The Preparation of 2,3-Dihydro-1*H*-pyrrolo[1,2-*a*]indole, 2,3-Dihydro-9-methyl-1*H*-pyrrolo[1,2-*a*]indole, 1,2,2a,3,4,5-Hexahydropyrrolo[3,2,1-*jk*]-carbazole, and 2,3,3a,4,5,6-Hexahydro-1*H*-pyrido[3,2,1-*jk*]carbazole

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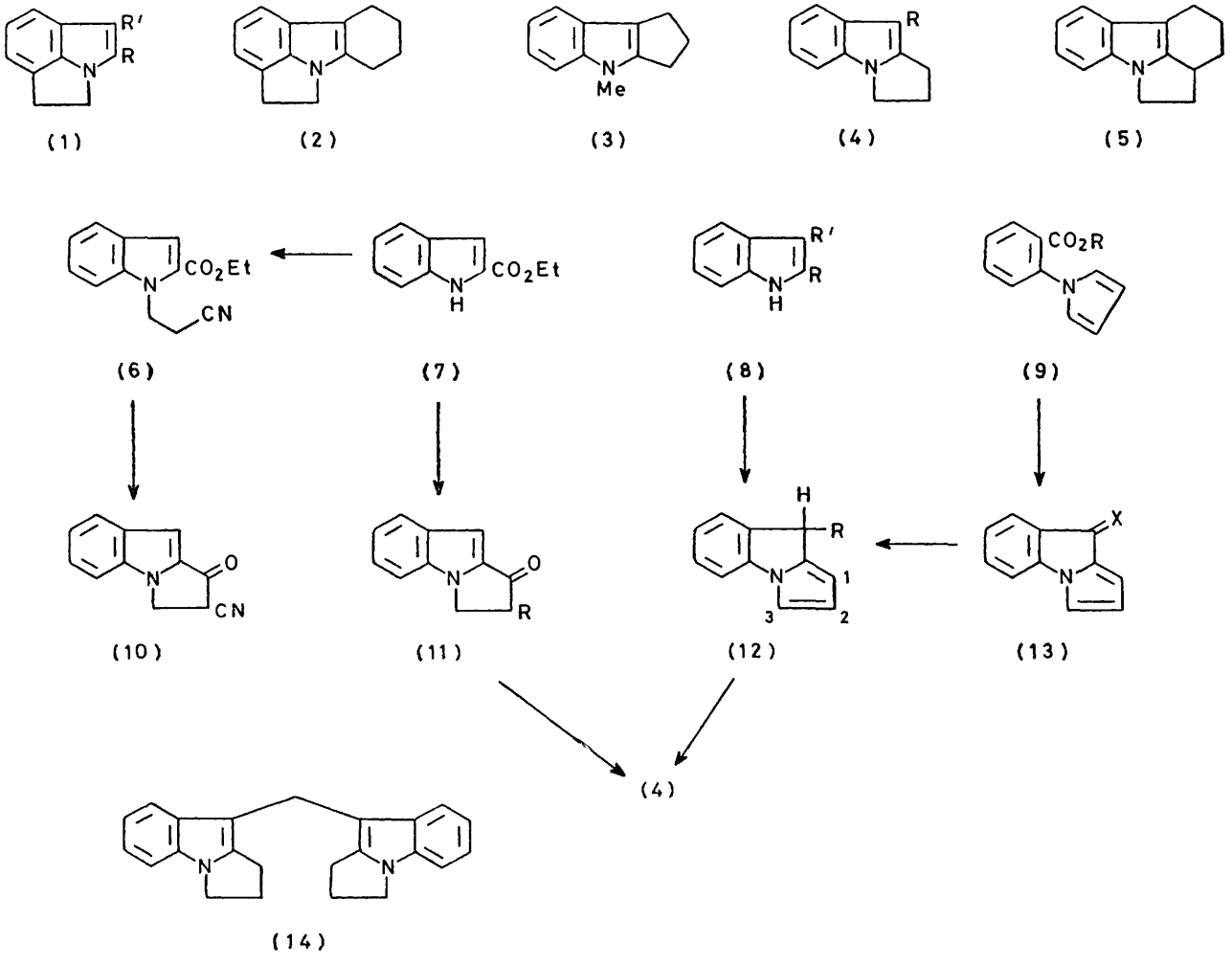
Several routes for the preparation of the four compounds listed in the title have been investigated to decide on methods suitable for obtaining the materials in quantity.

