Indolisation of 1-decalone and the reactions of the products with oxygen and with nucleophiles

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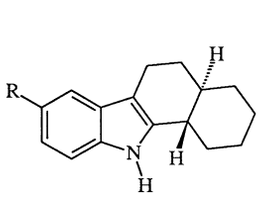
The regioselectivity of the Fischer indolisation of *trans*-1-decalone has been examined in order to define conditions which select either indole or indolenine products.† During the reactions aerial oxidation may occur and this can lead to some unexpected rearrangements. In addition, the reactions of the indolenines with nucleophiles have been studied with particular reference to the stereoselectivity of the additions.

When 4-isopropylphenylhydrazine is reacted with 1-decalone (80% *trans*) a mixture of hydrazones is formed, which in the presence of 4-sulfosalicylic acid cyclise to yield two main products: the indole (**1**, R = Pr^i) and the indolenine (**2**, R = Pr^i).†



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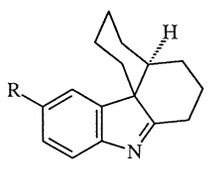

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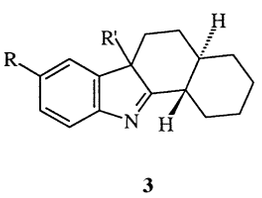

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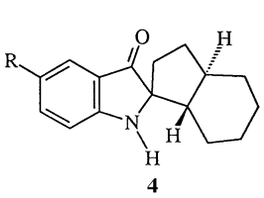

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A minor product is the hydroperoxide (**3**, R = Pr^i, R′ = OOH). A parallel set of results is obtained for the reaction of 4-*tert*-butylhydrazine with 1-decalone leading to **1** (R = Bu^t), **2** (R = Bu^t) and the hydroperoxide **3** (R = Bu^t, R′ = OOH). (NB Here the indolenines are represented as *cis*-fused decalin derivatives.) The *cis* form of the indolenine is shown by MM2 calculations[1] to have a global energy minimum of 106 kJ mol^{-1}, whereas the *trans* formulation would have a minimum energy of 142 kJ mol^{-1}; the *cis* assignment is confirmed by a X-ray crystal structure of the adduct **25**, (R = Pr^i, Nu = Ph) obtained when the indolenine **2** (R = Pr^i) is treated with phenyllithium (see Fig. 1).‡ The indole **1** (R = Pr^i) is unstable, particularly in solution and/or during chromatography and decomposes to the hydroperoxide **3** (R = Pr^i, R′ = OOH) and the hydroxy compound **3** (R = Pr^i, R′ = OH). The hydroperoxide is also unstable and, when heated in boiling ethanol, it is transformed into a mixture of the hydroxy compound and the spirocycle **4** (R = Pr^i). The propensity of tetrahydrocarbazoles to undergo aerial oxidation and give hydroperoxides is well known[2] and appears to depend upon the size of the carbocyclic ring since, although a solution of 1,2,3,4-tetrahydrocarbazole **5** exposed to air undergoes oxidation to the hydroperoxide **6**, its cycloheptano **7** and cyclopentano **8** analogues do not.[3] Similarly,

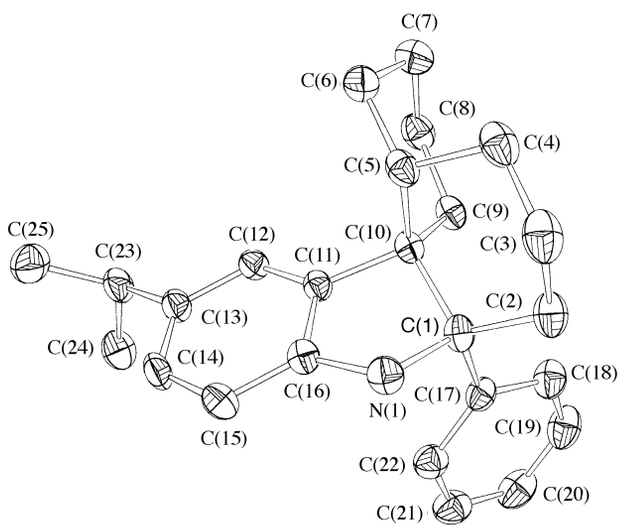
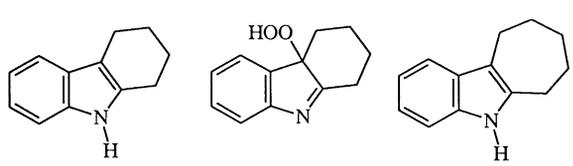
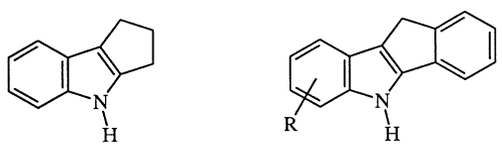


Fig. 1 Molecular plot of **25** (R = Pr^i, Nu = Ph) showing the labelling scheme used. Ellipsoids are represented at the 30% probability level.



5 **6** **7**



8 **9**

† 1-Decalone = decahydronaphthalen-1-one; indolenine = 3*H*-indole.

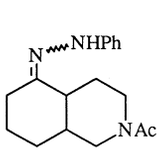
‡ *X-Ray crystallographic data for* **25**: $C_{25}H_{31}N$, M = 345.5, monoclinic, a = 14.766(2), b = 8.9146(9), c = 14.795(2) Å, β = 92.98(1)°, U = 1946.0 Å^3, space group $P2_1/c$, Z = 2, D_c = 1.18 g cm^{-3}, μ(Mo-Kα) = 0.70 cm^{-1}; F(000) = 752. Data were measured at room temperature on a CAD4 automatic four-circle diffractometer in the range $2 < \theta < 24°$. 3378 Reflections were collected of which 1713 were unique with $I \geqslant 2\sigma(I)$. Data were corrected for Lorentz and polarisation but not for absorption. In the final least squares cycles all atoms were allowed to vibrate anisotropically. Hydrogen atoms were included at calculated positions except in the instance of H1 (attached to N1) which was located in an advanced difference Fourier map and refined at a distance of 0.98 Å from the parent atom.

Final residuals after 10 cycles of least squares (240 parameters) were R = 0.0455, R_w = 0.0407, for a weighting scheme of $w = 2.7414/[\sigma^2(F) + 0.000\,207(F)^2]$. Maximum final shift/esd was 0.000. The maximum and minimum residual densities were 0.06 and −0.06 e Å^{-3}, respectively.

although we have synthesised many indenoindoles **9**, often on a large scale, at no time was C-9b hydroperoxidation observed.[4]

The proportions of the indole **3** (R = Pr^i) and the indolenine **4** (R = Pr^i) seem to depend upon the acid used in the Fischer indolisation reaction. For example, 4-sulfosalicylic acid in glacial acetic acid at 110 °C favours the indole (typically 5:1), whereas if toluene-*p*-sulfonic acid in toluene at 110 °C is used the ratio of products is 1:1. It has been suggested that for unsymmetrical ketones the nature of the ene–hydrazine formed (and consequently which cyclised product is obtained) depends upon the stereochemistry of the parent hydrazone.[5]

We have studied the reactions of other phenylhydrazines with 1-decalone under a variety of acid conditions and we note that the addition of acetate ion enhances the formation of the corresponding indolenines rather than the indoles. Typically, when 10% sodium acetate in acetic acid is used the ratio is 5:1 in favour of the indolenine. This is further increased if the phenylhydrazine hydrochloride (rather than the phenylhydrazine), sodium acetate and 1-decalone are similarly heated at *ca.* 100 °C. We are not the first to observe this effect and Bird and Wee[6] record that the hydrazone **10** undergoes selective cyclisation to the indole **11** when it is heated with acetic acid or acetic acid–hydrochloric acid, but when sodium acetate is added to the reaction a 3:2 mixture of **11** and **12** is produced.



