium methylide had to be used. No spiro-epoxides could be obtained from anthrone due to rapid enolisation, or from chroman-4-one due to competing attack of the sulphur ylide at C-2 with formation of the cyclopropyl ketone (**6**) in 29% yield.[12] A variety of other conditions were tried to prepare these epoxides, but without success. To investigate the effect of an electron-withdrawing group, the glycidic ester (**2h**) of 1-tetralone was prepared using the Darzen's reaction.[13]

Ring Opening of Epoxides with Azide.—In general, this proved to be a troublesome step. The epoxides (**2a–d**) could be opened to the corresponding azido alcohols (**3**) using sodium azide and lithium chloride in dimethylformamide (DMF). The presence of lithium chloride is necessary for this reaction, which presumably involves the *in situ* formation of lithium azide. The epoxide (**2d**) required a higher temperature (100 °C) and longer reaction time (48 h), compared with the epoxides (**2a–c**) (65 °C, 15 h). Also the epoxides (**2e–h**) failed to react under the above conditions, or under a variety of other conditions, including sodium azide/lithium chloride in refluxing methanol,[6] or refluxing aqueous dioxane.[14] Furthermore, use of trimethylsilyl azide, or the more reactive titanium complex, $Ti(OPr^i)_2(N_3)_2$[15] proved unsuccessful.

Dehydration of Azido Alcohols.—The dehydration of the azido alcohols (**3**) to the vinyl azides (**4**) was carried out using thionyl chloride in pyridine. However, the desired vinyl azide was always accompanied by the unwanted endocyclic double-bond isomer. Fortunately, with the exception of the azido alcohol (**3b**), the required exocyclic alkene was the major product, and could be readily separated by chromatography.

Thermolysis of Vinyl Azides.—When heated in boiling mesitylene (b.p. 162–164 °C), the azide (**4a**) was converted into the known[16] tetrahydrobenz[*cd*]indole (**5a**) in good yield (67%). Similarly the methoxy substituted tetrahydrobenz[*cd*]indoles (**5b**) (70%) and (**5c**) (67%), and the cyclohept[*cd*]indole (**5d**) (72%) were obtained by thermolysis of the corresponding azides.

Thus the current work represents a new approach to tetrahydrobenz[*cd*]indoles and related compounds in that the pyrrole ring is built onto a readily available bicyclic aromatic ketone.

Experimental

270 MHz ^{1}H NMR spectra were recorded on a JEOL GSX 270 spectrometer, and IR spectra were recorded on a Perkin-Elmer 1 710 FT-IR spectrometer. For other general points, see ref. 7.

Preparation of Epoxides

Spiro[1,2,3,4-*tetrahydronaphthalene*-1,2′-*oxirane*] (**2a**).—Sodium hydride dispersion in mineral oil (60%; 0.88 g, 22.1 mmol) was washed with light petroleum (3 × 10 ml) and allowed to dry under an atmosphere of nitrogen. Trimethylsulphoxonium iodide (4.9 g, 22.1 mmol) was added, followed by dry DMSO (20 ml), which was added dropwise over 30 min. After the ensuing effervescence had ceased, the mixture was stirred for a further 30 min, after which time 1-tetralone (2.50 g, 17.1 mmol) in dry DMSO (10 ml) was added slowly. The mixture was stirred at room temperature for a further 15 min, then at 55 °C for a further 15 h. The solution was allowed to cool and water (20 ml) was cautiously added. The resulting solution was extracted with ether (3 × 30 ml), the combined extracts being washed with water (2 × 30 ml) and brine (20 ml) before drying ($MgSO_4$). Evaporation under reduced pressure gave a brown oil which was distilled in a Kugelrohr apparatus (oven

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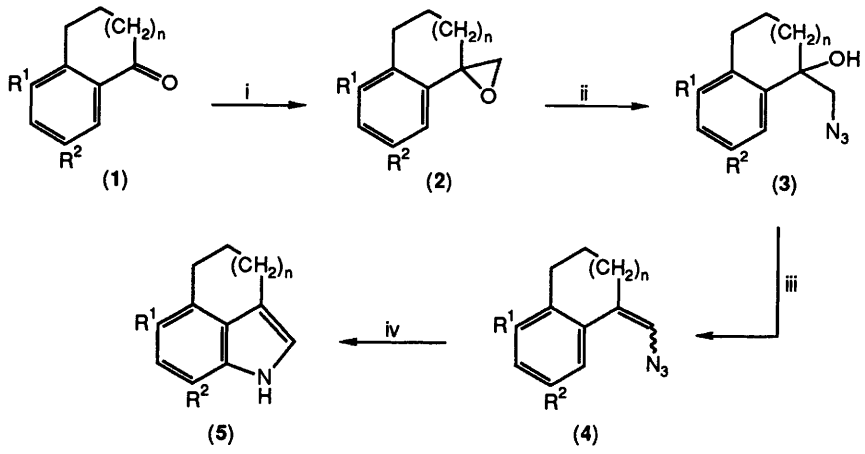
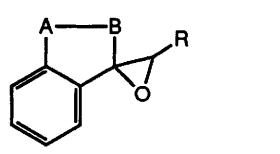


	R^1	R^2	n
a	H	H	1
b	OMe	H	1
c	H	OMe	1
d	H	H	2

Scheme. *Reagents and conditions:* i, $Me_2S^+OCH_2^-$, DMSO, 55 °C; ii, NaN_3, LiCl, DMF; iii, $SOCl_2$, pyridine, room temperature; iv, mesitylene, reflux.