We have investigated the reactions of 'strained' indoles with arenesulphonyl azides and noted the reactivity of indoles containing fused or bridging five-membered rings, *e.g.* (1),[1] (2),[2] and (3).[3] It was decided to extend this work by examining the reactions of indoles of types (4) and (5). Here we report the preparation of the indoles.

RESULTS AND DISCUSSION

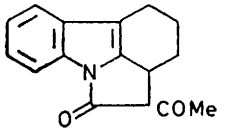
Syntheses of pyrrolo[1,2-*a*]indole systems have been briefly reviewed.[4] Most of the routes have been directed towards syntheses of the mitomycin antibiotics, molecules containing a quinonoid ring. Three routes to (4; R = H) were examined. Ethyl indole-2-carboxylate (7) was condensed with ethyl acrylate in the presence of sodium hydride forming (11; R = CO_2Et).[5] Hydrolysis, decarboxylation, and Wolff–Kishner reduction then afforded (4; R = H), the overall yield being only 1.5% (based on ethyl pyruvate). Treatment of (7) with acrylonitrile afforded (6) [6] and hence the cyanoketone (10) in good yield. However the nitrile (10) could not be hydrolysed to the desired acid. Since the overall yield of (4) was very poor a second route involving the reaction [7] of triphenylvinylphosphonium bromide [8] with



indole-2-carbaldehyde (8; R = CHO, R′ = H)[9] was examined. The n.m.r. spectrum of the product (12) of this reaction confirmed that the compound had the 9*H* structure[10] and was not in the 3*H* form.[7] Hydrogenation then afforded (4; R = H). Although the yields were satisfactory we considered that the route was unsuitable for large-scale synthesis. We then synthesised (4; R = H) from methyl anthranilate and 2,5-dimethoxytetrahydrofuran *via* (9),[11] (13; X = O),[10,11] (13; X = $NNHCONH_2$),[12] and (12; R = H). Modifications (see Experimental section) of the published methods gave a 26% overall yield of (4; R = H).

The reaction of 2-formyl-3-methylindole[13] with triphenylvinylphosphonium bromide afforded compound (12; R = Me); the n.m.r. spectrum of this compound showed clearly that it was in the 9*H* form (split CMe signal) and it did not have the 3*H* structure. Hydrogenation of (12; R = Me) was sluggish and only a 15% yield of (4; R = Me) was obtained. Compound (4; R = Me) was satisfactorily prepared by formylation of (4; R = H) giving (4; R = CHO).[5] Reduction (LAH) of (4; R = CHO) then afforded (4; R = Me) in good yield. During one reduction the di-indolylmethane (14) was isolated (15% yield). The structure of this compound was proved by its synthesis from (4; R = H) and formaldehyde. Compound (14) arises *via* the 3-indolylmethanol (4; R = CH_2OH) (see ref. 14 for further examples).

The synthesis of compound (5) proved to be more difficult. A derivative (15) of this ring system has been reported;[15] this compound was obtained by treating the pyridinium salt (16) with ethyl acetoacetate. All attempts to repeat this preparation failed; others[16] have also reported failure. 2-Acetylpyrrole has been condensed with triphenylvinylphosphonium bromide to form a pyrrolizine derivative;[7] and we therefore attempted to condense 1-oxotetrahydrocarbazole (17)[17] with triphenylvinylphosphonium bromide to obtain (18). Hydrogenation of (18) would then yield (5) [*cf.* the reduction (12)→(4)]. However, all attempts to prepare (18) gave either starting materials or tar. The ketone (17) was condensed with acrylonitrile affording (19; R = CN) in good yield; base-catalysed (NaH) cyclisation of this compound failed, and an attempt at cyclisation with polyphosphoric acid gave a good yield of the amide (19; R = $CONH_2$).



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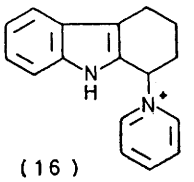

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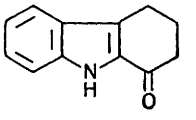

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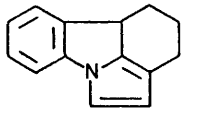

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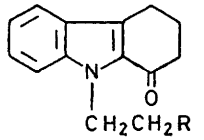
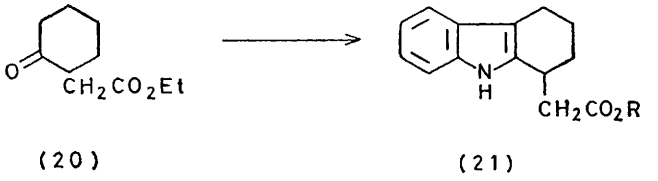


(19)