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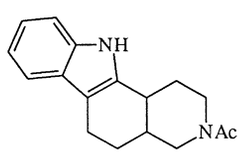

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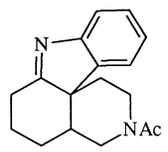

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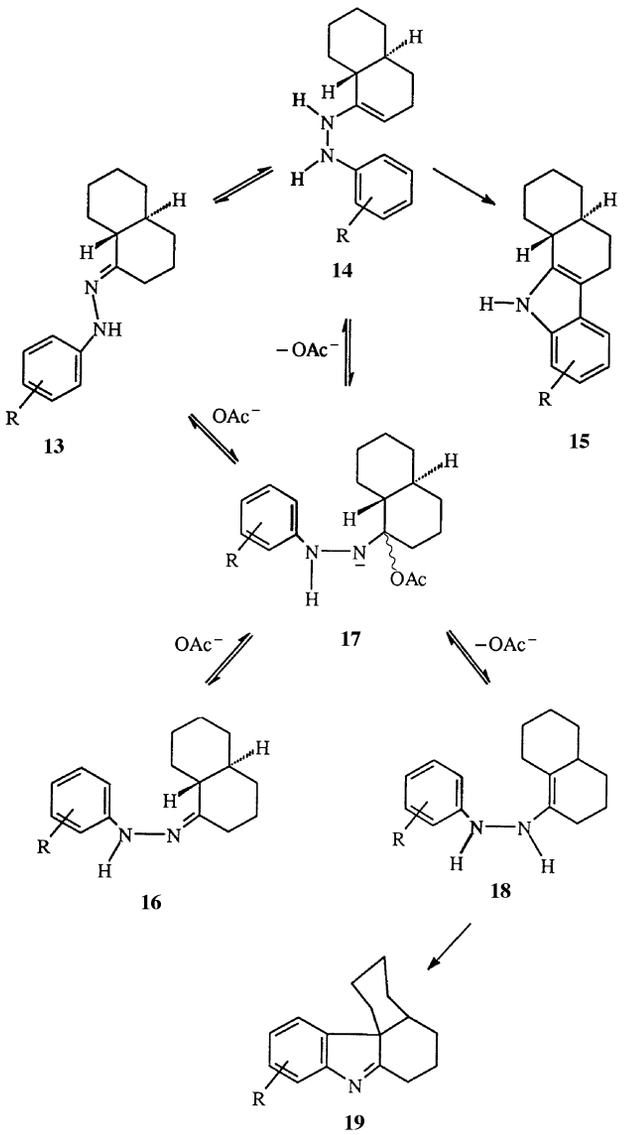
It is known that the balance of alternative indoles from unsymmetrical ketones is influenced by the strength of the acid used in the Fischer reaction,[7] but here we speculate that the acetate is not simply acting as a buffer. Our results suggest that in the absence of acetate anion the dominance of the indoles **15** reflects the natural preference for the less sterically constrained (*E*)-hydrazones **13** (over the *Z* forms **16**). These lead directly to the less substituted ene–hydrazines **14**, by prototropic rearrangement. However, when acetate ion is present this combines with either the (*E*)- or (*Z*)-hydrazones to afford a common tetrahedral intermediate **17**. This may lose acetate ion returning either hydrazone, but tends to favour the production of the more substituted ene–hydrazine **18**, from which the indolenines **19** are derived (Scheme 1). In essence the presence of acetate ion acts to facilitate the higher energy reaction pathway.

Reduction of the indoles with sodium cyanoborohydride in glacial acetic acid gives the corresponding indolines **20** as single diastereomers, and similar treatment of the indolenines yields the reduced derivatives **21** also as single diastereomers. Indolenines of the type **22**§ fail to react with nucleophiles such as phenyllithium and we argue this is because deprotonation at the α-position to the imine bond is more favoured than addition. However, the indolenines **2** readily undergo addition with nucleophiles such as PhLi, 4-Bu^{t}PhLi, BuLi and MeLi to give, after protonation, indolines of the type **25**. Models suggest that in the relatively planar anion **23** there should be effective overlap of the p-orbital carrying the formal negative charge and the imine π-system thus promoting anion formation, whereas in the anions **24** overlap of the p-orbital with the π system of the C=N bond is very poor. An X-ray crystal analysis of the phenyl derivative **25** (Nu = Ph; Fig. 1) shows that the phenyl substituent is α-orientated and that both cyclohexane rings assume chair conformations. In this case MM2 calculations indicate a global



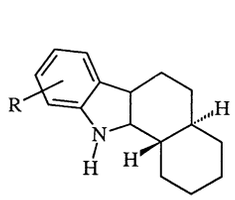
Scheme 1

energy minimum of 182.7 kJ mol^{-1}; other potential conformations are at least 20 kJ mol^{-1} less favourable.

When the indolenine **2** (R = Bu^t) is treated with *tert*-butyllithium and quenched with deuterium, 54% of the 'starting material' is recovered, of which 12% is the deuteriated analogue **26** (R = D), 6% is the hydroperoxide **26** (R = OOH) and 1.5% is the alcohol **26** (R = OH). When the procedure is repeated with air bubbling through the solution of base and imine before the addition of D_2O, more of the alcohol and less of the hydroperoxide is obtained. It was hoped that the site of deuteriation could be verified by ^{1}H NMR spectroscopy, but a comparison of the peak integrals over the two low-field, aliphatic proton resonances in the mixture of **2** (R = Bu^t) and **26** (R = D) proved to be inconclusive. However, in the ^{13}C NMR spectrum of the parent compound the carbon atom α to the indolenine (C-7) resonates at 29.1 ppm, whereas in the mixture an extra 1:1:1 triplet (*J* 20 Hz) appears at 28.8 ppm. These chemical shift positions are consistent with deprotonation and deuterium incorporation at C-7.

In the ^{1}H NMR spectrum of the alcohol **26** (R = OH), the multiplicity of a signal at 4.97 ppm (1 H, dd, *J* 3.0, 3.0 Hz) (assigned to the resonance of the H-7) is consistent with the stereospecific abstraction of the axial proton; the coupling constants being appropriate to one $H_{eq/ax}$ and one $H_{eq/eq}$ vicinal coupling. A COSY spectrum relates the C-7 equatorial proton to the adjacent C-6 methylene protons, which resonate at 2.32

§ Personal communication Dr C. Westerlund, Astra (Hässle), Mölndal, Sweden.



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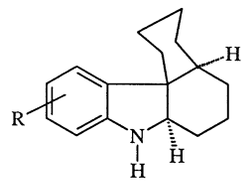

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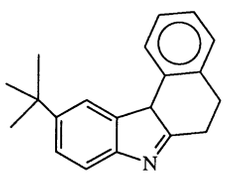

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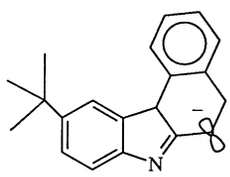

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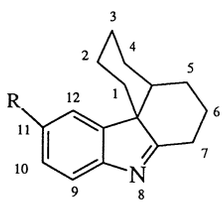

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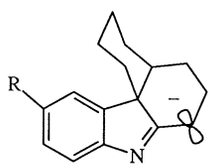

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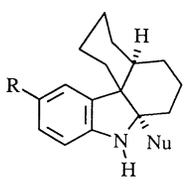

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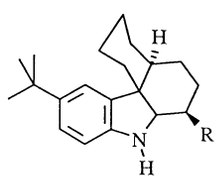


26

(1 H, dddd, *J* 13.5, $J_{eq/ax}$ 3.0, $J_{eq/eq}$ 3.0, $J_{eq/eq}$ 3.0 Hz) and 1.64 (1 H, dddd, J_{gem} 13.5, $J_{ax/ax}$ 13.5, $J_{ax/eq}$ 3.0, $J_{ax/eq}$ 3.0 Hz) and thus may be assigned as equatorial and axial protons, respectively. The constitution of the alcohol was confirmed by an X-ray crystal structure determination (Fig. 2).¶

When 4-methoxy-3,5-dimethylphenylhydrazine hydrochloride is reacted with 1-decalone in the presence of sodium acetate in acetic acid at 105 °C, two isomeric indolenines **27** (R = H) and **30** (R = H) (2:3) are formed as the major products, plus minor amounts of the indole **28** (R = H), its hydroperoxide **29** (R = H, R′ = OOH) and the corresponding alcohol **29** (R = H, R′ = OH). An X-ray crystal structure analysis of the indolenine **30** (R = H) confirms its unusual constitution (Fig. 3).‖ A similar compound (**30**, R = Me) is obtained when 4-methoxy-2,3,5-trimethylphenylhydrazine hydrochloride is reacted with 1-decalone. Although compound **30** (R = Me) has the same R_f as its isomer **28** (R = Me), a separation is possible by exploiting

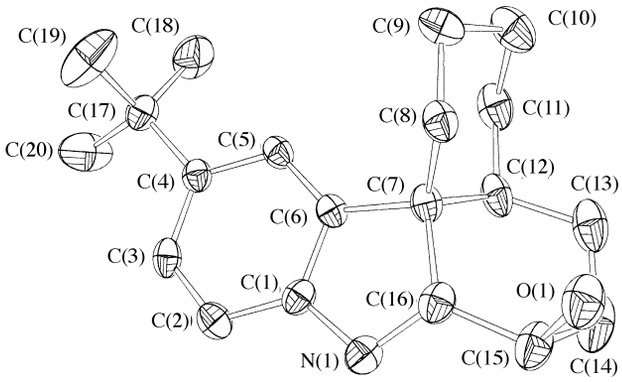
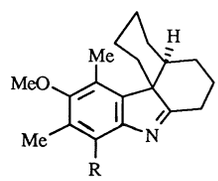


Fig. 2 Molecular plot of **26** (R = OH) showing the labelling scheme used. Ellipsoids are represented at the 30% probability level.



