The Reactions of 4-(1,2-Dimethylindol-3-yl)butyric Acid and of 3-(1,2-Dimethylindol-3-yl)propionic Acid with Trifluoroacetic Anhydride

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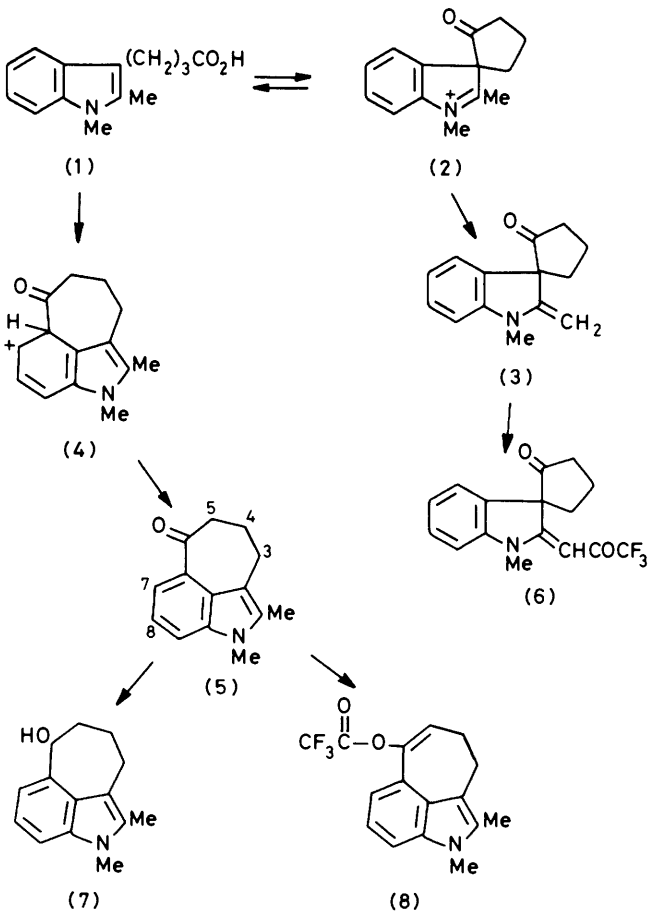
Treatment of 4-(1,2-dimethylindol-3-yl)butyric acid (1) with trifluoroacetic anhydride gives either 1-methyl-2-trifluoroacetylmethyleneindoline-3-spirocyclopentan-2'-one (6) or 1,2-dimethyl-6-oxo-3,4,5,6-tetrahydro-1*H*-cyclohept[*c,d*]indole (5) depending on the reaction conditions. 3-(1,2-Dimethylindol-3-yl)propionic acid (10; R = OH) reacts with trifluoroacetic anhydride to form 4,4a-dihydro-9-methyl-4a-[2,2,2-trifluoro-1-(2-hydroxy-9-methylcarbazol-3-yl)ethyl]carbazol-2(3*H*)-one (21).

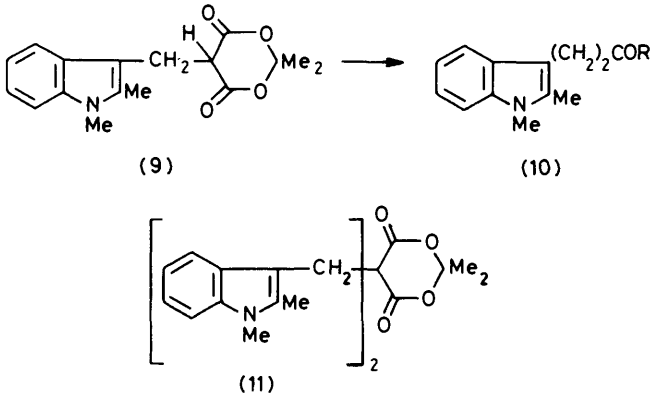
We have reported [1] that the indol-3-ylbutyric acid (1) reacts with trifluoroacetic anhydride (TFAA) to form the spiro-ketone (6). Attempts to repeat this reaction under the conditions described in ref. 1 with a fresh sample of the acid (1) did not yield (6); the only crystalline material isolated was the ketone (5). The i.r. spectrum of the compound contained a band at 1 650 cm^{-1} (CO),[2] and the n.m.r. spectrum contained signals at δ 2.3 (CMe) and 3.65 (NMe), and showed the presence of only three ' aromatic ' protons. Reduction of the ketone (5) yielded the corresponding alcohol (7). When the acid (1) was heated for a longer time with TFAA the *C*-methyl group of (5) was not attacked, the enoltrifluoroacetate (8) being isolated. However, heating the acid (1) with TFAA in benzene solution in the presence of sodium carbonate gave the known [1] compound (6). These results suggest that (1) can cyclise in two ways to form either (2) or (4), and that a stronger base is required to convert (2) into (3) than is needed to create the aromatic structure present in (5). We have already commented [3] on the reactions of 3-carboxy-1-methylindol-2-ylacetic acid with acetic anhydride in the presence and absence of base.