The successful route to (5) was developed from the keto-ester (20).[18] The Fischer synthesis gave the ester (21; R = Et);[16] using the conditions suggested by Palmer[19] the yield of (21; R = Et) was increased to 75%. Cyclisation of the acid (21; R = H) gave a



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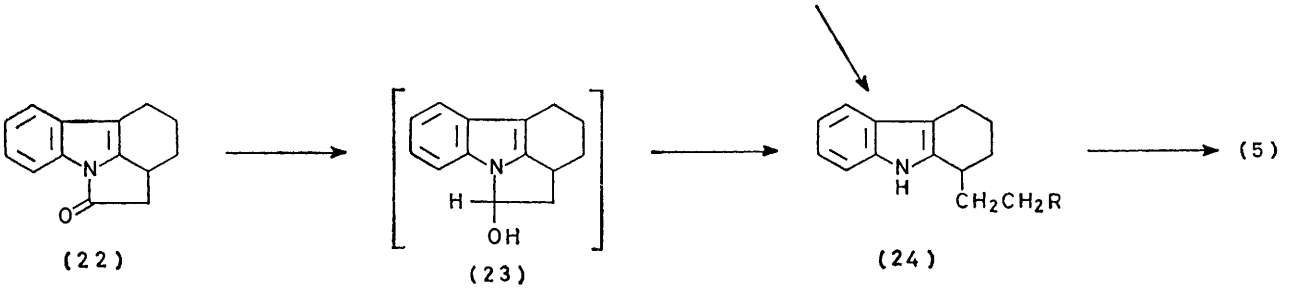

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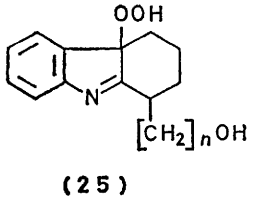

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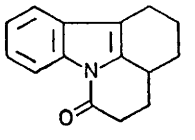

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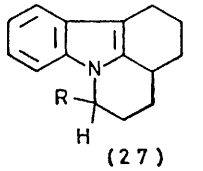

(27)

moderate yield of the amide (22). LAH reduction of (22) produced the alcohol (24; R = OH), presumably *via* (23), the carbinolamine ring of (23) opening to the aldehyde form which was then reduced. Diborane afforded a mixture of products; (5) could not be detected (t.l.c.) in the mixture. Reduction of the ester (21; R = Et) afforded the alcohol (24; R = OH); on one occasion the hydroperoxyindolenine (25; $n = 2$) was isolated (10% yield). The hydroperoxy compound (25; $n = 3$) has been isolated [20] from a similar LAH reduction. Treatment of the alcohol (24; R = OH) with tosyl chloride gave (24; R = OTs); the reaction conditions are critical. In some experiments mixtures of products were obtained including the unstable chloride (24; R = Cl). The pure tosyl derivative cyclised in the presence of $KOBu^t$ giving an excellent yield of (5).

The amide (26) [21] was reduced by diborane, and by sodium borohydride in pyridine,[22] to the alcohol (27; R = OH). However sodium borohydride in THF containing trifluoroacetic acid [23] gave an excellent yield of (27; R = H).

EXPERIMENTAL

General details and instruments use have been reported previously.[24] U.v. spectra were recorded on solutions in ethanol and n.m.r. spectra on solutions in $CDCl_3$ unless otherwise stated; i.r. spectra were recorded on Nujol mulls. Column and t.l.c. chromatography were carried out on silica using chloroform as eluant unless otherwise stated.

2,3-*Dihydro*-1H-*pyrrolo*[1,2-a]*indole* (4; R = H).—(*a*) Recrystallised (EtOH) ethyl pyruvate phenylhydrazone (40 g) was dissolved in AcOH (200 ml; 50 °C) and $BF_3{\cdot}Et_2O$ (25 g) added. After boiling for 3 h water (150 ml) was added and the solid collected. Recrystallisation (EtOH) gave (7) (55% yield), m.p. 119—121 °C.[25] Using unpurified phenylhydrazone or formic acid as reaction medium gave very poor yields.