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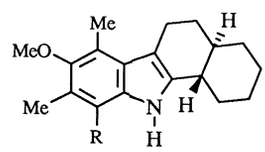

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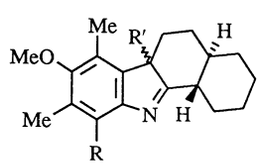

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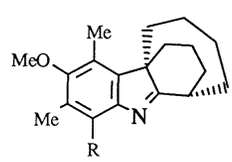

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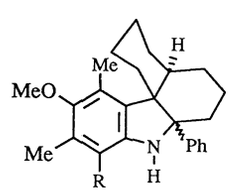

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¶ *X-Ray crystallographic data for* **26**: $C_{20}H_{27}NO$, *M* = 297.4, orthorhombic, *a* = 12.313(3), *b* = 14.397(3), *c* = 19.309(4) Å, *U* = 3423.9 Å^3, space group *Pncn* (No. 52), *Z* = 8, D_c = 1.15 g cm^{-3}, μ(Mo-Kα) = 0.70 cm^{-1}, *F*(000) = 1296. Data were measured at room temperature on a CAD4 automatic four-circle diffractometer in the range $2 < \theta < 24°$. 2683 Reflections were collected of which 1176 were unique with $I \geqslant 2\sigma(I)$. Data were corrected for Lorentz, polarisation and extinction (extraction parameter = 0.001 29). In the final least squares cycles all atoms were allowed to vibrate anisotropically. Hydrogen atoms were included at calculated positions except in the instance of the H1 (attached to O1) which was located in an advanced difference Fourier and refined at a distance of 0.96 Å from the parent atom.

A study of the supramolecular array associated with this structure revealed that pairs of molecules are hydrogen bonded. In particular H1 of the molecule as presented in the ORTEP plot bonds to N1 of the lattice neighbour generated *via* the operator $0.5 - x$, $0.5 - y$, *z*. (H1–N1a; 1.983 Å) The reciprocal bond between N1 of the molecule in the asymmetric unit and H1a of the same lattice neighbour also exists. Final residuals after 10 cycles of least squares (205 parameters) were $R = 0.0576$, $R_w = 0.0563$, for a weighting scheme of $w = 2.4957/[\sigma^2(F) + 0.001\,398(F)^2]$. Maximum final shift/esd was 0.000. The maximum and minimum residual densities were 0.07 and −0.09 e Å^{-3}, respectively.

‖ *X-Ray crystallographic data for* **30**: $C_{19}H_{25}NO$, *M* = 283.4, monoclinic, *a* = 15.341(3), *b* = 10.683(2), *c* = 19.893(3) Å, β = 103.13(2)°, *U* = 3175.0 Å^3, space group $P2_1/n$, *Z* = 8, D_c = 1.19 g cm^{-3}, μ(Mo-Kα) = 0.70 cm^{-1}, *F*(000) = 1232. Data were measured at room temperature on a CAD4 automatic four-circle diffractometer in the range $2 \leqslant \theta \leqslant 24°$. 5495 reflections were collected of which 2162 were unique with $I \geqslant 2\sigma(I)$. Data were corrected for Lorentz and polarisation but not for absorption. The asymmetric unit consisted of 2 enantiomeric molecules which were geometrically equivalent within the bounds of experimental error except for the comparative ring systems involving C7–C16 and C26–C35, which is probably a consequence of some disorder in the C34 position, which could not be successfully refined. In the final least squares cycles all atoms were all allowed to vibrate anisotropically. Hydrogen atoms were included at calculated positions. Final residuals after 10 cycles of least squares (381 parameters) were $R = 0.0688$, $R_w = 0.0621$, for a weighting scheme of $w = 3.6148/[\sigma^2(F) + 0.000\,301(F)^2]$. Maximum final shift/esd was 0.001. The maximum and minimum residual densities were 0.11 and −0.11 e Å^{-3}, respectively.

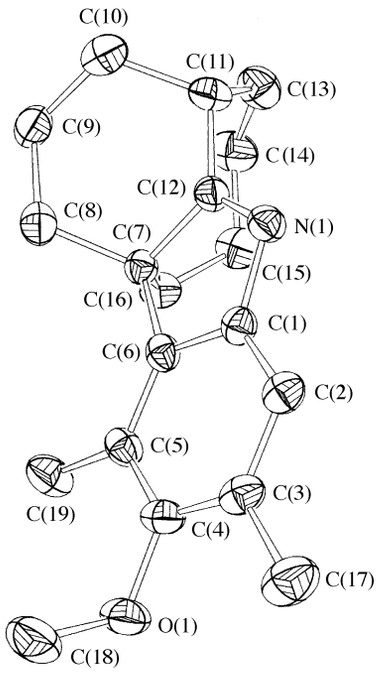
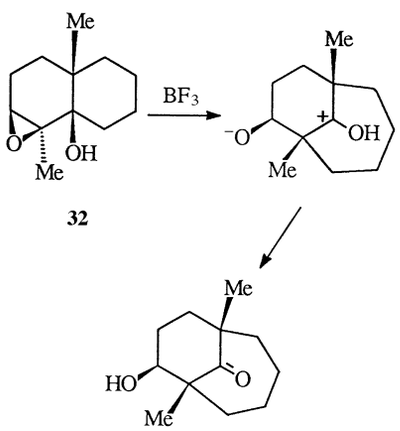


Fig. 3 Molecular plot of one molecule in the asymmetric unit of **30** (R = H) showing the labelling scheme used. Ellipsoids are represented at the 30% probability level.

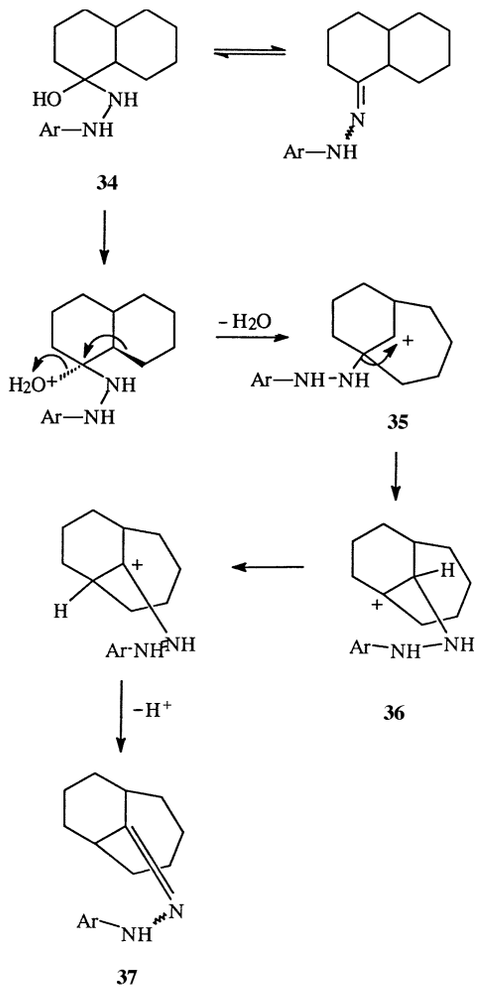
the lack of reactivity of **30** (R = Me) towards phenyllithium (see below).

In order to understand the origin of the new tetracyclic compounds, we heated 1-decalone, the indole **28** (R = H) and its oxygenated derivatives in separate experiments with sodium acetate and acetic acid to see if they might also rearrange. Such changes do not occur. Neither do we observe the formation of a rearranged indolenine in the reaction between 4-methoxyphenylhydrazine hydrochloride and 1-decalone; this gives only the usual indolenine **2** (R = OMe) and indole **1** (R = OMe). This result shows that rearrangement is not contingent upon the presence of a 4-methoxy group in the hydrazine. However, the hydroxyepoxide **32** is known to undergo a pinacol-type rearrangement to give the bicyclo[4.3.1]decan-10-one **33**.[8] A possible mechanism is shown in Scheme 2. We propose that a



Scheme 2

similar mechanism operates in our reactions. Thus, since the rearrangement only occurs when there is steric compression generated by an aryl methyl *ortho* to the developing heterocycle, the normal indolenine forming reaction is relatively slow. This allows an alternative elimination–rearrangement pathway, leading to the cation **35**, to become competitive. This intermediate then undergoes a 1,2-sigmatropic shift of the hydrazinyl group (possibly through an aziridinium species) leading to the tertiary carbocation **36**. Finally, proton migration and deprotonation afford the hydrazone **37**, which then undergoes a conventional Fischer-type annulation to afford the rearranged indolenine (Scheme 3).