We have also examined the reaction of compound (10; R = OH), the lower homologue of (1), with TFAA. Neidlein [4] had treated the acid chloride (10; R = Cl) with aluminium chloride in benzene in an attempt to make the tricyclic ketone (12), but obtained the ketone (10; R = Ph), although cyclisations of β-indol-3-ylpropionic acids to form derivatives of benz[*cd*]indole have been accomplished.[5] The acid (10; R = OH) was prepared by the known [4,5a] route from β-propiolactone and 1,2-dimethylindole. Since the reaction of Meldrum's acid with indole and aldehydes has been used [6] to prepare β-indol-3-ylpropionic acids, we examined the reaction between 1,2-dimethylindole, formaldehyde, and Meldrum's acid in the presence of DL-proline, compound (9) being obtained. This was then boiled with ethanol–pyridine in the presence of copper powder [6] and the crude ester (10; R = OEt) hydrolysed to the acid (10; R = OH). Under different reaction conditions 1,2-dimethylindole reacted with Meldrum's acid and formaldehyde to give the bis-condensation product (11). The n.m.r. spectrum of Meldrum's acid contains a signal at δ 1.76 from the CMe_2 group; [7] in the n.m.r. spectrum of the dioxane (9) these two methyl groups are non-equivalent,[7] having δ 1.60 and 1.75, but the signal from the protons of the CMe_2 group in compound (11) appears as a sharp singlet at δ 0.5 (1.26 p.p.m. upfield of the corresponding signal in Meldrum's acid). The structure of (11) has been determined by *X*-ray crystallography; [8] the indolyl rings are held above and below the ring of the Meldrum's acid portion of the molecule forming a ' sandwich ' structure, the protons of the CMe_2 group being shielded by the indole rings.

Boiling a benzene solution of the acid (10; R = OH) with TFAA did not afford the ketone (12) but yielded a crystalline



solid of molecular formula $C_{28}H_{23}F_3N_2O_2$. The molecular formula was supported by the mass spectrum of the compound which contained a small signal at *m/z* 476 (confirmed by field-ionization mass spectroscopy); major peaks appeared at 279 ($C_{15}H_{12}F_3NO$), 210 (279 − CF_3), and 199 ($C_{13}H_{13}NO$). The u.v. spectrum was complex and the i.r. spectrum contained broad bands at 3 400—3 000 and 1 570 cm^{-1}, suggesting the presence of a hydrogen-bonded OH group and a conjugated CO group. The compound did not give a strong ferric chloride colour indicating the absence of an enolised β-diketonic structure. The ^1H n.m.r. spectrum of the compound included signals at 2.45 and 3.70 assigned to two *N*-methyl groups, but no signals corresponding to *C*-methyl groups. There were signals present at δ 4.95 (1 H, q, *J* 11 Hz), 5.1 (1 H, s), and signals indicating the presence of 10 ' aromatic ' protons including singlets at δ 6.45 and 6.75; there was also a



singlet at δ 10.5 (exchanged with D_2O). The ^{19}F n.m.r. spectrum consisted of a doublet (J 11 Hz) 15.5 p.p.m. downfield of CF_3CO_2H. This suggested the presence of a CF_3CH group in the molecule (F–H coupling constants for this type of structure are *ca.* 9 Hz [9]).