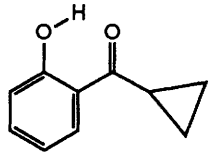


(**2e**) A-B = $Me_2CCH_2CH_2$, R = H

(**2f**) A-B = $CH_2CH_2C_6H_4$, R = H

(**2g**) A-B = $(CH_2)_5$, R = H

(**2h**) A-B = $(CH_2)_3$, R = CO_2Et



(**6**)

temperature, 110 °C, 0.45 mmHg) (lit.,[17] no b.p. given) to give the title compound (**2a**) (1.77 g, 65%) as a colourless liquid (Found: C, 82.5; H, 7.8. Calc. for $C_{11}H_{12}O$, C, 82.5; H, 7.6%); ν_{max}(film) 2 940, 2 863, 1 493, 1 457, 1 039, 918, 841, 786, 759, and 724 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.82–1.91 (1 H, m, 2-CH), 2.00–2.24 (3 H, m, 2-CH and 3-CH_2), 2.90–2.98 (2 H, m, 4-CH_2), 3.03 (1 H, d, *J* 5 Hz, 3'-CH), 3.07 (1 H, d, *J* 5 Hz, 3'-CH), and 7.10–7.25 (4 H, m, 5-, 6-, 7-, and 8-H); *m/z* 160 (M^+, 40%), 159 (24), 132 (24), 131 (100, *M* − CHO), 129 (50), 128 (26), 115 (27), and 91 (25, $C_7H_7^+$).

5-*Methoxyspiro*[1,2,3,4-*tetrahydronaphthalene*-1,2'-*oxirane*] (**2b**).—This compound was prepared from sodium hydride (60%; 0.30 g, 7.38 mmol), trimethylsulphoxonium iodide (1.62 g, 7.38 mmol), and 5-methoxy-1-tetralone (1.0 g, 5.67 mmol) as described above. Work-up and purification gave the *title compound* (**2b**) (0.63 g, 59%) as a colourless liquid, b.p. 95 °C at 0.30 mmHg (Kugelrohr) (Found: C, 75.5; H, 7.6. $C_{12}H_{14}O_2$ requires C, 75.8; H, 7.4%); ν_{max}(film) 2 941, 1 583, 1 474, 1 440, 1 341, 1 259, 1 186, 1 052, 780, and 718 cm^{-1}; δ_H(270 MHz; $CDCl_3$) 1.70–1.78 (1 H, m, 2-CH), 1.92–2.15 (3 H, m, 2-CH and 3-CH_2), 2.83 (2 H, t, *J* 4.5 Hz, 4-CH_2), 2.96 (1 H, d, *J* 5.4 Hz, 3'-CH), 3.00 (1 H, dd, *J* 5.4 and 1.2 Hz, 3'-CH), 3.83 (3 H, s, OMe), 6.73 (1 H, d, *J* 8.1 Hz, 6-H), 6.74 (1 H, d, *J* 8.1 Hz, 8-H), and 7.15 (1 H, t, *J* 8.1 Hz, 7-H); *m/z* 190 (M^+, 44%), 162 (18), 161 (100, *M* − CHO), 159 (17), 129 (10), 128 (10), 115 (16), and 91 (13, $C_7H_7^+$).

7-*Methoxyspiro*[1,2,3,4-*tetrahydronaphthalene*-1,2'-*oxirane*] (**2c**).—This compound was prepared from sodium hydride (60%; 0.30 g, 7.38 mmol), trimethylsulphoxonium iodide (1.62 g, 7.38 mmol), and 7-methoxy-1-tetralone (1.0 g, 5.67 mmol) as described above. Work-up and purification gave the *title compound* (**2c**) (0.51 g, 48%) as a colourless liquid, b.p. 110 °C at 0.23 mmHg (Kugelrohr) (Found: C, 75.8; H, 7.6. $C_{12}H_{14}O_2$ requires C, 75.8; H, 7.4%); ν_{max}(film) 2 938, 2 861, 2 837, 1 614, 1 500, 1 466, 1 435, 1 296, 1 236, 1 044, 918, 837, and 810 cm^{-1}; δ_H(270 MHz; $CDCl_3$) 1.78–2.00 (1 H, m, 2-CH), 1.95–2.12 (3 H, m, 2-CH and 3-CH_2), 2.79–2.85 (2 H, m, 4-CH_2), 2.96–2.97 (2 H, m, 3'-CH_2), 3.76 (3 H, s, OMe), 6.61 (1 H, d, *J* 2.9 Hz, 8-H), 6.77 (1 H, dd, *J* 8.3 and 2.9 Hz, 6-H), and 7.03 (1 H, d, *J* 8.3 Hz, 5-H); *m/z* 190 (M^+, 30%), 176 (12), 162 (15), 161 (100, *M* − CHO), 146 (9), and 91 (9, $C_7H_7^+$).