Scheme 3 Ar = 4-methoxy-3,5-dimethylphenyl or 4-methoxy-2,3,5-trimethylphenyl

It is probable that the relative stereochemistry of the hydroxy group in the first intermediate **34** also influences the selection of the reaction pathway, since a synchronous rearrangement necessitates that this group and the migrating sigma bond must assume a *trans*-diaxial relationship. For a *trans*-fused decalin system this requires the left hand cyclohexane ring to assume a boat conformation. It should be noted that for a bicyclo-[4.3.1]decan-10-one only a *cis*-fused configuration is acceptable; the *trans* form is 90 kJ mol^{-1} more strained.[9]

Presumably the unreactive nature of indolenines of type **30** towards phenyllithium is due to steric problems, whereas we observe that the indolenines **27** react with phenyllithium to give *two* isomeric indolines (ratio 5:2), which have the same R_f. These indolines are the isomers **31** in which the phenyl group is either α- or β-orientated and the ^{1}H NMR spectrum of the mixture is not affected by an increase in temperature (up to 140 °C in [$^2H_7$]DMF). That two phenyl adducts should form in these cases must reflect, in part at least, the steric effects imposed upon the indolenines **27** by the methyl group at C-12, since for the indolenines **25** (R = Pr^i or Bu^t), unsubstituted at C-12, only the α-phenyl derivatives are observed. Single products **25**, [R = Pr^i, Bu^t, Ph; where Nu can be Me, Bu, Ph, 4-$Bu^tC_6H_4$, $(CH_2)_6N(Bn)_2$ or $(CH_2)_4OPh$] are also formed in the reactions of methyl-, butyl- and 4-(*tert*-butylphenyl)-,

6-(*N*,*N*-dibenzylamino)hexyl- and 5-phenyl-4-oxabutyllithiums with either of the indolenines **2** (R = Pr^i) or **2** (R = Bu^t).

Experimental

Light petroleum refers to the fraction bp range 60–80 °C. ^{1}H and ^{13}C NMR spectra were recorded at 270 or 400 MHz for solutions in deuteriochloroform, unless stated otherwise. *J* Values are given in Hz. IR spectra were obtained as Nujol mulls. All chromatographic procedures used silica gel as the solid phase. Mass spectra were recorded using a VG AutoSpec spectrometer in the EI mode, unless noted otherwise.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, 1997, Issue 1. Any request to the CCDC for this material should quote full literature citation and reference number 207/106. All structures were solved by direct methods and refined using the SHELX[10,11] suite of programs.

2,3,4,4a,5,6,11,11b-Octahydro-8-isopropyl-1*H*-benzo[*a*]carbazole 1 (R = Pr^i) and 1,2,3,4,4a,5,6,7-octahydro-11-isopropylbenzo[*d*]carbazole 2 (R = Pr^i)

Small scale reaction. 4-Isopropylphenylhydrazine (3.7 g) and 1-decalone (3.2 g) in ethanol (40 cm^3) were heated to 50 °C and the solution was allowed to cool to room temperature overnight. The solvent was removed to give the crude hydrazone, which was redissolved in glacial acetic acid (60 cm^3) and 4-sulfosalicylic acid (6.0 g) and the solution was heated to 120 °C for 2.5 h under an atmosphere of nitrogen. The acetic acid was then removed and the residue partitioned between ethyl acetate (50 cm^3) and water (50 cm^3). The organic phase was collected and the aqueous layer was extracted with ethyl acetate (3 × 25 cm^3). The combined organic phases were washed with saturated aqueous sodium hydrogen carbonate (2 × 15 cm^3), dried and evaporated to give a red–brown oil (5.0 g). This was chromatographed on silica gel (40 g) eluting with 3% ethyl acetate in light petroleum to afford the indole **1** (R = Pr^i) (3.2 g, 57%) as an unstable oil; *m*/*z* 267 (100%); ν_{max}/cm^{-1} 3425; δ_H 1.20 (2 H, m), 1.29 (6 H, d, *J* 7), 1.30–2.20 (11 H, m), 2.64–2.85 (1 H, m), 2.99 (1 H, septet, *J* 7.0), 6.99 (1 H, dd, *J* 8.0, 1.0), 7.21 (1 H, d, *J* 8.0), 7.29 (1 H, d, *J* 1.0), 7.69 (1 H, br s).

Further elution with 4% ethyl acetate in light petroleum gave more of the indole **1** (R = Pr^i) (0.6 g) contaminated with another component and elution with 15–25% ethyl acetate in light petroleum then yielded the indolenine **2** (R = Pr^i) as an oil (0.7 g, 12%); *m*/*z* 267 (100%), 253 (95); ν_{max}/cm^{-1} 1610 (C=N); δ_H 1.03 (1 H, br d, *J* 11.0), 1.30 (6 H, d, *J* 7.0), 1.36–1.82 (7 H, m), 1.84–2.28 (5 H, m), 2.57 (1 H, ddd, *J* 13.5, 13.5, 5.5), 2.80 (1 H, dddd, *J* 13.4, 5.5, 2.5, 2.5), 2.98 (1 H, septet, *J* 7.0), 7.22 (1 H, dd, *J* 8.0, 1.5), 7.52 (1 H, d, *J* 8.0), 7.61 (1 H, d, *J* 1.5).

Larger scale reaction. A. The reaction was repeated using 4-isopropylphenylhydrazine (17 g) and 1-decalone (18 g), however this time the crude hydrazone (36.0 g) was dissolved in toluene (150 cm^3) and to the stirred solution was added toluene-*p*-sulfonic acid (PTSA) (17.0 g). The reaction mixture was placed in an oil bath at 130 °C for 15 min and at the end of this time a further addition of PTSA (11.0 g) was made and the reaction mixture was heated under Dean–Stark conditions in toluene for a further 1 h. The reaction mixture was cooled and washed with water (2 × 100 cm^3) and then with saturated aqueous sodium hydrogen carbonate (2 × 50 cm^3). The organic phase was dried and evaporated to give a brown oil (32 g) which rapidly solidified. ^{1}H NMR spectroscopic analysis showed the reaction mixture to consist of a 2:3 mixture of the indolenine **2** (R = Pr^i) and the indole **1** (R = Pr^i). This mixture was then chromatographed giving the indolenine (11.5 g, 38%) and indole (17.1 g, 57%) (yields based on the starting hydrazine).

B. The 4-isopropylphenylhydrazine hydrochloride (40 g), 1-decalone (32 g), freshly fused sodium acetate (34.5 g) and glacial acetic acid (300 cm^3) were heated in an oil bath firstly at 60 °C for 30 min and then at 110 °C for 2 h. The solvent was removed and the residue was partitioned between ethyl acetate (100 cm^3) and water (50 cm^3). The organic layer was collected, washed with brine (4 × 15 cm^3) and then saturated aqueous sodium hydrogen carbonate (2 × 10 cm^3), dried and evaporated. The residue was triturated with light petroleum (25 cm^3) and the solid which formed was collected and washed sparingly with light petroleum, until the filtrate was almost colourless. The colourless powder (30 g) which remained consisted of a 2:1 mixture of the indolenine **2** (R = Pr^i) and the indole **1** (R = Pr^i). The washings and the filtrate were combined and evaporated to afford a brown oil (27 g),which was chromatographed on silica gel (150 g), eluting with ethyl acetate–light petroleum to give impure indole (5.1 g) (5–10% ethyl acetate) and pure indolenine (17.3 g) (15–30% ethyl acetate).

2,3,4,4a,5,6,6a,11b-Octahydro-6a-hydroperoxy-8-isopropyl-1*H*-benzo[*a*]carbazole 3 (R = Pr^i, R′ = HOO) and 3a,4,5,6,7,7a-hexahydro-5′-isopropylspiro[indane-1,2′-indolin]-3′-one 4 (R = Pr^i)

A second reaction was carried out in a similar manner to the above small scale procedure, except that the first fraction eluted from the column with 3% ethyl acetate in light petroleum and was allowed to stand in contact with air. After a few minutes, this solution deposited colourless crystals of the hydroperoxide **3** (120 mg), mp 134 °C (EtOH); *m*/*z* 299 (3%), 283 (100), 188 (80); ν_{max}/cm^{-1} 3080, 1610, 1600; δ_H 1.26 (6 H, d, *J* 7.0), 1.21–1.38 (5 H, m), 1.52–2.00 (6 H, m), 2.20 (1 H, ddd, *J* 14.0, 2.0, 2.0), 2.45–2.58 (2 H, m), 2.94 (1 H, septet, *J* 7.0), 7.24 (1 H, dd, *J* 7.5, 1.5), 7.26 (1 H, d, *J* 1.5), 7.47 (1 H, d, *J* 7.5), 8.01 (1 H, s) (Found: C, 76.1; H, 8.5; N, 4.6. $C_{19}H_{25}NO_2$ requires C, 76.25; H, 8.4; N, 4.65%).