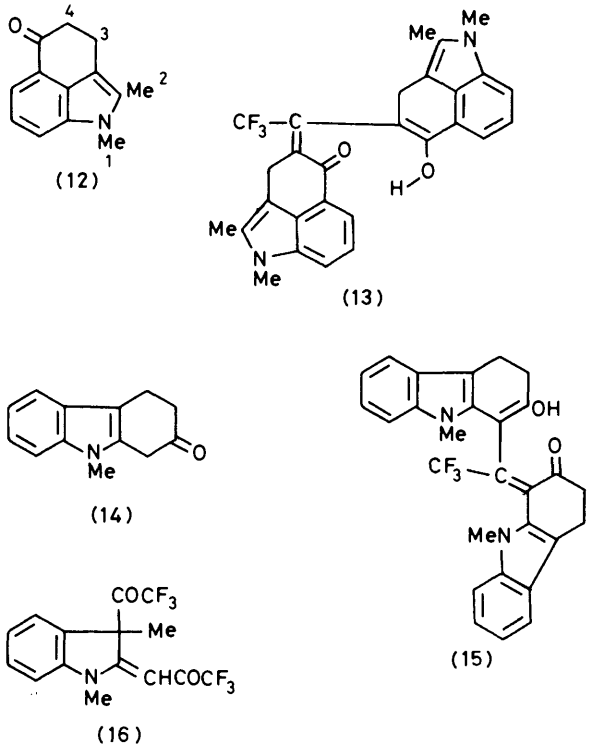
It seemed unlikely that the acid (10; R = OH) would cyclise onto C-3 of the indole ring forming a structure analogous to compound (3) but containing a four-membered ring, and we first considered structures that could be formed from (12). This compound could trifluoroacetylate on C-4 or on the C–Me group, and condensation of this product with a second molecule of (12) would give rise to a variety of structures, one of which, (13), is illustrated. Alternatively two molecules of (12) could undergo an aldol condensation followed by trifluoroacetylation of the product, this pathway giving rise to another set of structures. However, all the structures formed by these two routes contain at least one C–Me group. Cyclisation of the acid (10; R = OH) to form the carbazole (14) would give rise to another series of compounds, *e.g.* (15), by trifluoroacetylation and condensation.

Having considered and rejected structures derived from compounds (12) and (14) we examined structures derived from the trifluoroacetyl derivative (17); this structure is formed from (10; R = OH) by trifluoroacetylation at C-3 followed by cyclisation [*cf.* the formation of (16) by the reaction of 1,2,3-trimethylindole with TFAA [1,10]]. Condensation of two molecules of (17) gives the dimer (19) [*via* (18), route *a*]. Isomerisation of (19) to (20), followed by loss of the $COCF_3$ group, finally affords structure (21) (Scheme 1).

Structure (21) fits all the spectroscopic data, cleavage at C-4a giving rise to the C_{15} and C_{13} fragments in the mass spectrum. The signal at δ 4.95 (q) in the ^1H n.m.r. spectrum is assigned to the $HCCF_3$ proton, that at 5.1 to C=CHCO,[1] and the two signals at δ 6.45 and 6.75 to the protons at positions 1 and 4 of the carbazole ring. This structure is also supported by the ^{13}C n.m.r. spectrum; in particular, the proton-decoupled spectrum contains a quartet (J 25 Hz) at 43.0 (CF_3C), 50.3 (C-4a), 93.7 (C=*C*CO), and 171.0 (*C*=CCO). Assignments were made using published data on compound (22),[1] enaminones,[11] indole alkaloids,[12] carbazoles,[13] and substituted benzenes,[14] and are shown in the Figure.

Structure (21) has been confirmed by an *X*-ray crystallographic determination.[15] In the crystal the molecules exist as dimers with hydrogen-bonding between the OH group of one molecule and the C=O group of another.