Spiro[6,7,8,9-*tetrahydro*-5H-*benzocycloheptene*-5,2'-*oxirane*] (**2d**).—This compound was prepared from sodium hydride (60%; 1.13 g, 28.2 mmol), trimethylsulphoxonium iodide (6.20 g, 28.2 mmol), and 1-benzosuberone (3.47 g, 21.7 mmol) as described above. Work-up and purification gave the *title compound* (**2d**) (3.35 g, 89%) as a colourless liquid, b.p. 80 °C at 0.20 mmHg (Kugelrohr) (Found: C, 82.8; H, 8.4. $C_{12}H_{14}O$ requires C, 82.7; H, 8.1%); ν_{max}(film) 2 928, 2 854, 1 489, 1 444, 942, 876, 761, and 748 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.42–2.07 (6 H, m, 6-, 7-, and 8-CH_2), 2.74 (1 H, dd, *J* 5.5 and 1.2 Hz, 3'-CH), 2.80–2.89 (2 H, m, 9-CH_2), 2.96 (1 H, d, *J* 5.5 Hz, 3'-CH), 7.08 (1 H, m, 3-H), 7.15 (1 H, d, *J* 3.5 Hz, 4-H), 7.17 (1 H, d, *J* 3.5 Hz, 1-H), and 7.36 (1 H, m, 2-H); *m/z* 174 (M^+, 47%), 173 (72), 145 (100, *M* − CHO), 143 (21), 129 (49), 128 (32), 115 (29), and 91 (19, $C_7H_7^+$).

4,4-*Dimethylspiro*[1,2,3,4-*tetrahydronaphthalene*-1,2'-*oxirane*] (**2e**).—This compound was prepared from sodium hydride (60%; 0.298 g, 7.46 mmol), trimethylsulphoxonium iodide (1.64 g, 7.46 mmol), and 4,4-dimethyl-1-tetralone[10] (1.0 g, 5.74 mmol) as described above. Work-up and purification gave the *title*

compound (**2e**) (0.79 g, 73%) as a colourless liquid, b.p. 100 °C at 0.46 mmHg (Kugelrohr) (Found: C, 82.95; H, 8.8. $C_{13}H_{16}O$ requires C, 82.9; H, 8.6%); ν_{max}(film) 2 960, 2 865, 1 489, 1 455, 1 030, 979, 879, 856, and 762 cm^{-1}; δ_H(270 MHz; $CDCl_3$) 1.33 (3 H, s, Me), 1.38 (3 H, s, Me), 1.61–1.72 (1 H, m, 2-CH), 1.80–1.95 (2 H, m, 3-CH_2), 2.21–2.35 (1 H, m, 2-CH), 2.91 (1 H, dd, *J* 5.4, 1.5 Hz, 3'-CH), 2.97 (1 H, d, *J* 5.4 Hz, 3'-CH), 7.05 (1 H, dd, *J* 7.8, 1.7 Hz, 8-H), 7.13 (1 H, td, *J* 7.3, 1.5 Hz, 7-H), 7.22 (1 H, td, *J* 7.3, 1.7 Hz, 6-H), and 7.31 (1 H, dd, *J* 7.8, 1.5 Hz, 5-H); *m/z* 188 (M^+, 26%), 159 (100, *M*-CHO), 143 (20), 129 (14), 128 (21), 117 (43), 115 (14), and 91 (14, $C_7H_7^+$).

Spiro[10,11-*dihydro*-5H-*dibenzo*[ad]*cycloheptene*-5,2'-*oxirane*] (**2f**).—Sodium hydride (60%; 1.25 g, 31.21 mmol) was washed with light petroleum under a nitrogen atmosphere as described above, and dry DMSO (50 ml) and THF (50 ml) were added. The mixture was cooled to 0 °C, and trimethylsulphonium iodide (6.37 g, 31.21 mmol) in DMSO (10 ml) was added over 3 min, followed by dibenzosuberone (5.0 g, 24.01 mmol) in THF (10 ml); the mixture gradually turned orange–brown. The cooling bath was removed and stirring was continued at room temperature for 15 h. Work-up and purification gave the *title compound* (**2f**) (4.82 g, 90%) as a colourless crystalline solid, m.p. 80–81 °C (Found: C, 86.5; H, 6.4. $C_{16}H_{14}O$ requires C, 86.45; H, 6.35%); ν_{max}(film) 3 012, 1 489, 1 448, 1 302, 1 018, 924, 782, and 585 cm^{-1}; δ_H(270 MHz; $CDCl_3$) 2.97–3.10 (2 H, m, 10- and 11-CH), 3.10 (2 H, s, 3'-CH_2), 3.40–3.55 (2 H, m, 10- and 11-CH), 7.10–7.25 (6 H, m, 1-, 2-, 3-, 7-, 8-, and 9-H), and 7.50–7.55 (2 H, m, 4- and 6-H); *m/z* 222 (M^+, 46%), 221 (100), 193 (32, *M* − CHO), 192 (10), 191 (31), 189 (19), 178 (14), and 165 (12).