The mother liquor from which the hydroperoxide crystallised was set aside for 4 days during which time more solid separated (1.18 g). This was shown to be a mixture consisting mainly of the hydroperoxide **3** (R = Pr^i, R′ = OOH) and the hydroxy compound **3** (R = Pr^i, R′ = OH). This material (520 mg) in ethanol was heated at reflux for 1 h during which time a yellow colour developed. Removal of the solvent gave a gum which was chromatographed on silica gel (10 g) eluting with 3% ethyl acetate in light petroleum. Early fractions afford the indole **1** (R = Pr^i) (44 mg). Further elution with the same eluent gave the spirocyclic indolin-3-one **4** (R = Pr^i) as yellow prisms (266 mg), mp 170–171 °C; *m*/*z* 283 (100%), 255 (70), 188 (85); ν_{max}/cm^{-1} 3300, 1680; δ_H 1.09–1.18 (6 H, m), 1.22 (3 H, d, *J* 7.0), 1.25 (1 H, m), 1.32–1.51 (3 H, m), 1.56–1.76 (4 H, m), 1.90–2.05 (2 H, m), 2.28 (1 H, ddd, *J* 15.0, 11.0, 2.0), 2.85 (1 H, septet, *J* 7.0), 4.53 (1 H, s), 6.79 (1 H, d, *J* 8.5), 7.33 (1 H, dd, *J* 8.5, 2.0), 7.45 (1 H, d, *J* 2.0) (Found: C, 80.4; H, 8.8; N, 4.8. $C_{19}H_{25}NO$ requires C, 80.6; H, 8.8, N, 4.95%).

2,3,4,4a,5,6,6a,11b-Octahydro-6a-hydroxy-8-isopropyl-1*H*-benzo[*a*]carbazole 3 (R = Pr^i, R′ = OH)

When the column used to purify the first two components in the previous experiment was eluted with 12% ethyl acetate in light petroleum the indolinol **3** (R = Pr^i, R′ = OH) (112 mg) was obtained as colourless needles, mp 145–147 °C (EtOH–H_2O); *m*/*z* 283 (100%), 188 (30); ν_{max}/cm^{-1} 3200; δ_H 1.25 (6 H, d, *J* 7.0), 1.24–1.36 (4 H, m), 1.45–1.65 (3 H, m), 1.65–1.87 (4 H, m), 2.05 (1 H, dd, *J* 13.5, 1.0), 2.26 (1 H, s), 2.40–2.52 (2 H, m), 2.93 (1 H, septet, *J* 7.0), 7.18 (1 H, dd, *J* 8.0, 2.0), 7.26 (1 H, d, *J* 2.0), 7.42 (1 H, d, *J* 8.0); δ_C 24.20, 24.34 (2 × q), 25.8, 26.0, 26.6, 28.5, 33.6, 37.9 (6 × t), 34.0, 44.0, 47.0, 120.1, 120.2, 127.2 (6 × d), 82.0, 141.6, 146.6, 151.3, 189.2 (5 × s) (Found: C, 80.2; H, 9.0; N, 5.0. $C_{19}H_{25}NO$ requires C, 80.6; H, 8.8; N, 4.95%).

The following compounds were similarly prepared from 4-*tert*-butylphenylhydrazine and 1-decalone.

8-*tert*-Butyl-2,3,4,4a,5,6,11,11b-octahydro-1*H*-benzo[*a*]-carbazole 1 (R = Bu^t). Physical data: mp 98 °C; ν_{max}/cm^{-1} 1635, 1610; δ_H 1.03 (1 H, br d, *J* 13), 1.35 (9 H, s), 1.35–1.53 (3 H, m), 1.64 (1 H, br d, *J* 14.0), 1.67–1.80 (3 H, m), 1.87–2.25 (5 H, m), 2.56 (1 H, ddd, *J* 13.5, 13.5, 5.0), 2.79 (1 H, br d, *J* 13.5), 7.38 (1 H, dd, *J* 8.0, 2.0), 7.52 (1 H, d, *J* 8.0), 7.79 (1 H, d, *J* 2.0); δ_C 19.6 (t), 21.4 (t), 26.2 (t), 26.9 (d), 27.2 (t), 28.0 (t), 29.1 (t), 31.6 (q), 34.5 (s), 40.8 (d), 57.3 (s), 119.0 (d), 121.59 (d), 124.3 (d), 145.2 (s), 146.7 (s), 151.9 (s), 189.2 (s); *m*/*z* 281 (30%), 266 (100) (Found: C, 85.1; H, 10.0; N, 5.0. $C_{20}H_{27}N$ requires C, 85.4; H, 9.6; N, 5.0%).

1,2,3,4,4a,5,6,7-Octahydro-11-*tert*-butylbenzo[*d*]carbazole 2 (R = Bu^t). Physical data: mp 98 °C; ν_{max}/cm^{-1} 1635; δ_H 1.03 (1 H, br d, *J* 13), 1.38 (9 H, s), 1.35–1.53 (3 H, m), 1.64 (1 H, br d, *J* 14), 1.67–1.80 (3 H, m), 1.87–2.25 (5 H, m), 2.56 (1 H, ddd, *J* 13.5, 13.5, 5.0), 5.79 (1 H, br d, *J* 13.5), 7.38 (1 H, dd, *J* 8.0, 2.0), 7.52 (1 H, d, *J* 8.0), 7.79 (1 H, d, *J* 2.0); δ_C 31.6 (*C*H$_3$), 19.6, 21.4, 26.2, 26.9, 27.2, 28.0, 29.1 (*C*H$_2$), 40.8, 119.0, 121.5, 124.3 (*C*H), 34.5, 57.3, 145.2, 146.7, 151.9, 189.2 (*C*); *m*/*z* 281 (M^+, 30%), 266 (100) (Found: C, 85.1; H, 10.0; N, 5.0. $C_{20}H_{27}N$ requires C, 85.4; H, 9.6; N, 5.0%).

8-*tert*-Butyl-2,2a,3,4,5,6,6a,11b-octahydro-6a-hydroperoxy-1*H*-benzo[*a*]carbazole 3 (R = Bu^t, R′ = OOH). Physical data: mp 136–138 °C; ν_{max}/cm^{-1} 3100, 1600, 890, 855; δ_H 1.23–1.38 (3 H, m), 1.38 (9 H, s), 1.43–1.60 (1 H, m), 1.68 (1 H, br d, *J* 13), 1.72–1.85 (3 H, m), 1.83–1.99 (1 H, m), 2.10–2.12 (1 H, m), 2.39 (1 H, br d, *J* 14), 2.45 (1 H, dddd, *J* 13.5, 13.5, 13.5, 3.0), 2.78 (1 H, ddd, *J* 13.5, 13.5, 3.6), 5.21 (1 H, dd, *J* 3.0, 3.0), 7.42 (1 H, dd, *J* 8.0, 2.0), 7.58 (1 H, d, *J* 8.0), 7.81 (1 H, d, *J* 2.0), 11.5 (1 H, br s); *m*/*z* 314 (M^+, 100%), 297 (18) (Found: M^+, 313.203 827. $C_{20}H_7NO_2$ requires *M*, 313.204 179).

8-*tert*-Butyl-2,2a,3,4,5,6,6a,11b-octahydro-6a-hydroxy-1*H*-benzo[*a*]carbazole 3 (R = Bu^t, R′ = OH). Physical data: mp 147–148 °C; ν_{max}/cm^{-1} 3110, 1600; δ_H 0.92 (1 H, br d, *J* 13), 1.25–1.42 (1 H, m), 1.35 (9 H, s), 1.48 (1 H, br d, *J* 14), 1.63–1.73 (3 H, m), 1.64 (1 H, dddd, *J* 14.0, 14.0, 3.5, 3.5), 1.73–1.85 (2 H, m), 2.10–2.20 (1 H, m), 2.58 (1 H, dddd, *J* 13.5, 13.5, 13.5, 3.5), 2.87 (1 H, br ddd, *J* 13.5, 13.5, 3.5), 4.69 (1 H, br s), 4.97 (1 H, dd, *J* 3.0, 3.0); *m*/*z* 298 (100%) (Found: C, 80.4; H, 9.30; N, 4.7. $C_{20}H_{27}NO$ requires C, 80.8; H, 9.1; N, 4.7%).