Sodium hydride (0.005 mol) was added to a solution of ethyl acrylate (0.005 mol) and (7) (0.005 mol) in dioxan (50 ml). The mixture was refluxed for 8 h and then kept at room temperature for 16 h. The usual work-up gave a gum, and chromatography afforded (11; R = CO_2Et) (yield 30%), needles, m.p. 103 °C (EtOH) (lit.,[5] 100 °C); τ 2.34 (1 H, d, *J* 8 Hz), 2.55 (4 H, m, Ar), 5.18—5.95 [5 H, m, C(2)H + C(3)H_2 + OCH_2CH_3], and 8.75 [3 H, t, *J* 7 Hz, OCH_2-CH_3]. Hydrolysis (aqueous AcOH) [5] of (11; R = CO_2Et) gave (11; R = H), needles, (AcOH), m.p. 145—148 °C (lit.,[5] 145—146 °C); τ 2.27 (1 H, d, *J* 8 Hz), 2.55—3.0 (3 H, m), 3.06 [1 H, s, C(9)H], 5.70 [2 H, t, *J* 7 Hz, C(3)H_2], and 6.89 [2 H, t, *J* 7 Hz, C(2)H_2]. Reduction [5] of (11; R = H) afforded (4; R = H) which was purified by chromatography followed by recrystallisation ($CHCl_3$–MeOH) (yield 25%), m.p. 78—80 °C (lit.,[5,12] 79—80 °C); τ 2.4—3.1 (3 H, m), 3.84 [1 H, s, C(9)H], 5.95 [2 H, t, *J* 7 Hz, C(3)H_2], 7.00 [2 H, t, *J* 7 Hz, C(1)H_2], and 7.2—7.6 [2 H, m, C(2)H_2]; *m/e* 157 (M^+, 100%), 156 (83%), 154 (12%), 129 (156 − C_2H_3, 17%, *m** 106.6), and 128 (14%).

Compound (6) (m.p. 85—86 °C, lit.,[6] 86—87 °C) (2.4 g) was dissolved in Et_2O (250 ml) containing NaH (0.3 g), and the mixture stirred for 18 h. Water (200 ml) was then added and the aqueous layer separated and acidified (conc. HCl). The ***nitrile*** (10) was collected and recrystallised (EtOH), needles, m.p. 175 °C (decomp.) (yield 85%) (Found: C, 73.3; H, 4.1; N, 14.3. $C_{12}H_8N_2O$ requires C, 73.5; H, 4.1; N, 14.2%); $\lambda_{max.}$ 242 (sh), 262 (sh), 282 (sh), and 325 nm (ε 16 100, 3 800, 3 400, and 20 400); $\nu_{max.}$ 1 538, 1 715, and 2 260 cm^{-1}; τ 2.15—2.95 (5 H, m), 5.16 [1 H, q, *J* 12 and 6 Hz, C(3)H], 5.44 [1 H, q, *J* 12 and 10 Hz, C(3)H], and 5.76 [1 H, q, 10 and 6 Hz, C(2)H]; *m/e* 196 (M^+, 61%), 143 (100%, *m** 104.3), 115 (143 − CO, 63%, *m** 92.4), and 114 (14%). All attempts at hydrolysis gave tars.

(*b*) Reduction (LAH) of (7) gave (8; R = CH_2OH, R′ = H) which was oxidised to the aldehyde (8; R = CHO, R′ = H) [9] (yield 45%). This aldehyde was treated with sodium hydride and triphenylvinylphosphonium bromide [7,8] affording 9*H*-pyrrolo[1,2-*a*]indole (12; R = H) (yield 76%), plates (EtOH), m.p. 90—91 °C (lit.,[10] 90—91 °C); τ 2.5—3.05 (5 H, m), 3.64 [1 H, t, *J* 3 Hz, C(2)H], 3.85—4.0 [1 H, m, C(1)H], and 6.20 [2 H, s, C(9)H_2]; *m/e* 155 (M^+, 95%), 154 (100%), 128 (9%), and 127 (18%). Hydrogenation in ethanol (Rh–C, 5%, 3 atm, 5 h) gave (4; R = H) (yield 75%), m.p. 78—80 °C. At atmospheric pressure hydrogenation was very slow (48 h) (yield 25% of pure material).

(*c*) Methyl anthranilate (151 g, 1 mol) was converted [11] into methyl 2-(1-pyrrolyl)benzoate (9; R = Me) and hence into the acid (9; R = H) (yield 85%), m.p. 105.5—106.5 °C (lit.,[11] 106—107 °C). Phosphorus pentachloride (18 g) was added to a solution of (9; R = H) (15 g) in benzene (300 ml). After 1 h stannic chloride (15 ml) was added and the mixture stirred (0.75 h). Ice (500 g) and HCl (2M, 500 ml) were then added. The solid which separated was collected and extracted with benzene (200 ml); the benzene layer of the filtrate was then separated and the aqueous layer extracted with benzene. The combined organic layers were concentrated yielding (13; X = O) (yield 90%), m.p. 115—120 °C (lit.,[11,12] 121—122, 122—122.5 °C). Extraction of the reaction mixture with chloroform followed by distillation [10] of the product gave only a 10% yield, most of the material decomposing during distillation. Recrystallisation of the distillate gave yellow prisms, m.p. 123—124 °C. The semicarbazone, m.p. 210—212 °C (lit.[12] 212—214 °C), yield 90%, was reduced [12] giving (12; R = H), m.p. 87—90 °C (lit.[12] 89—90 °C) which was reduced to (4; R = H) [see under (*b*)].