Chromatography of the mother-liquors from the preparation of compound (21) gave a small quantity of crystalline material, m.p. 152—155 °C. High resolution mass spectrometry suggested a molecular formula $C_{15}H_{10}F_3NO_2$, the major fragmentation peaks being *m/z* 224, $C_{14}H_{10}NO_2$, ($M - CF_3$) and 196 ($M - COCF_3$). The i.r. spectrum of the



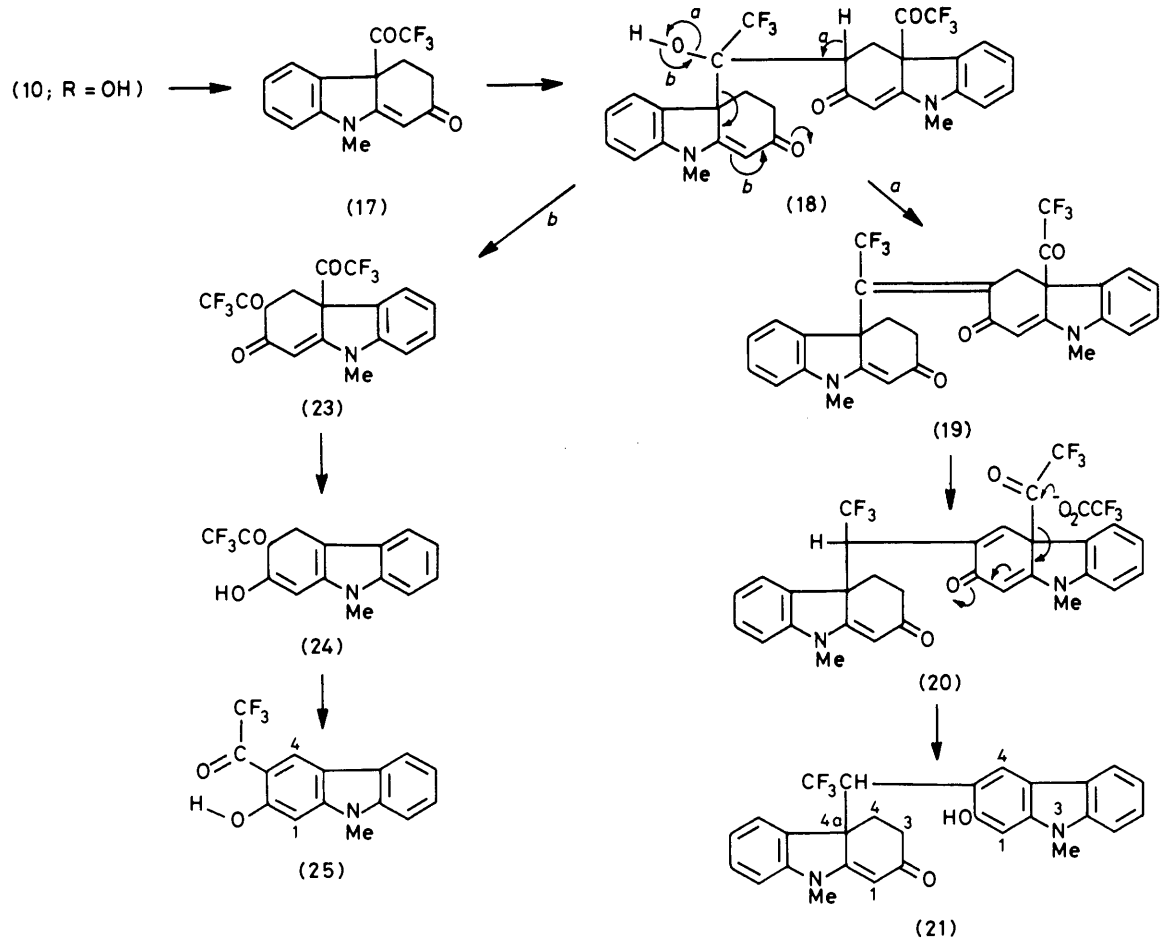
compound contained a broad band at 3 400, and bands at 1 640 and 1 620 cm^{-1}, indicating the presence of a hydrogen-bonded OH group and a carbonyl group. The compound gave an intense colouration with ferric chloride solution suggesting the presence of an enolised β-diketonic structure. The n.m.r. spectrum contained signals at δ 3.8 (3 H, s), 6.9 (1 H, s), 7.3—8.0 (4 H, m), 8.4 (1 H, s), and 11.6 (1 H, s, exchanged with D_2O). This compound is assigned structure (25); had the material been formed by the trifluoroacetylation of either carbazole (14) or (17) a 1-substituted carbazole would have been obtained. Structure (25) explains the ferric chloride colouration and the presence of two 1 H singlets in the n.m.r. spectrum of the compound. Structure (25) could be formed by cleavage of compound (18) (route *b*) giving the carbazole (23), followed by loss of the angular $COCF_3$ group to give (24) and oxidation then yielding (25).