2,3,4,4a,5,6,6a,11,11a,11b-Decahydro-8-isopropyl-1*H*-benzo[*a*]-carbazole 20 (R = Pr^i) (hydrochloride salt)

The crude indole **1** (R = Pr^i) (3.2 g) in glacial acetic acid (30 cm^3) was treated with sodium cyanoborohydride (0.76 g) in portions over a period of 3 h. The solvent was then removed and the residue extracted into ethyl acetate (30 cm^3), washed with water (15 cm^3) and saturated aqueous sodium hydrogen carbonate (15 cm^3). The solvent was evaporated and the residue mixed with silica gel (1.0 g) and added to a column of silica gel (40 g). Elution with 3–4% ethyl acetate in light petroleum gave a gum, which when treated with diethyl ether saturated with hydrogen chloride gave the hydrochloride salt of the title compound as colourless prisms (2.3 g, 71%), mp 262–268 °C (EtOH); *m*/*z* 269 (100%), 254 (90), 172 (75); δ_H($CDCl_3$–CD_3SOCD_3) 1.24 (6 H, d, *J* 7.0), 1.1–2.2 (14 H, m), 2.95 (1 H, septet, *J* 7.0), 3.22 (1 H, m), 3.92 (1 H, m), 7.20 (1 H, d, *J* 8.0), 7.23 (1 H, s), 7.38 (1 H, d, *J* 8.0), 11.6 (2 H, br s); δ_C($CDCl_3$–CD_3SOCD_3) 23.9, 24.0 (*C*H$_3$), 25.8, 26.4, 29.7, 30.1, 31.2, 33.4 (*C*H$_2$), 33.7, 35.5, 41.5, 41.9, 65.2, 119.8, 122.2, 125.9 (*C*H), 133.5, 141.6, 150.1 (*C*) (Found: C, 74.2; H, 9.4; N, 4.6. $C_{19}H_{28}NCl$ requires C, 74.6; H, 9.2; N, 4.6%).

1,2,3,4,4a,5,6,7,7a,8-Decahydro-11-isopropylbenzo[*d*]carbazole 21 (R = Pr^i) (hydrochloride salt)

The indolenine **2** (R = Pr^i) (0.7 g) in glacial acetic acid (12 cm^3) was treated with sodium cyanoborohydride (0.23 g) in portions over 1.5 h. After the removal of the solvent, the residue was extracted with hot light petroleum (5 × 15 cm^3) and the combined extracts were evaporated to a smaller volume (*ca*. 20 cm^3) and then treated with diethyl ether (20 cm^3), previously saturated with hydrogen chloride. After standing for 24 h, the reaction product was filtered off as colourless crystals (0.62 g, 87%), mp 193–194 °C (EtOH–Et_2O, 1:7); *m*/*z* 269 (90%), 212 (100); δ_H 1.25 (6 H, d, *J* 6.5), 1.30–2.20 (15 H, m), 2.94 (1 H, septet, *J* 6.5), 4.03 (1 H, br s), 7.20 (1 H, br d, *J* 7.5), 7.31 (1 H, br s), 7.65 (1 H, d, *J* 7.5), 11.31, 11.80 (1 H, br s); δ_C 19.2, 22.7, 23.2, 25.1, 26.5, 27.7, 33.4 (*C*H$_2$), 24.1 (*C*H$_3$), 34.4, 36.2, 63.8, 121.1, 122.1, 126.1 (*C*H), 47.6, 132.7, 144.7, 150.4 (*C*) (Found: C, 74.3; H, 9.2; N, 4.5. $C_{19}H_{28}NCl$ requires C, 74.6; H, 9.2; N, 4.6%).

1,2,3,4,4a,5,6,7,7a,8-Decahydro-7a-methyl-11-isopropylbenzo-[*d*]carbazole 25 (R = Pr^i, Nu = Me) (hydrochloride salt)

The indolenine **2** (R = Pr^i) (270 mg) in dry THF (10 cm^3) was cooled to −78 °C and treated with 1.4 M methyllithium in THF (2.1 cm^3) over a period of 10 min. The reaction mixture was maintained at this temperature for a further 30 min and then allowed to warm to room temperature. Excess reagent was destroyed by the addition of saturated aqueous ammonium chloride (0.8 cm^3) and the organic layer was collected. The aqueous phase was then extracted with ethyl acetate (3 × 15 cm^3) and the combined organic phases were dried and evaporated to afford an oil which was chromatographed on silica gel (5 g) eluting with 1% ethyl acetate in light petroleum. An oil was obtained and this was converted into the hydrochloride salt of the title compound **25** (R = Pr^i, Nu = Me) by treatment with diethyl ether (5 cm^3) and the addition of diethyl ether (0.5 cm^3), previously saturated with hydrogen chloride. This product was obtained as colourless micro-prisms (181 mg, 63%), mp 182–184 °C (Et_2O); ν_{max}/cm^{-1} 2680–2510; δ_H 1.26 (6 H, d, *J* 7.0), 1.40–1.75 (12 H, m), 1.75–2.05 (4 H, m), 2.05–2.15 (2 H, m), 2.93 (1 H, septet, *J* 7.0), 7.18 (1 H, dd, *J* 8.0, 1.5), 7.37 (1 H, s), 7.59 (1 H, d, *J* 8.0), 11.31 (1 H, br s), 11.66 (1 H, br s) (Found: C, 74.8; H, 9.5; N, 4.2. $C_{20}H_{30}NCl$ requires C, 75.1; H, 9.4; N, 4.4%).

1,2,3,4,4a,5,6,7,7a,8-Decahydro-11-isopropyl-7a-phenylbenzo-[*d*]carbazole 25 (R = Pr^i, Nu = Ph)

Small scale reaction. The indolenine **2** (R = Pr^i) (700 mg) in THF was cooled at 0 °C and treated with 0.9 M phenyllithium in THF (2.1 cm^3) over a period of 20 min. The reaction mixture was then allowed to warm to room temperature and more reagent (5 cm^3) was added. After a few minutes excess reagent was destroyed by the addition of saturated aqueous ammonium chloride (3.0 cm^3) and the solvent layer was collected. The aqueous phase was then extracted with ethyl acetate (3 × 15 cm^3) and the combined organic phases were dried and evaporated to afford an oil which was chromatographed on silica (50 g) eluting with light petroleum. This afforded biphenyl, which was discarded. The eluent was then changed to 1–2% ethyl acetate in light petroleum and this gave the title compound (425 mg, 47%) as colourless prisms, mp 155–156 °C (light petroleum); ν_{max}/cm^{-1} 2295, 1605; δ_H 0.80–0.92 (1 H, m), 1.02–1.13 (1 H, ddd, *J* 13.5, 4.0, 4.0), 1.19 (3 H, d, *J* 7.0), 1.20 (3 H, d, *J* 7.0), 1.14–1.34 (2 H, m), 1.36–1.53 (3 H, m), 1.54–2.00 (8 H, m), 2.31 (1 H, m), 2.84 (1 H, septet, *J* 7.0), 3.84 (1 H, br s), 6.62 (1 H, d, *J* 8.0), 6.93 (1 H, dd, *J* 8.0, 1.5), 6.93 (1 H, dd, *J* 8.0, 1.0), 7.09 (1 H, d, *J* 1.0), 7.12–7.22 (3 H, m), 7.40 (1 H, br d, *J* 8.0) (Found: C, 86.7; H, 9.0; N, 4.1. $C_{25}H_{31}N$ requires C, 88.0; H, 9.0; N, 4.05%).

Larger scale preparation. The indolenine **2** (R = Pr^i) (11.3 g, 4.23 mmol) was dissolved in THF (100 cm^3, Na dried) and to the stirred solution under N_2 at 0 °C was added PhLi (25 cm^3, 1.8 M, 45.0 mmol) *via* a syringe over 20 min. Further additions amounting to (10 cm^3, 18.0 mmol) of the reagent were made over 2.5 h (after this treatment TLC analysis of the reaction mixture still showed the presence of a minor component with the same R_f as the starting material). The solution was then held at room temperature for 0.5 h before saturated aqueous ammo-

nium chloride (4.0 cm^3) was added to destroy the excess reagent. This treatment gave a clear yellow solvent layer which was decanted from a precipitate of inorganic solids. The latter were washed with diethyl ether (4 × 10 cm^3) and the combined washings and solvent layer were dried and evaporated to afford a brown oil (12.5 g). Treatment of this oil with light petroleum (20 cm^3) caused a solid to form which, after trituration, was collected and washed with small portions of light petroleum until the filtrate was colourless. The residue was then twice suspended in boiling light petroleum (15 cm^3) to remove last traces of soluble impurities and finally it was dried under reduced pressure. This afforded the title compound as a colourless microcrystalline powder (5.25 g, mp 153–155 °C).