2,3-*Dihydro*-9-*methyl*-1H-*pyrrolo*[1,2-a]*indole* (4; R = Me).—(*a*) Phosphorus oxychloride (25 ml) was added dropwise to dimethylformamide (20 g) at 10 °C. 1,2-Dichloroethane (100 ml) was added followed by 3-methylindole (26 g) in dichloroethane (150 ml) at 10—20 °C. The mixture was then boiled (15 min). Ice (100 g) was then added followed by sodium hydroxide solution (2N) to pH 9. The mixture was then boiled (5 min), cooled, and the organic phase separated. Evaporation of the solvent and recrystallisation of the residue (MeOH) gave prisms, m.p. 136—141 °C (lit.,[13] 138—140 °C) (yield 20%). 2-Formyl-3-methylindole (3.3 g) was added during 10 min to a suspension of NaH (0.5 g) in ether (150 ml). After stirring for 10 min triphenylvinylphosphonium bromide (7.4 g) was added, the mixture boiled (20 h), the solution filtered, and the solvent was removed. The crude product was extracted with pentane (5 × 25 ml) (yield 80%). Sublimation (40 °C/0.01 mmHg) of a sample gave 9-*methyl*-9H-*pyrrolo*[1,2-a]-*indole* (12; R = Me), prisms, m.p. 48—49 °C (Found: C, 85.2; H, 6.4; N, 8.3. $C_{12}H_{11}N$ requires C, 85.2; H, 6.5; N, 8.3%); $\lambda_{max.}$ 264 and 292 nm (ε 16 900 and 2 500); τ 2.6—3.05 (5 H, m), 3.65 [1 H, t, *J* 2.5 Hz, C(2)H], 3.85—3.95

[1 H, m, C(1)H], 6.01 [1 H, q, *J* 8 Hz, C(9)H], and 8.52 [3 H, d, *J* 8 Hz, C(9)Me]; *m/e* 169 (M^+, 57%), 168 (27%), 155 (13%), 154 (100%, *m** 140.3), and 127 (8%, *m** 104.7). Hydrogenation of (12; R = Me) (10 g) for 6 d [5% Rh–C (2 g), in EtOH (150 ml), 3 atm, room temperature] gave a mixture containing starting material (t.l.c.). Chromatography (silica, cyclohexane) gave (4; R = Me), yield 15%, identical with the sample described below.

(*b*) Compound (4; R = H) was converted (Vilsmeir–Haack) [5] to (4; R = CHO), m.p. 154 °C (lit.,[5] 151—154 °C) using dichloromethane as solvent, which gave a better yield (65%) than using dimethylformamide as solvent.[5] The aldehyde (4; R = CHO) (3.6 g) was extracted (Soxhlet) during 40 h into a boiling suspension of $LiAlH_4$ (3.0 g) in ether (500 ml), and the usual work-up followed by chromatography (silica, cyclohexane) gave (4; R = Me) (yield 90%) as an oil which darkened slowly at room temperature. At 0 °C it formed a stable colourless solid, m.p. 15—18 °C (Found: C, 84.2; H, 7.6; N, 8.0. $C_{12}H_{13}N$ requires C, 84.2; H, 7.6; N, 8.2%); $\lambda_{max.}$ 230, 280 (sh), 286, and 293 (sh) nm (ε 31 000, 4 700, 5 200, and 4 900); τ 2.45—3.35 (4 H, m), 6.06 [2 H, t, *J* 7 Hz, C(3)H_2], 7.12 [2 H, t, *J* 7 Hz, C(1)H_2], 7.3—7.6 [2 H, m, C(2)H_2], and 7.78 (3 H, s, CMe); *m/e* 171 (M^+, 100%), 170 (92%), 156 (11%), 143 (15%, *m** 119.5), and 115 (7%). During one reduction a yellow solid (16% yield) separated after the ether had been removed and cyclohexane added. Recrystallisation (benzene–cyclohexane) afforded plates. 9,9′-*Bis*-[2,3-*dihydro*-1H-*pyrrolo*-[1,2-a]*indolyl*]*methane* (14) had m.p. 188—189.5 °C (Found: C, 84.7; H, 6.7; N, 8.4. $C_{23}H_{22}N_2$ requires C, 84.7; H, 6.8; N, 8.6%); $\lambda_{max.}$ 232, 286, and 295 (sh) nm (ε 72 400, 12 800, and 11 600); τ 2.4—2.6 and 2.75—3.12 (8 H, m, Ar), 5.9 [2 H, s, C(9)CH_2], 6.08 (4 H, t, *J* 8 Hz), and 7.25—7.75 (8 H, m); *m/e* 326 (M^+, 100%), 325 (53%), 298 (11%, *m** 270.3), 297 (9%), 170 (38%), 169 (68%), and 163 (16%). Concentration of the mother-liquors gave (4; R = Me) (yield 60%). A solution of (4; R = H) (0.5 g) in AcOH (0.4 ml) and EtOH (5 ml) containing formalin (0.3 ml) was boiled (5 min) and then cooled. Compound (14) separated (yield 90%), flakes (EtOH–EtOAc), m.p. 187—191 °C; identical with the sample isolated above.