When a solution of the acid (10; R = OH) was dissolved in neat TFA containing TFAA, 1,2-dimethyl-3-trifluoroacetylindole (27) was isolated (Scheme 2). The ketone (27) may be formed by reaction of the acid with TFAA to form the mixed anhydride which is attacked at C-3 by the TFAA forming compound (26); loss of the $CH_2CH_2CO_2H$ side-chain from (26) then gives (27). This suggestion is supported by the fact that treating compound (9) with TFAA in pyridine affords 1,2-dimethyl-3-trifluoroacetylindole (27), presumably *via* the intermediate (28).

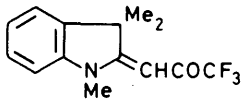
The formation of compounds (21) and (27) in these reactions and other observations [1,10] show that trifluoroacetylation of 3-substituted indoles at C-3 is a common occurrence.

Experimental

General details and instruments used have been reported.[1] U.v. spectra were determined for solutions in ethanol and n.m.r. spectra for solutions in $CDCl_3$ unless otherwise stated. ^{13}C Chemical shifts are in p.p.m. from Me_4Si and ^{19}F shifts in p.p.m. from CF_3CO_2H. ^{13}C Assignments are supported by the



Scheme 1.



(22)

observation of C–H coupling but only the completely decoupled values are quoted. I.r. spectra were recorded for Nujol mulls.

1,2-*Dimethyl*-6-*oxo*-3,4,5,6-*tetrahydro*-1H-*cyclohept*[cd]-*indole* (5).—4-(1,2-Dimethylindol-3-yl)butyric acid (1) (3 g) was dissolved in dry benzene (60 ml), the solution cooled to 0 °C, stirred, and TFAA (6 ml) added dropwise. The mixture was then boiled under reflux for 30 min, cooled, the benzene solution washed with sodium carbonate solution and dried ($MgSO_4$). The benzene was removed under reduced pressure affording a yellow solid. The *ketone* (5) (0.7 g) formed yellow cubes, m.p. 138—139 °C (from ethanol) (Found: C, 78.8; H, 7.1; N, 6 5. $C_{14}H_{15}NO$ requires C, 78.9; H, 7.0; N, 6.6%); $\lambda_{max.}$ 249 and 370 nm (ε 14 600 and 5 700); $\nu_{max.}$ 1 650 cm^{-1}; δ 2.1—2.3 (2 H, m), 2.3 (3 H, s, CMe), 2.85—2.95 (2 H, m), 2.96—3.0 (2 H, m), 3.65 (3 H, s, NMe), 7.18 (1 H, m, 8-H), 7.44 (1 H, dd, *J* 9 and 1.5 Hz, 9-H), and 7.86 (1 H, dd, *J* 9 and 1.5 Hz, 7-H); *m/z* 213 (M^+, 100%), 198(18), 183(15), and 157 ($M - C_3H_4O$, 68).

The above experiment was repeated but the time of refluxing was increased to 45 min. T.l.c. showed the presence of two