Spiro[7,8,9,10-*tetrahydrobenzo-octene*-5,2'-*oxirane*] (**2g**).—This compound was prepared from sodium hydride (60%; 0.149 g, 3.73 mmol), trimethylsulphonium iodide (0.76 g, 3.73 mmol), and 7,8,9,10-tetrahydrobenzocyclo-octen-5(6*H*)-one[11] (0.50 g, 2.87 mmol) as described for compound (**2a**). Work-up and purification gave the *title compound* (**2g**) (0.28 g, 52%) as a colourless liquid, b.p. 100 °C at 0.34 mmHg (Kugelrohr) (Found: C, 82.7; H, 8.6. $C_{13}H_{16}O$ requires C, 82.9; H, 8.6%); ν_{max}(film) 2 932, 2 859, 1 495, 1 447, 964, 927, 813, 761, and 701 cm^{-1}; δ_H(270 MHz; $CDCl_3$) 1.45–2.08 (8 H, m, 5-, 6-, 7-, and 8-CH_2), 2.36 (2 H, d, *J* 4.9 Hz, 4-CH_2), 3.00 (1 H, d, *J* 3.7 Hz, 3'-CH), 3.04 (1 H, d, *J* 3.9 Hz, 3'-CH), and 7.23–7.37 (4 H, m, ArH); *m/z* 188 (M^+, 39%), 159 (5, *M* − CHO), 131 (14), 129 (22), 117 (15), 115 (17), 94 (22), and 91 (100, $C_7H_7^+$).

Ethyl Spiro[1,2,3,4-*tetrahydronaphthalene*-1,2'-*oxirane*]-3'-*carboxylate* (**2h**).—To a mixture of 1-tetralone (5.0 g, 34.2 mmol) and ethyl chloroacetate (6.76 g, 55.1 mmol) under nitrogen at −10 °C was added an ethanolic solution of sodium ethoxide, prepared by cautiously dissolving sodium metal (1.26 g, 54.7 mmol) in dry ethanol (10 ml). The mixture was stirred at −5 °C for 3 days and then allowed to warm to room temperature. Water (30 ml) was cautiously added and the resulting solution was extracted with ether (3 × 50 ml). The combined extracts were washed with water (4 × 50 ml) and brine (30 ml), dried ($MgSO_4$), and evaporated under reduced pressure to give a brown oil which was distilled in a Kugelrohr apparatus (oven temperature, 130 °C, 0.46 mmHg) to give the *title compound* (**2h**) (1.58 g, 20%) as a colourless liquid (Found: C, 72.5; H, 7.1. $C_{14}H_{16}O_3$ requires C, 72.4; H, 6.9%); ν_{max}(film) 2 940, 1 729 (ester C=O), 1 494, 1 452, 1 298, 1 250, 1 093, 1 046, and 744 cm^{-1}; δ_H(270 MHz; $CDCl_3$) 1.31 (3 H, t, *J* 7.2 Hz, CH_2CH_3), 1.75—1.95 (2 H, m, 3-CH_2), 2.05–2.15 (2 H, m, 2-CH_2), 2.75–2.82 (2 H, m, 4-CH_2), 3.63 (1 H, s, 3'-CH), 4.30 (2 H, q, *J* 7.2 Hz, CH_2CH_3), 6.98–7.02 (1 H, m, 8-H), and 7.12–7.26 (3 H, m, 5-, 6-, and 7-H); *m/z* 232 (M^+, 17%), 132 (11), 131 (100), 130 (8), 129 (14), 115 (8), and 91 (13, $C_7H_7^+$).

(2-*Hydroxyphenyl*) *Cyclopropyl Ketone* (**6**).—Sodium hydride dispersion in mineral oil (60%; 0.18 g, 4.39 mmol) was washed with light petroleum (3 × 10 ml) and allowed to dry under an atmosphere of nitrogen. Trimethylsulphoxonium iodide (0.97 g, 4.39 mmol) was added, followed by dry DMSO (10 ml), which was added dropwise over 30 min. After the ensuing effervescence had ceased, the mixture was stirred for a further 30 min, after which time chroman-4-one (0.50 g, 3.37 mmol) in dry DMSO (5 ml) was added slowly to produce a clear orange solution from the grey–white slurry. The mixture was stirred at room temperature for a further 15 min and then at 55 °C for a further 1 h. After this it was allowed to cool and water (20 ml) was cautiously added. The resulting solution was extracted with ether (3 × 30 ml) and the combined extracts were washed with water (2 × 30 ml) and brine, (20 ml) dried ($MgSO_4$), and evaporated under reduced pressure to give a brown oil. This was distilled in a Kugelrohr apparatus (oven temperature, 110 °C, 0.46 mmHg) to give the *title compound* (**6**) (0.16 g, 29%) as a colourless oil (Found: C, 73.8; H, 6.35. $C_{10}H_{10}O_2$ requires C, 74.05; H, 6.22%); ν_{max}(film) 3 011, 2 800–3 200 (H-bonded OH), 1 635 (C=O), 1 608, 1 489, 1 448, 1 404, 1 284, 1 209, 1 157, 994, and 753 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.04–1.13 (2 H, m, cyclopropyl CH_2), 1.26–1.32 (2 H, m, cyclopropyl CH_2), 2.63–2.75 [1 H, m, cyclopropyl $CH(CH_2)_2$], 6.89–6.99 (2 H, m, 3- and 5-H), 7.45 (1 H, td, *J* 6.8, 1.5 Hz, 4-H), 7.96 (1 H, dd, *J* 7.8, 1.5 Hz, 6-H), and 12.50 (1 H, s, OH); *m/z* 162 (M^+, 74%), 161 (15), 134 (14), 121 (100, *M* − cyclopropyl), 93 (15), and 65 (20).