1,2,2a,3,4,5-*Hexahydropyrrolo*[3,2,1-jk]*carbazole* (5).—A solution of (17) (1.85 g) in MeCN (200 ml) containing acrylonitrile (0.52 g) and ' Triton B ' (10 drops) was set aside at room temperature for 18 h. The solution was then acidified (AcOH) and partitioned between chloroform and water. The organic phase was evaporated and the residue recrystallised (EtOH) (yield 50%). 3-(1,2,3,4-*Tetrahydro*-1-*oxocarbazol*-9-*yl*)*propiononitrile* (19; R = CN) formed needles, m.p. 113—113.5 °C (Found: C, 75.3; H, 6.1; N, 11.6. $C_{15}H_{14}N_2O$ requires C, 75.5; H, 5.9; N, 11.8%); $\lambda_{max.}$ 237 and 306 nm (ε 9 500 and 12 350); $\nu_{max.}$ 1 542, 1 654, and 2 255 cm^{-1}; τ 2.3—2.95 (4 H, m), 5.25 [2 H, t, *J* 7 Hz, NCH_2], 7.00 [2 H, t, *J* 6 Hz, C(2)H_2], 7.15 [2 H, t, *J* 7 Hz, CH_2CN], 7.35 [2 H, t, *J* 6 Hz, C(4)H_2], and 7.6—7.95 [2 H, m, C(3)H_2]; *m/e* 238 (M^+, 27%), 199 (13%), and 198 (100%, *m** 164.7). A solution of the nitrile (0.5 g) in polyphosphoric acid (2 ml) was heated (100 °C, 1 h) and the solution poured into water. Extraction (EtOAc) gave a solid which was recrystallised from ethanol. The *amide* (19; R = $CONH_2$) formed prisms, m.p. 172 °C (yield 90%) (Found: C, 70.1; H, 6.2; N, 10.6. $C_{15}H_{16}N_2O_2$ requires C, 70.2; H, 6.3; N, 10.9%); $\lambda_{max.}$ 239 and 308 nm (ε 16 000 and 19 700); $\nu_{max.}$ 1 535, 1 645, 1 685, 3 200, and 3 370 cm^{-1}; τ 2.3—3.0 (4 H, m), 3.55 and 4.15 (each 1 H, s, exchanged with D_2O), 5.23 (2 H, t, *J* 7 Hz), 7.00 (2 H, t, *J* 6 Hz), 7.2—7.4 (4 H, m), and 7.65—7.95 (2 H, m); *m/e* 256 (M^+, 89%), 212 (24%), 211 (22%), 198 (89%), and 185 (100%, *m** 133.7).

Ethyl 2-oxocylohexylacetate (20) had b.p. 78—81 °C at 0.2 mmHg (lit.,[18] 95—101 °C at 0.5 mmHg) and gave a phenylhydrazone (rods, from ethanol), m.p. 108—110 °C (yield 80%). This phenylhydrazone (132 g) was dissolved in a mixture of concentrated sulphuric acid and ethanol (20% v/v, 500 ml).[19] The solution was boiled (30 min) and then the solution was concentrated to half-volume. Water (1 l) was added, and ether extraction then afforded (21; R = Et) (yield 75%), prisms (MeOH), m.p. 70—72 °C (lit.,[16] 72—73 °C). Hydrolysis (KOH–MeOH) of the ester gave (21; R = H), prisms (PhH), m.p. 142—144 °C (lit.,[15] 137—138 °C).