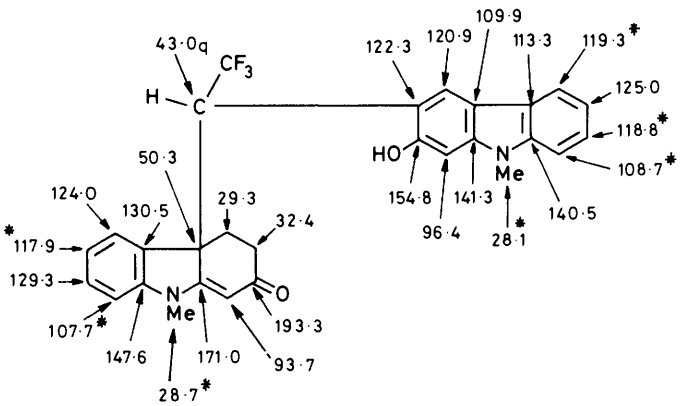
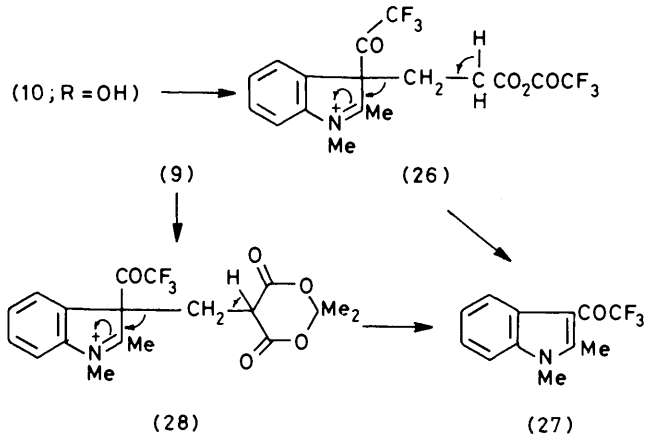


Figure. ^{13}C N.m.r. absorptions of compound (21). Signals whose assignments are uncertain are marked *

compounds of R_F 0.26 [compound (5)] and R_F 0.79. The faster running compound was isolated by chromatography (SiO_2/CH_2Cl_2). Recrystallisation of the product from ethanol gave the *enoltrifluoroacetate* (8) as needles (100 mg) m.p. 92 °C (Found: C, 62.3; H, 4.5; N, 4.5. $C_{16}H_{14}F_3NO_2$ requires C, 62.1; H, 4.5; N, 4.5%); $\lambda_{max.}$ 244 and 336 nm (ε 24 300 and 5 900); $\nu_{max.}$ 1 805 cm^{-1}; δ 2.3 (3 H, s, CMe), 2.45—2.70 (2 H, m), 2.8—3.05 (2 H, m), 3.6 (3 H, s, NMe), 5.95 (1 H, t, *J* 6 Hz, 5-H), and 6.85—7.3 (3 H, m); *m/z* 309 (M^+, 100%), 212 ($M - COCF_3$, 58), and 184 (212 – CO, 30). The com-



Scheme 2.

pound did not give a colour with ferric chloride solution, showing that it was not the β-diketone formed by acylation at C-5. Reduction of the ketone (5) (0.50 g) by $LiAlH_4$ in Et_2O gave 1,2-*dimethyl*-6-*hydroxy*-3,4,5,6-*tetrahydro*-1H-*cyclohept*-[cd]*indole* (7) (0.45 g), m.p. 134—136 °C (from ethanol) (Found: C, 78.6; H, 7.9. $C_{14}H_{17}NO$ requires C, 78.2; H, 7.4%); $\lambda_{max.}$ 232 and 296 nm (ε 36 900 and 8 300); $\nu_{max.}$ 3 450—3 000 cm^{-1}; δ 1.75 (1 H, s, exchanged with D_2O), 2.10—2.45 (4 H, m), 2.3 (3 H, s), 2.70—2.95 (2 H, m), 3.6 (3 H, s), 5.0—5.15 (1 H, m), and 2.85 (3 H, narrow m, Ar); *m/z* 215 (M^+, 64%), 196(100), 181(58), and 158(73).

TFAA (6 ml) was added dropwise with stirring to a cold (0 °C) solution of the acid (1) (2 g) in benzene (40 ml) containing anhydrous sodium carbonate (0.5 g). After the initial reaction had subsided the mixture was heated under reflux for 45 min, cooled, and water added. The benzene solution was washed with sodium carbonate solution, with water, dried, and the solvent removed under reduced pressure. The solid so obtained was recrystallised from ethanol affording the spiroketone (6) (1.1 g), m.p. 175—176 °C, identical (i.r. and n.m.r.) with an authentic sample.[1]

β-(1,2-*Dimethylindol*-3-*yl*)*propionic Acid* (10; R = OH).—(*a*) 1,2-Dimethylindole was heated with β-propiolactone,[4,5a] m.p. 154—156 °C (reported 153—154 °C and 159 °C).