Preparation of Azido Alcohols

1-*Azidomethyl*-1,2,3,4-*tetrahydronaphthalen*-1-*ol* (**3a**).—To the epoxide (**2a**) (0.81 g, 5.1 mmol) was added lithium chloride (0.28 g, 6.5 mmol), followed by sodium azide (0.44 g, 6.7 mmol) and dry DMF (10 ml). The mixture was stirred and heated at 65 °C for 15 h. The mixture was allowed to cool and water (30 ml) was added. The solution was extracted with ether (1 × 50, 2 × 30 ml) and the combined extracts were washed with water (2 × 30 ml) and brine (30 ml), dried ($MgSO_4$), and evaporated under reduced pressure to give a green–brown oil. This was purified by column chromatography (dichloromethane) to give the *title compound* (**3a**) (0.55 g, 53%) as a pale brown oil (Found: M^+, 147.0808. $C_{11}H_{13}N_3O - CH_2N_3$ requires 147.0810); ν_{max}(film) 3 391 (OH), 2 938, 2 104 (N_3), 1 451, 1 387, 1 350, 1 279, 1 085, 795, 764, and 733 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.72–1.95 (3 H, m, 2-CH and 3-CH_2), 2.09 (1 H, s, OH), 2.19–2.28 (1 H, m, 2-CH), 2.76–2.83 (2 H, m, 4-CH_2), 3.41 (1 H, d, *J* 12 Hz, $CHHN_3$), 3.59 (1 H, d, *J* 12 Hz, $CHHN_3$), 7.06–7.11 (1 H, m, 5-H), 7.16–7.26 (2 H, m, 6-H and 7-H), and 7.53–7.57 (1 H, m, 8-H); *m/z* 147 ($M^+ - CH_2N_3$, 100%), 144 (94), 118 (66), 115 (48), 91 (31, $C_7H_7^+$), 90 (31), and 89 (15).

1-*Azidomethyl*-5-*methoxy*-1,2,3,4-*tetrahydronaphthalen*-1-*ol* (**3b**).—The epoxide (**2b**) (0.54 g, 2.8 mmol) was treated with lithium chloride (0.16 g, 3.7 mmol), and sodium azide (0.24 g, 3.7 mmol) in dry DMF (10 ml) as described above to give the *title compound* (**3b**) (0.39 g, 59%) as a very pale brown oil which solidified *in vacuo* (Found: M^+, 233.1169. $C_{12}H_{15}N_3O_2$ requires 233.1164); ν_{max}(film) 3 571 (OH), 2 099 (N_3), 1 582, 1 345, 1 310, 1 261, 1 031, 937, 793, and 727 cm^{-1}; δ_H(270 MHz; $CDCl_3$) 1.69–1.79 (2 H, m, 3-CH_2), 1.90–1.97 (1 H, m, 2-CH), 2.18 (1 H, s, OH), 2.18–2.25 (1 H, m, 2-CH), 2.64–2.72 (2 H, m, 4-CH_2), 3.41 (1 H, d, *J* 12.7 Hz, $CHHN_3$), 3.59 (1 H, d, *J* 12.7 Hz, $CHHN_3$), 3.83 (3 H, s, OMe), 6.78 (1 H, dd, *J* 7.3 and 2.0 Hz, 6-H), and 7.17–7.26 (2 H, m, 7-H and 8-H); *m/z* 233 (M^+, 3%), 177 (*M* − CH_2N_3, 100%), 176 (26), 174 (14), 148 (13), 121 (29), and 91 (19, $C_7H_7^+$).

1-*Azidomethyl*-7-*methoxy*-1,2,3,4-*tetrahydronaphthalen*-1-*ol*

(**3c**).—The epoxide (**2c**) (0.10 g, 0.53 mmol) was treated with lithium chloride (29 mg, 0.68 mmol), and sodium azide (44 mg, 0.68 mmol) in dry DMF (10 ml) as described above to give the *title compound* (**3c**) (65 mg, 53%) as a pale brown oil (Found: M^+, 233.1172. $C_{12}H_{15}N_3O_2$ requires 233.1164); ν_{max}(film) 3 455 (OH), 2 936, 2 102 (N_3), 1 612, 1 500, 1 455, 1 283, 1 238, 1 042, 867, and 811 cm^{-1}; δ_H(270 MHz; $CDCl_3$) 1.77 (1 H, s, OH), 1.80–1.95 (2 H, m, 3-CH_2), 2.17–2.25 (2 H, m, 2-CH_2), 2.71–2.74 (2 H, m, 4-CH_2), 3.41 (1 H, d, *J* 12.7 Hz, CH*H*N_3), 3.59 (1 H, d, *J* 12.7 Hz, C*H*HN_3), 3.81 (3 H, s, OMe), 6.80 (1 H, dd, *J* 8.4 and 2.6 Hz, 6-H), 7.02 (1 H, d, *J* 8.5 Hz, 5-H), and 7.10 (1 H, d, *J* 2.6 Hz, 8-H); *m/z* 233 (M^+, 9%), 178 (12), 177 (M – $CH_2N_3^+$, 100%), 176 (17), 121 (19), 86 (13), 84 (21), and 49 (25).