The combined mother liquid and light petroleum washings were evaporated and the residue obtained subjected to column chromatography [120 g, SiO_2, eluting with ethyl acetate in light petroleum (0→4%, then 4% and then 4→25%)]. This gave biphenyl (1.2 g) (light petroleum only), title compound (1.2 g) (3→4% ethyl acetate in light petroleum) and starting indolenine (4.5 g) (25% ethyl acetate in light petroleum). The total yield of products was thus 6.45 g, 45% (73%, if the recovered starting material was taken into account).

7a-Butyl-1,2,3,4,4a,5,6,7,7a,8-decahydro-11-isopropylbenzo-[*d*]carbazole 25 (R = Pr^i, Nu = Bu) (hydrochloride salt)

The indolenine **2** (R = Pr^i) (7.0 g, 26.2 mmol) in THF (Na dried, 110 cm^3) at 0 °C under N_2, was treated with BuLi (20 cm^3, 1.5 M, 30 mmol) over 20 min and the reaction mixture was allowed to reach room temperature and then kept at this temperature overnight. The excess reagent was decomposed by the careful addition of saturated aqueous NH_4Cl (7.0 cm^3) and the organic layer was then separated and the residue was washed with diethyl ether (4 × 20 cm^3). The combined organic layer and extracts were dried and treated with Et_2O (10 cm^3) previously saturated with HCl. From this solution the hydrochloride salt of the title compound gradually separated. It was washed repeatedly (5 × 3 cm^3) with cold acetone affording a colourless microcrystalline solid (6.1 g, 64%), mp 211–215 °C (EtOH); ν_{max}/cm^{-1} 2700–2500, 1610, 1605; δ_H 0.92 (3 H, t, *J* 7.0), 1.25 (6 H, d, *J* 7.0), 1.26–2.20 (21 H, m), 2.93 (1 H, septet, *J* 7.0), 7.15 (1 H, d, *J* 8.0), 7.24 (1 H, s), 7.71 (1 H, d, *J* 8.0), 11.32 (1 H, br s), 11.47 (1 H, br s) (Found: C, 76.4; H, 10.3; N, 3.9. $C_{23}H_{35}N\cdot HCl$ requires C, 76.35; H, 10.9; N, 3.9%).

7a-(4-*tert*-Butylphenyl)-1,2,3,4,4a,5,6,7,7a,8-decahydro-11-isopropylbenzo[*d*]carbazole 25 (R = Pr^i, Nu = 4-$Bu^tC_6H_4$)

The indolenine **2** (R = Pr^i) (5.3 g, 20 mmol) and 4-*tert*-butylphenyl bromide (5.11 g, 24 mmol) in dry THF (75 cm^3) under N_2 at 0 °C was treated with Bu^tLi (30 cm^3, 1.7 M in pentane, 50 mmol) over 0.5 h, then the reaction mixture was heated at 45 °C for a further 2 h. Saturated aqueous NH_4Cl (10 cm^3) was added and the solvent evaporated. The residue was partitioned between ethyl acetate and water. The combined extracts were dried and evaporated. The residue was treated with acetone (7 cm^3), the mixture allowed to stand for 30 min, filtered and the residue washed with acetone (4 × 1 cm^3) until a colourless filtrate was obtained. After this treatment the residue consisted of colourless crystals of the title compound (1.33 g), mp 202–203 °C. The filtrate was evaporated and the residue subjected to column chromatography. Elution with 1% ethyl acetate in light petroleum gave more of the title compound (180 mg), whereas 40% ethyl acetate in light petroleum produced the starting indolenine (3.6 g). Yield 19% (adjusted for recovered indolenines 61%); ν_{max}/cm^{-1} 3380, 1610; δ_H 1.11 (1 H, ddd, *J* 14.0, 3.5, 3.5), 1.20 (3 H, d, *J* 7.0), 1.22 (3 H, d, *J* 7.0), 1.26 (9 H, s), 1.30–2.00 (14 H, m), 2.30 (1 H, m), 2.80 (1 H, septet, *J* 7.0), 3.84 (1 H, br s), 6.62 (1 H, d, *J* 8.0), 6.92 (1 H, dd, *J* 8.0, 1.5), 7.12 (1 H, d, *J* 1.5), 7.18 (2 H, d, *J* 8.5), 7.28 (2 H, br d, *J* 8.5) (Found: C, 86.6; H, 9.6; N, 3.4. $C_{29}H_{39}N$ requires C, 86.8; H, 9.7; N, 3.5%).

11-*tert*-Butyl-1,2,3,4,4a,5,6,7a,8,12b-decahydro-7a-(4-phenoxybutyl)benzo[*d*]carbazole 25 [R = Bu^t, Nu = $(CH_2)_4OPh$] (hydrochloride salt)

The title compound was formed in 64.5% yield from **2** (R = Bu^t) and 4-phenoxybutyllithium (prepared from the corresponding bromide by treatment with *tert*-butyllithium as in the previous experiment); mp 211–213 °C; ν_{max}/cm^{-1} 2660–2434; 1.29 (9 H, m), 1.30–2.0 (21 H, m), 3.97 (2 H, t, *J* 6.2), 6.9 (3 H, m), 7.25 (3 H, m), 7.42 (1 H, d, *J* 0.5), 7.7 (1 H, dd, *J* 7.7, 0.5), 11.4 (1 H, br s, exchanged by D_2O), 11.6 (1 H, br s, exchanged by D_2O); *m*/*z* 431 (25%, M^+), 282 (100).

11-*tert*-Butyl-1,2,3,4,4a,5,6,7a,8,12b-decahydro-7a-[6-(*N*,*N*-dibenzylamino)hexyl]benzo[*d*]carbazole 25 [R = Bu^t, Nu = $(CH_2)_6NBn_2$] (dihydrochloride)

The title compound was formed in 42.5% yield from **2** (R = Bu^t) and 6-(*N*,*N*-dibenzylamino)hexyllithium; mp 150–154 °C; ν_{max}/cm^{-1} 3354, 2602; δ_H 1.1–2.6 (25 H, m), 1.3 (9 H, s), 2.8 (1 H, br s), 4.08 (2 H, q, *J* 7.5), 4.5 (2 H, m), 4.7 (1 H, dd, *J* 14.0, 4.5), 7.23 (1 H, d, *J* 1.8), 7.27 (1 H, dd, *J* 8.0, 1.9), 7.61 (1 H, d, *J* 8.0), 7.4–7.8 (10 H, m), 11.2 (2 H, br s, exchanged by D_2O), 12.2 (1 H, br s, exchanged by D_2O); *m*/*z* (EI) 282 (100%); (CI) 521 (90, M^+) (Found: C, 75.2; H, 8.7; N, 4.0. $C_{40}H_{56}N_2Cl_2$ requires C, 75.6; H, 8.8; N, 4.4%).

11-*tert*-Butyl-1,2,3,4,4a,5,6,7-octahydro[7β-^{2}H]benzo[*d*]-carbazole 26 (R = D)

tert-Butyllithium (1 M, 1.2 cm^3, 1.7 mmol) was added to a solution of the indolenine **2** (R = Bu^t) (0.28 g, 1 mmol) in dry THF (10 cm^3) under N_2. After the addition, air (*ca.* 35 cm^3) was slowly bubbled into the reaction mixture *via* a syringe. D_2O (0.8 cm^3, 40 mmol) was then introduced and the next day saturated aqueous NH_4Cl (0.5 cm^3) was added. The organic layer was removed and evaporated to give a colourless residue, which was partitioned between water and ethyl acetate. The ethyl acetate layer was collected and evaporated to afford an oil (300 mg) and this was then chromatographed. Fraction 1 (15% ethyl acetate–light petroleum) (152 mg) contained the deuteriated compound **26** (R = D) (12%), fraction 2 (20% ethyl acetate–light petroleum) (50 mg) contained the hydroperoxide **26** (R = OOH) (17%) and fraction 3 (30% ethyl acetate–light petroleum) gave the alcohol **26** (R = OH) (4%). When the same procedure was carried out without air being drawn through the reaction mixture, the respective yields were 54, 6 and 1.5%. The structure of the alcohol **26** (R = OH) is confirmed by an X-ray crystal structure determination. [NB The ^{13}C NMR spectrum of the deuteriated compound is essentially the same as that of the parent (**26**, R = H), see above, except after the addition of D_2O the quartet at 29.1 ppm becomes a triplet at 28.8 ppm].