(*b*) 1,2-Dimethylindole (5.1 g), Meldrum's acid (5.25 g) and DL-proline (0.26 g) were dissolved in acetonitrile (20 ml). The solution was stirred, warmed to 40 °C, and formaldehyde (40% aqueous solution; 1.5 ml) added *slowly* (2—3 min). After 0.5 h more formaldehyde (1.0 ml) was added. The mixture was stirred for a further 5 h and then ethanol (40 ml) was added. The solution was kept at 0 °C overnight, and the solid collected (5.5 g); concentrating the mother-liquors gave more product (2.3 g). 2,2-*Dimethyl*-5-(1,2-*dimethylindol*-3-*ylmethyl*)-1,3-*dioxane*-4,6-*dione* (9) formed prisms, m.p. 135—136 °C (from ethanol) (Found: C, 67.7; H, 6.3; N, 4.6. $C_{17}H_{19}NO_4$ requires C, 67.8; H, 6.3; N, 4.7%); $\nu_{max.}$ 1 755 and 1 790 cm^{-1}; δ 1.60 (3 H, s), 1.75 (3 H, s), 2.58 (3 H, s), 3.70 (2 H, d, *J* 5 Hz), 3.72 (3 H, s), 3.82 (1 H, t, *J* 5 Hz), 7.15—7.40 (3 H, m), and 7.68 (1 H, d, *J* 8 Hz); *m/z* 301 (M^+, 16%), 199(16), 171(19), and 158(100). Compound (9) (1.08 g) was dissolved in a mixture of pyridine and ethanol (10 : 1; 22 ml) and copper powder (100 mg) was added. The mixture was boiled under reflux for 3 h, the copper filtered off, and the solvents removed under reduced pressure. The residue was hydrolysed by boiling (1 h) with potassium hydroxide (0.56 g) in 75% ethanol–water (10 ml). The solution was diluted with water and acidified (2M-HCl), yielding the acid (10; R = OH) (0.55 g), identical (m.p., i.r., n.m.r.) with the sample prepared under (*a*).

1,2-Dimethylindole (5.2 g), Meldrum's acid (5.0 g), and DL-proline (0.3 g) were dissolved in acetonitrile (20 ml). The solution was warmed to 40 °C, stirred, and formaldehyde solution (5 ml) poured in. After 15 min a solid started to separate and more acetonitrile (20 ml) was added to facilitate stirring. After 3 h the solid was collected and recrystallised from acetonitrile. 2,2-*Dimethyl*-5,5-*bis*(1,2-*dimethylindol*-3-*ylmethyl*)-1,3-*dioxane*-2,4-*dione* (11) formed prisms, m.p. 229—233 °C (8.0 g) (Found: C, 73.4; H, 6.6; N, 6.2. $C_{28}H_{30}N_2O_4$ requires C, 73.4; H, 6.6; N, 6.1%); $\nu_{max.}$ 1 730 and 1 770 cm^{-1}; δ 0.5 (6 H, s), 2.4 (6 H, s), 3.6 (6 H, s), 3.7 (4 H, s), and 7.0—7.8 (8 H, m); *m/z* 458 (M^+, 4%), 356(2), 302(4), and 158(100).