A solution of (21; R = H) (5 g) in Ac_2O (100 ml) was boiled under reflux for 18 h, cooled, and poured into water. The mixture was basified (NaOH aqueous) and extracted (EtOAc). Evaporation of the organic phase gave a gum; chromatography of this gum afforded 2a,3,4,5-*tetrahydropyrrolo*[3,2,1-jk]*carbazol*-1(2H)-*one* (22) (1.42 g), prisms, m.p. 90—92 °C, from pentane (Found: C, 79.4; H, 6.2; N, 6.7. $C_{14}H_{13}NO$ requires C, 79.6; H, 6.2; N, 6.6%); $\lambda_{max.}$ 238, 262, and 290 nm (ε 19 400, 10 900, and 2 600); $\nu_{max.}$ 1 688 and 1 740 cm^{-1}; τ 2.05—2.2 [1 H, m, C(9)H], 2.5—2.8 (3 H, m), 6.6—6.9 (1 H, m), 7.1—7.5 (1 H, m), and 7.6—8.8 (7 H, m); *m/e* 211 (M^+, 100%), 184 (8%), 183 ($M^+ - 28$, 68%, *m** 158.7), 168 (34%), and 155 (183 − 28, 46%, *m** 131.3). Compound (22) (0.5 g) was reduced ($LiAlH_4$) in Et_2O giving (24; R = OH) (0.3 g), m.p. 106—109 °C, as the only crystalline product.

Reduction ($LiAlH_4$, 12 g) of the ester (21; R = Et) (60 g) in Et_2O (900 ml) gave the alcohol (24; R = OH) as an oil which solidified on standing. 2-(1,2,3,4-*Tetrahydrocarbazol*-1-*yl*)*ethanol* (24; R = OH) was recrystallised from benzene–cyclohexane yielding prisms, (39.5 g), m.p. 108—109 °C (Found: C, 78.2; H, 8.0; N, 6.8. $C_{14}H_{17}NO$ requires C, 78.1; H, 7.9; N, 6.5%); $\lambda_{max.}$ 228, 275 (sh), 280, and 292 (sh) (ε 25 000, 5 300, 5 700, and 5 000); $\nu_{max.}$ ($CHCl_3$) 3 360, 3 480, and 3 625 cm^{-1}; τ 1.3 (1 H, NH), 2.4—3.05 (4 H, m), 6.28 (2 H, t, *J* 7 Hz, CH_2OH), 6.9—7.2 (1 H, m), 7.80 (1 H, s, exchanged D_2O), and 7.6—8.6 (6 H, m); *m/e* 215 (M^+, 40%), 171 (18%), 170 (100%, *m** 134.4), and 168 (17%). Distillation of one reaction product (5-g scale) yielded an oil, b.p. 180—190 °C at 0.3 mmHg which solidified on standing. The addition of benzene–cyclohexane gave a solid (yield 10%); 2-(1,2,3,4-*tetrahydro*-4a-*hydroperoxycarbazol*-1-*yl*)*ethanol* (25; *n* = 2) formed prisms, m.p. 140—145 °C (Found: C, 67.5; H, 6.7; N, 5.7. $C_{14}H_{17}NO_3$ requires C, 68.0; H, 6.9; N, 5.6%); $\lambda_{max.}$ 219 and 250 (sh) (ε 26 000 and 5 500); $\nu_{max.}$ 1 590 and 2 800—3 300 cm^{-1}; τ [$(CD_3)_2SO$] 2.45—3.1 (4 H, m), 6.1—6.35 (2 H, m, CH_2OH), 6.7—7.05 (1 H, m), 4.68 and 5.6—6.5 [each 1 H, br, exchanged with D_2O], and 7.35—9.1 (8 H, m); *m/e* 231 ($M^+ - O$, 17%), 214 (19%), 213 (54%), 194 (26%), 187 (100%), 186 (29%), 185 (30%), and 170 (68%). The mother-liquors yielded (24; R = OH) (70%).

An ice-cold solution of (24; R = OH) (10 g) in dry pyridine (30 ml) was added dropwise to a solution of pure tosyl chloride (10 g) in pyridine (30 ml) at 0 °C. The solution was stirred at 0 °C for 2 h and refrigerated for 24 h. Then ice–water (200 ml) followed by cold H_2SO_4 (1M, 50 ml) was added and the mixture set aside at 0 °C overnight. The crude tosylate was collected and washed copiously with water (yield 15.2 g), m.p. 123—124 °C. The *tosylate* (24;

R = OTs) formed prisms, m.p. 125—126 °C from benzene–light petroleum (Found: C, 68.5; H, 6.2; N, 3.6; S, 8.7. $C_{21}H_{23}NO_3S$ requires C, 68.3; H, 6.2; N, 3.8; S, 8.7%); $\nu_{max.}$ 3 400 cm^{-1}; *m/e* 369 (M^+, 42%), 197 (M − TsOH, 39%, *m** 105.2), 170 (100%, *m** 78.3), 169 (73%), and 168 (51%).