1,2,3,4,4a,5,6,7-Octahydro-11-methoxy-10,12-dimethylbenzo[*d*]carbazole 27 (R = H), 1,4a-butano-1,2,3,4-tetrahydro-6-methoxy-5,7-dimethylcarbazole 30 (R = H), 2,3,4,4a,5,6,6a,11b-octahydro-6a-hydroxy-8-methoxy-7,9-dimethyl-1*H*-benzo[*a*]carbazole 29 (R = H, R′ = OH) and 2,3,4,4a,5,6,6a,11b-octahydro-6a-hydroperoxy-8-methoxy-7,9-dimethylbenzo[*a*]carbazole 29 (R = H, R′ = OOH)

Fused sodium acetate (0.85 g) in warm glacial acetic acid (20 cm^3) was treated with 4-methoxy-3,5-dimethylphenylhydrazine hydrochloride (1.01 g, 5 mmol) and 1-decalone (0.8 g, mmol). The mixture was heated at 105 °C for 1 h and the solvents were then removed under reduced pressure. The residue was partitioned between ethyl acetate and water and the organic phase was washed with saturated aqueous $NaHCO_3$, dried and evaporated. The residue was chromatographed, eluting at first with 5% ethyl acetate in light petroleum and then with 10% ethyl acetate to give the imine **30** (R = H) (0.35 g, 25%) and finally with 15% ethyl acetate to give the imine **27** (R = H) (0.39 g, 28%).

30 (R = H): mp 104–106 °C; ν_{max}/cm^{-1} 1570; δ_H 1.02 (1 H, m), 1.27 (1 H, ddd, *J* 13.1, 13.0, 4.4), 1.6–1.8 (6 H, m), 1.84–1.89 (2 H, m), 1.94–1.99 (1 H, dm), 2.0–2.17 (3 H, m), 2.32 (3 H, s), 2.33 (3 H, s), 2.5 (1 H, dd, *J* 13.7, 4.0), 3.3 (1 H, q, *J* 5.4), 3.7 (3 H, s), 7.19 (1 H, s); *m*/*z* 283 (100%, M^+), 268 (80, M − 15).

27 (R = H): ν_{max}/cm^{-1} 1594; δ_H 1.15 (1 H, br d, *J* 10), 1.4–1.6 (3 H, m), 1.72–1.85 (4 H, m), 1.97–2.17 (4 H, m), 2.34 (3 H, s), 2.42–2.53 (1 H, m), 2.56 (1 H, ddd, *J* 13.5, 13, 7.5), 2.66 (3 H, s), 2.77 (1 H, ddd, *J* 13.2, 4.5, 2.8), 3.71 (3 H, s), 7.26 (1 H, s); *m*/*z* 283 (100%, M^+), 268 (80).

The initial combined fractions from the column on evaporation yielded a 6:5 mixture of **29** (R = H, R′ = OH) and **29** (R = H, R′ = OOH) (0.2 g, 20%).

29 (R = H, R′ = OH): δ_H([$^2H_6$]DMSO) 1.0–2.50 (14 H, m), 2.22 (3 H, s), 2.28 (3 H, s), 3.61 (3 H, s), 5.59 (1 H, s, exchanged by D_2O), 7.05 (1 H, s); *m*/*z* 299 (100%, M^+), 284 (30).

29 (R = H, R′ = OOH): δ_H([$^2H_6$]DMSO) 1.0–2.50 (14 H, m), 2.3 (3 H, s), 2.26 (3 H, s), 3.63 (3 H, s), 7.05 (1 H, s), 11.52 (1 H, s, exchanged by D_2O); *m*/*z* 315 (5%, M^+), 299 (100).

1,2,3,4,4a,5,6,7,7a,8-Decahydro-11-methoxy-10,12-dimethyl-7a-phenylbenzo[*d*]carbazole 31 (R = H)

To **27** (R = H) (1.25 g, 4.4 mmol) in dry THF (30 cm^3) was added phenyllithium (6 cm^3, 1 M) at 0 °C under N_2. After an hour, the mixture was warmed to room temperature and left for another hour, before saturated aqueous NH_4Cl (0.5 cm^3) was added. The solvents were removed under reduced pressure and the residue was partitioned between ethyl acetate and water. The organic phase was dried and evaporated and the residue was column chromatographed on silica eluting with 1% ethyl acetate in light petroleum to give the title compound. It was dissolved in diethyl ether and diethyl ether saturated with HCl was added to convert it into the hydrochloride salt. However, the ^{1}H NMR spectrum showed that the salt was a mixture of two isomers in the ratio 6:7. This proved inseparable by column chromatography, mp 178–180 °C; ν_{max}/cm^{-1} 3380br, 1572; *m*/*z* 361 (100%, M^+) (Found: C, 75.5; H, 8.2; N, 3.5. $C_{25}H_{32}NOCl$ requires C, 75.5; H, 8.05; N, 3.5%).

1,2,3,4,4a,5,6,7-Octahydro-11-methoxy-9,10,12-trimethylbenzo[*d*]carbazole 27 (R = Me), 1,4a-butano-1,2,3,4-tetrahydro-6-methoxy-5,7,8-trimethylcarbazole 30 (R = Me), 2,3,4,4a,5,6,6a,11b-octahydro-6a-hydroxy-8-methoxy-7,9,10-trimethylbenzo[*a*]carbazole 29 (R = Me, R′ = OH) and 2,3,4,4a,5,6,6a,11b-octahydro-6a-hydroperoxy-8-methoxy-7,9,10-trimethylbenzo[*a*]carbazole 29 (R = Me, R′ = OOH)

The first two compounds were obtained as a 2:3 mixture from 4-methoxy-2,3,5-trimethylphenylhydrazine hydrochloride and 1-decalone by an analogous experiment to that used to synthesise **27** (R = H) and **30** (R = H). Unlike the latter pair of compounds, however, they could not be separated.

27 (R = Me): δ_H 0.9–2.1 (13 H, m), 2.23 (3 H, s), 2.34 (3 H, s), 2.46 (3 H, s), 2.9 (2 H, m), 3.68 (3 H, s).

30 (R = Me): δ_H 1.0–2.2 (14 H, m), 2.24 (3 H, s), 2.30 (3 H, s), 2.48 (3 H, s), 3.38 (1 H, dd, *J* 7.0, 7.0), 3.69 (3 H, s).

Also isolated as a mixture were: **29** (R = Me, R′ = OH): δ_H([$^2H_6$]DMSO) 1.0–2.5 (14 H, m), 2.14 (3 H, s), 2.23 (3 H, s), 2.32 (3 H, s), 3.60 (3 H, s), 5.51 (1 H, s, exchanged by D_2O); *m*/*z* 313 (100%, M^+); and **29** (R = Me, R′ = OOH): δ_H([$^2H_6$]DMSO) 1.0–2.5 (14 H, m), 2.13 (3 H, s), 2.25 (3 H, s), 2.33 (3 H, s), 3.58 (3 H, s), 11.46 (1 H, s, exchanged by D_2O); *m*/*z* 329 (5%, M^+), 313 (100).

When the mixture of **27** (R = Me) and **30** (R = Me), was treated with phenyllithium (1 equiv.) another mixture formed. This consisted of unreacted **30** (R = Me), plus diastereomers **31** (R = Me). The diastereomers (as a 5:2 mixture) could be separated from the indoline **30** (R = Me) by chromatography eluting with 5% ethyl acetate in light petroleum. Major isomer: δ_H 0.9–2.0 (14 H, m), 2.08 (3 H, s), 2.13 (3 H, s), 2.23 (3 H, s), 2.48 (1 H, ddd, *J* 13.0, 12.8, 1.8), 3.61 (3 H, s), 7.09–7.20 (4 H, m), 7.3 (1 H, d, *J* 8). Minor isomer: δ_H 0.9–2.0 (14 H, m), 1.99 (3 H, s), 2.20 (3 H, s), 2.31 (3 H, s), 2.70 (1 H, ddd, *J* 12.5, 12.5, 12.5), 3.63 (3 H, s), 7.09–7.24 (4 H, m), 7.98 (1 H, d, *J* 8.0).

The mixed diastereomers formed mixed hydrochloride salts on treatment with diethyl ether saturated with HCl, mp 175–176 °C (decomp.) (Found: C, 75.9; H, 8.4; N, 3.5. $C_{26}H_{34}NOCl$ requires C, 75.8; H, 8.3; N, 3.4%).

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