4,4a-*Dihydro*-9-*methyl*-4a-[2,2,2-*trifluoro*-1-(2-*hydroxy*-9-*methylcarbazol*-3-*yl*)*ethyl*]*carbazol*-2(3H)-*one* (21).—The acid (10) (2.0 g) was dissolved in benzene (40 ml), the solution cooled to 0 °C, stirred and TFAA (4 ml) added dropwise. The solution was then boiled for 5 min, cooled, and aqueous sodium carbonate added. The organic phase was washed with water, dried, the solvent removed, and the residue taken up in a little methanol. After 2 days the solid which had separated was collected and recrystallised from ethyl acetate. *Compound* (21) formed clear prisms, m.p. 213—215 °C (0.5 g); the crystals contained solvent (i.r. and n.m.r.). Solvent-free material was obtained by recrystallisation from ethanol (Found: C, 70.3; H, 5.0; F, 12.1; N, 5.8. $C_{28}H_{23}F_3N_2O_2$ requires C, 70.6; H, 4.8; F, 12.0; N, 5.9%); $\lambda_{max.}$ 214, 238, 264, 300, 326, and 334 nm (ε 24 500, 45 500, 22 500, 16 500, 16 000, and 16 500); $\nu_{max.}$ 3 400—3 000 and 1 570br cm^{-1}; δ[$(CD_3)_2SO$] 2.0—2.1 (1 H, m), 2.4—2.55 (1 H, m), 2.45 (3 H, s), 2.65—2.80 (1 H, m), 2.9—3.0 (1 H, m), 3.70 (3 H, s), 4.95 (1 H, q, *J* 11 Hz), 5.1 (1 H, s), 6.45 (1 H, s), 6.70 (1 H, d, *J* 8 Hz), 6.75 (1 H, s), 7.0—7.6 (7 H, m), and 10.5 (1 H, s, exchanged with D_2O); δ (^{19}F) − 15.5 p.p.m. (downfield of CF_3CO_2H) (d, *J* 11 Hz); *m/z* 476 (M^+, 7%), 279(70), 210(60), 199(100), and 157(25). Recrystallisation of compound (21) from nitromethane afforded needles containing solvent (Found: N, 7.2. $C_{29}H_{26}F_3N_3O_4$ requires N, 7.8%). This sample was used in the *X*-ray crystallographic determination of the structure.

2-*Hydroxy*-9-*methyl*-3-*trifluoroacetylcarbazole* (25).—After compound (21) had been collected the mother-liquors were evaporated to dryness and the residue chromatographed (SiO_2/CH_2Cl_2). The fourth fraction yielded a crystalline solid (*ca.* 10 mg), m.p. 152—153 °C (Found: M^+ 293.0665. $C_{15}H_{10}F_3NO_2$ requires *M*, 293.0664; *m/z* 224.0711. $C_{14}H_{10}NO_2$ requires 224.0711); $\lambda_{max.}$ 205, 230, 270sh, 281, 300sh, 312, 334sh, and 370 nm; *m/z* 293 (50%), 224(100), and 196(10). Other spectral data have been reported in the main section. A dilute alcoholic solution of the compound gave an intense green-brown colouration with ferric chloride solution.

1,2-*Dimethyl*-3-*trifluoroacetylindole* (27).—(*a*) The acid (10; R = OH) (0.62 g) was dissolved in TFA (20 ml) and TFAA (10 ml) was added. The mixture was kept at room temperature overnight under nitrogen and then boiled under reflux for 4.5 h, cooled and poured into water. The solid which separated was collected and dried. Recrystallisation from light petroleum (b.p. 60—80 °C) gave compound (27) as plates, m.p. 106—107 °C (0.22 g), identical (i.r., n.m.r.) with the material prepared under (*c*).

(*b*) Compound (9) (0.8 g) was dissolved in pyridine (4 ml), stirred at 0 °C and TFAA (4 ml) added. Next day the solution was poured into ice, the solid collected, washed with water,

and dried, yield (0.37 g), identical (m.p., i.r., n.m.r.) with the material prepared under (*c*).

(*c*) A solution of TFAA (4 ml) in dry diethyl ether (8 ml) was added dropwise to a cold (0 °C), stirred solution of 1,2-dimethylindole (2 g) in diethyl ether (12 ml). After 30 min ice–water was added, the ether allowed to evaporate, and the solid which formed collected. The *ketone* (27) (1.62 g) formed needles from methanol, plates from light petroleum, m.p. 109—110 °C (Found: C, 59.7; H, 4.1; N, 5.7. $C_{12}H_{10}F_3NO$ requires C, 59.8; H, 4.1; N, 5.8%); $\lambda_{max.}$ 210, 253, 268, and 323 nm (ε 33 500, 15 000, 9 100, and 12 600); $\nu_{max.}$ 1 660 cm^{-1}; δ 2.8 (3 H, s), 3.7 (3 H, s), 7.2—7.4 (3 H, m), and 7.9—8.2 (1 H, m); *m/z* 241 (M^+, 38%) and 172(100).

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