5-*Azidomethyl*-6,7,8,9-*tetrahydro*-5H-*benzocyclohepten*-5-*ol* (**3d**).—The epoxide (**2d**) (1.0 g, 5.74 mmol) was treated with lithium chloride (0.30 g, 7.08 mmol), and sodium azide (0.46 g, 7.08 mmol) in dry DMF (20 ml) at 100 °C for 48 h as described above to give the *title compound* (**3d**) (0.88 g, 71%) as a pale yellow oil (Found: M^+, 161.0963. $C_{12}H_{15}N_3O - CH_2N_3$ requires 161.0966); ν_{max}(film) 3 451 (OH), 2 930, 2 857, 2 104 (N_3), 1 484, 1 447, 1 293, and 761 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.45–1.58 (1 H, m, 6-CH), 1.73–1.96 (4 H, m, 7- and 8-CH_2), 2.10–2.19 (1 H, m, 6-CH), 2.22 (1 H, s, OH), 2.83–2.89 (2 H, m, 9-CH_2), 3.57 (1 H, d, *J* 12 Hz, CH*H*N_3), 3.66 (1 H, d, *J* 12 Hz, C*H*HN_3), 7.08 (1 H, dd, *J* 7.5 and 1.5 Hz, 1-H), 7.16 (1 H, td, *J* 7.5 and 1.5 Hz, 2-H), 7.23 (1 H, td, *J* 7.5 and 2 Hz, 3-H), and 7.69 (1 H, dd, *J* 7.5 and 2 Hz, 4-H); *m/z* 161 (M – $CH_2N_3^+$, 100%), 160 (63), 132 (22), 131 (42), 117 (27), 104 (33), and 91 (68, $C_7H_7^+$).

Preparation of Vinyl Azides

1-*Azidomethylene*-3,4-*dihydronaphthalene* (**4a**).—The azido alcohol (**3a**) (0.25 g, 1.23 mmol) dissolved in dry pyridine (10 ml) was treated at room temperature with thionyl chloride (0.25 ml, 0.41 g, 3.44 mmol). The solution was stirred at room temperature for 15 min and then water (25 ml) was cautiously added. The mixture was extracted with ether (3 × 30 ml) and the combined extracts were washed with water (3 × 30 ml), saturated aqueous copper sulphate (3 × 30 ml), water (2 × 30 ml), and brine (30 ml) dried ($MgSO_4$), and evaporated under reduced pressure to give a golden oil. This was purified by column chromatography (light petroleum) to give first the title compound (**4a**) (0.13 g, 56%) as a very pale brown oil which was characterised on the basis of IR and NMR data; ν_{max}(film) 2 936, 2 104 (N_3), 1 633, 1 450, 1 278, and 764 cm^{-1}; δ_H(200 MHz; $CDCl_3$) 1.78 (2 H, quintet, *J* 6 Hz, 3-CH_2), 2.47 (2 H, td, *J* 6 and 2 Hz, 2-CH_2), 2.75 (2 H, t, *J* 6 Hz, 4-CH_2), 6.71 (1 H, t, *J* 2 Hz, C=C*H*N_3), 7.10–7.15 (3 H, m, 5-, 6-, and 7-H), and 7.41 (1 H, dd, *J* 9 and 4 Hz, 8-H). This was followed by the isomeric dehydration product, 1-azidomethyl-3,4-dihydronaphthalene (34 mg, 15%), obtained as a pale brown oil; ν_{max}(film) 2 930, 2 099 (N_3), 1 573, 1 460, 1 265, and 789 cm^{-1}; δ_H(200 MHz; $CDCl_3$) 2.36 (2 H, m, 3-CH_2), 2.80 (2 H, t, *J* 8 Hz, 4-CH_2), 4.11 (2 H, s, CH_2N_3), 6.13 (1 H, t, *J* 4.5 Hz, 2-CH), and 7.14—7.28 (4 H, m, 5-, 6-, 7-, and 8-H).