A solution of the alcohol (24; R = OH) 1.1 g) in pyridine (10 ml) containing tosyl chloride (1.0 g) was set aside at room temperature for 24 h. The usual work-up gave an oil and chromatography (silica–benzene) gave 1-(2-*chloroethyl*)-1,2,3,4-*tetrahydrocarbazole* (24; R = Cl) (0.32 g) as an unstable oil; $\lambda_{max.}$ 228, 276 (sh), 283, and 291 nm (ε 53 700, 11 600, 12 200, 10 600); $\nu_{max.}$ 3 425 cm^{-1}; τ 2.1 (1 H, s, exchanged with D_2O), 2.45—3.05 (4 H, m), 6.36 (2 H, t, *J* 7 Hz, CH_2Cl), 6.75—7.05 (1 H, m), 7.31 (2 H, t, *J* 6 Hz), and 7.6—8.5 (6 H, m); *m/e* 233 (M^+, 34%), 171 (22%), 170 (100%, *m** 124.0), and 168 (24%); the isotope peaks (omitted) showed the presence of Cl in the molecule. Further elution of the column gave (24; R = OTs) (0.3 g).

A solution of (24; R = OTs) (15.2 g) in dry Bu^tOH (60 ml) was added to a solution of potassium (2.34 g) in Bu^tOH (30 ml). The mixture was boiled (30 min), cooled, water added, and the mixture extracted (Et_2O). Chromatography (silica–CH_2Cl_2) of the product gave 1,2,2a,3,4,5-*hexahydropyrrolo*[3,2,1-jk]*carbazole* (5), m.p. 32—33 °C (yield 95%) (Found: C, 85.4; H, 7.5; N, 6.8. $C_{14}H_{15}N$ requires C, 85.3; H, 7.6; N, 7.1%); $\lambda_{max.}$ 232, 279 (sh), 282, and 292 (sh) nm (ε 27 500, 6 000, 6 200, and 5 300); τ 2.45—2.65 (1 H, m), 2.7—3.1 (3 H, m), 5.8—6.35 [2 H, m, C(1)H_2], and 6.7—9.3 (9 H, m); *m/e* 197 (M^+, 54%), 170 (12%), 169 (100%, *m** 145.0), 168 (54%), and 167 (20%).

2,3,3a,4,5,6-*Hexahydro*-1H-*pyrido*[3,2,1-jk]*carbazole* (27; R = H).—3,3a,4,5-tetrahydropyrido[3,2,1-*jk*]carbazole-1-(2*H*)-one (26) had m.p. 124—125 °C (lit.,[21] 125—126 °C), *m/e* 225 (M^+). A solution of the amide (0.02 mol) in methylene chloride was reduced with diborane.[26] Chromatography gave starting material (0.64 g) and 2,3,3a,4,5,6-hexahydro-1*H*-pyrido[3,2,1-*jk*]carbazole (27; R = OH) (2.8 g), prisms, (benzene–light petroleum), m.p. 131—133 °C (lit.,[20] 134—136 °C) (Found: C, 79.3; H, 7.6; N, 7.3. Calc. for $C_{15}H_{17}NO$: C, 79.3; H, 7.5; N, 6.2%); $\nu_{max.}$ 3 400 (br) cm^{-1}. Reduction by $NaBH_4$ in pyridine [22] gave a mixture of (26) and (27; R = OH).

To a stirred solution of compound (26) (0.01 mol) in tetrahydrofuran (25 ml) containing $NaBH_4$ (0.05 mol) was added trifluoroacetic acid (0.05 mol) during 10 min. The mixture was boiled (4 h), the solvent removed *in vacuo* and water added. Extraction ($CHCl_3$, 3 × 50 ml) gave an oil which crystallised on addition of MeOH. Recrystallisation (MeOH) gave (27; R = H), prisms, m.p. 80—81 °C (lit.,[20] 82—84 °C) (yield 83%) (Found: C, 85.2; H, 8.0; N, 6.6%. Calc. for $C_{15}H_{17}N$: C, 85.3; H, 8.1; N, 6.6%); $\lambda_{max.}$ 232 and 285 nm (ε 39 600 and 9 100); τ 2.4—3.1 (4 H, m), 5.6—5.85 (1 H, m), 6.15—6.6 (1 H, m), 7.0—7.4 (3 H, m), and 7.6—9.0 (8 H, m).

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