1-*Azidomethylene*-3,4-*dihydro*-5-*methoxynaphthalene* (**4b**).—The azido alcohol (**3b**) (0.12 g, 0.52 mmol) was treated at room temperature with thionyl chloride (0.68 ml, 1.10 g, 9.28 mmol) in dry pyridine (10 ml) as described above. Work-up gave an oil which was purified by column chromatography (light petroleum) to give first the title compound (**4b**) (35.4 mg, 32%) as a very pale brown oil which was characterised on the basis of IR and NMR data; ν_{max}(film) 2 924, 2 109 (N_3), 1 623, 1 572, 1 474, 1 455, 1 435, 1 328, 1 253, 1 127, and 780 cm^{-1}; δ_H(270 MHz; $CDCl_3$) 1.79 (2 H, quintet, *J* 6.4 Hz, 3-CH_2), 2.45 (2 H, td, *J* 6.4 and 1.5 Hz, 2-CH_2), 2.71 (2 H, t, *J* 6.4 Hz, 4-CH_2), 3.82 (3 H, s, OMe), 6.70–6.74 (2 H, m, C=C*H*N_3 and 6-H), and 7.04–7.14 (2 H, m, 7- and 8-H). This was followed by the isomeric dehydration product, 1-azidomethyl-3,4-dihydro-5-methoxynaphthalene (50.5 mg, 46%), obtained as a pale brown oil; ν_{max}(film) 2 938, 2 099 (N_3), 1 574, 1 462, 1 439, 1 347, 1 325, 1 261, 1 048, and 781 cm^{-1}; δ_H(270 MHz; $CDCl_3$) 2.30–2.38 (2 H, m, 3-CH_2), 2.81 (2 H, t, *J* 8.3 Hz, 4-CH_2), 3.85 (3 H, s, OMe), 4.12 (2 H, d, *J* 0.7 Hz, CH_2N_3), 6.15 (1 H, t, *J* 4.6 Hz, 2-H), 6.84 (1 H, d, *J* 8.3 Hz, 6-H), 6.94 (1 H, d, *J* 7.8 Hz, 8-H), and 7.20 (1 H, t, *J* 8.1 Hz, 7-H).

1-*Azidomethylene*-3,4-*dihydro*-7-*methoxynaphthalene* (**4c**).—The azido alcohol (**3c**) (17 mg, 0.076 mmol) was treated at room temperature with thionyl chloride (0.10 ml, 0.16 g, 1.37 mmol) in dry pyridine (5 ml) as described above. Work-up gave an oil which was purified by column chromatography (dichloromethane) to give the title compound (**4c**) (12 mg, 71%) as a pale brown oil which was characterised on the basis of IR and NMR data; ν_{max}(film) 2 928, 2 099 (N_3), 1 627, 1 602, 1 497, 1 466, 1 274, 1 241, 1 223, and 1 044 cm^{-1}; δ_H(270 MHz; $CDCl_3$) 1.72–1.82 (2 H, m, 3-CH_2), 2.45 (2 H, td, *J* 5.5 and 1.8 Hz, 2-CH_2), 2.69 (2 H, t, *J* 6.3 Hz, 4-CH_2), 3.80 (3 H, s, OMe), 6.71 (1 H, m, C=C*H*N_3), 6.74 (1 H, dd, *J* 8.5 and 2.7 Hz, 6-H), 6.94 (1 H, d, *J* 2.7 Hz, 8-H), and 7.01 (1 H, d, *J* 8.5 Hz, 5-H).

5-*Azidomethylene*-6,7,8,9-*tetrahydro*-5H-*benzocycloheptene* (**4d**).—The azido alcohol (**3d**) (0.76 g, 3.5 mmol) was treated at room temperature with thionyl chloride (0.72 ml, 1.17 g, 9.81 mmol) in dry pyridine (10 ml) as described above. Work-up gave an oil which was purified by column chromatography (light petroleum) to give first the title compound (**4d**) (0.23 g, 33%) as a pale yellow oil which was characterised on the basis of IR and NMR data; ν_{max}(film) 2 927, 2 854, 2 104 (N_3), 1 635, 1 446, 1 297, 1 252, and 758 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.69—1.78 (4 H, m, 7- and 8-CH_2), 2.34–2.41 (2 H, m, 6-CH_2), 2.75 (2 H, t, *J* 5.2 Hz, 9-CH_2), 6.21 (1 H, s, C=C*H*N_3), and 7.09–7.20 (4 H, m, 1-, 2-, 3-, and 4-H). This was followed by the isomeric dehydration product, 5-azidomethyl-8,9-dihydro-7*H*-benzocycloheptene (0.12 g, 17%) obtained as a colourless oil; ν_{max}(film) 2 931, 2 861, 2 108 (N_3), 1 602, 1 451, 1 209, and 815 cm^{-1}; δ_H(270 MHz; $CDCl_3$) 2.32–2.39 (4 H, m, 7- and 8-CH_2), 2.89 (2 H, t, *J* 7.1 Hz, 9-CH_2), 4.13 (2 H, s, CH_2N_3), 6.26 (1 H, t, *J* 4.7 Hz, 6-H), and 7.07–7.30 (4 H, m, 1-, 2-, 3-, and 4-H).

Preparation of Indoles

1,3,4,5-*Tetrahydrobenz*[cd]*indole* (**5a**).—A solution of the azide (**4a**) (72 mg, 0.39 mmol) in mesitylene (10 ml) under nitrogen was quickly heated to reflux for 45 min. The solution was allowed to cool and the solvent was removed under reduced pressure. The residue was chromatographed (dichloromethane) to give the title compound (**5a**) (41 mg, 67%) as a colourless crystalline solid, m.p. 54–56 °C (lit.,[16] 55–56 °C); ν_{max}(Nujol) 3 411 (indole NH), 2 928, 1 606, 1 445, 1 345, 1 083, 1 028, 775, and 749 cm^{-1}; δ_H(270 MHz; $CDCl_3$) 2.06 (2 H, quintet, *J* 6 Hz, 4-CH_2), 2.87 (2 H, td, *J* 6 and 1.2 Hz, 3-CH_2), 2.95 (2 H, t, *J* 6 Hz, 5-CH_2), 6.82 (1 H, d, *J* 1.2 Hz, 2-H), 6.84 (1 H, d, *J* 1 Hz, 6-H), 7.11 (2 H, m, 7-H and 8-H), and 7.72 (1 H, br s, 1-H); *m/z* 157 (M^+, 100%), 156 (90), 130 (23), 129 (35), 128 (16), and 104 (19).

6-*Methoxy*-1,3,4,5-*tetrahydrobenz*[cd]*indole* (**5b**).—A solution of the azide (**4b**) (20 mg, 0.093 mmol) in mesitylene (10 ml) under nitrogen was quickly heated to reflux for 45 min. Work-up and chromatography (dichloromethane) gave the *title compound* (**5b**) (12.2 mg, 70%) as a colourless crystalline solid, m.p. 94–95 °C (Found: M^+, 187.0997. $C_{12}H_{13}NO$ requires

187.0997); ν_{max}($CHCl_3$) 3 482 (indole NH), 3 053, 2 985, 2 937, 1 504, 1 440, 1 265, 1 240, 1 064, 783, and 757 cm^{-1}; δ_H(270 MHz; $CDCl_3$) 1.99–2.08 (2 H, m, 4-CH_2), 2.83 (2 H, td, *J* 5.6 and 1.1 Hz, 3-CH_2), 2.91 (2 H, t, *J* 5.9 Hz, 5-CH_2), 3.87 (3 H, s, OMe), 6.84 (1 H, t, *J* 1.1 Hz, 2-H), 6.86 (1 H, d, *J* 8.4 Hz, 7-H), 7.10 (1 H, d, *J* 8.4 Hz, 8-H), and 7.67 (1 H, br s, 1-H); *m/z* 187 (M^+, 77%), 172 (38), 157 (33), 156 (36), 150 (45), 57 (100), and 41 (48).

8-*Methoxy*-1,3,4,5-*tetrahydrobenz*[cd]*indole* (**5c**).—A solution of the azide (**4c**) (12 mg, 0.053 mmol) in mesitylene (10 ml) under nitrogen was quickly heated to reflux for 45 min. Work-up and chromatography (dichloromethane) gave the title compound (**5c**) (6.7 mg, 67%) as a colourless crystalline solid, m.p. 70–71 °C (lit.,[4] 71–72 °C) (Found: M^+, 187.1001. Calc. for $C_{12}H_{13}NO$, 187.0997); ν_{max}(Nujol) 3 481 (indole NH), 3 007, 2 936, 1 519, 1 404, 1 280, 1 255, 1 065, and 795 cm^{-1}; δ_H(270 MHz; $CDCl_3$) 1.99–2.08 (2 H, m, 4-CH_2), 2.81–2.86 (2 H, m, 3-CH_2), 2.86–2.91 (2 H, m, 5-CH_2), 3.93 (3 H, s, OMe), 6.56 (1 H, d, *J* 7.6 Hz, 7-H), 6.73 (1 H, dt, *J* 7.6 and 1.0 Hz, 6-H), 6.83 (1 H, t, *J* 1.0 Hz, 2-H), and 7.97 (1 H, br s, 1-H); *m/z* 187 (M^+, 100%), 186 (17), 172 (45), 156 (8), 154 (9), 149 (28), and 144 (7).

3,4,5,6-*Tetrahydrocyclohept*[cd]*indole* (**5d**).—A solution of the azide (**4d**) (0.21 g, 1.04 mmol) in mesitylene (10 ml) under nitrogen was quickly heated to reflux for 45 min. Work-up and chromatography (dichloromethane) gave the *title compound* (**5d**) (0.13 g, 72%) as a colourless crystalline solid, m.p. 65–67 °C (Found: M^+, 171.1044. $C_{12}H_{13}N$ requires 171.1048); ν_{max}(Nujol) 3 392 (indole NH), 2 926, 2 855, 1 462, 1 418, 1 378, 1 363, 775, and 748 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.90–2.08 (4 H, m, 4- and 5-CH_2), 2.97 (2 H, t, *J*, 5.3 Hz, 3-CH_2), 3.17 (2 H, t, *J* 5.6 Hz, 6-CH_2), 6.91 (1 H, dd, *J* 7.5 and 1.3 Hz, 7-H), 6.98 (1 H, t, *J* 1.3 Hz, 2-H), 7.09 (1 H, t, *J* 7.5 Hz, 8-H), 7.19 (1 H, d, *J* 7.5 Hz, 9-H), and 7.94 (1 H, br s, 1-H); *m/z* 171 (M^+, 100%), 170 (48), 143 (54), 130 (15), 115 (15), 77 (13), and 71 (14).

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