Reactions of some Indolyl Alcohols and Indolyl-olefins with Arenesulphonyl Azides

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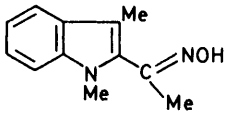
The reactions of 1,3-dimethylindol-2-ylmethanols with arenesulphonyl azides afford 2-arenesulphonylamino-1,3-dimethylindoles as the major products, the side chain being lost, whilst hexahydro-5-methylcyclohept[*b*]indol-6-ol yields 2-arenesulphonylimino-2'-hydroxy-1-methylindoline-3-spirocyclohexanes. From the reaction between 5-methyl-5,8,9,10-tetrahydrocyclohepta[*b*]indole and *p*-chlorobenzenesulphonyl azide three products have been isolated and shown to be 2-*p*-chlorophenylsulphonylimino-1-methylindoline-3-spirocyclohex-2'-ene, 6-*p*-chlorophenylsulphonylimino-5,6,7,8,9,10-hexahydro-5-methylcyclohepta[*b*]indole and 2'-*p*-chlorophenylsulphonylaminomethylene-2-*p*-chlorophenylsulphonylimino-1-methylindoline-3-spirocyclopentane.

ALTHOUGH we have examined the reactions of arenesulphonyl azides with a wide range of indoles containing alkyl and aryl groups our examination of the reactions



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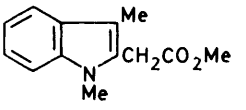

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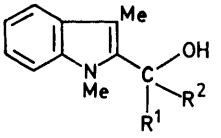
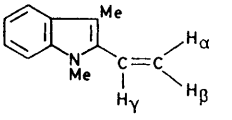


(3) $R^1 = H, R^2 = Me$
(4) $R^1 = R^2 = Me$
(5) $R^1 = R^2 = H$

of substituted indoles has been limited to carbonyl derivatives, for example (1) [1] and (2).[2] This work has now been extended to alcohols and olefins of types (3)—(5) and (6) and (7). It was necessary to examine both types of compound since dehydration of the alcohols (3) and (4) to form olefins readily occurs.

Compound (3) was obtained by reduction of the known [1] 2-acetyl-1,3-dimethylindole. Treatment of 2-acetyl-1,3-dimethylindole with methylmagnesium iodide yielded compound (4). It was impossible to purify this alcohol since on chromatography or just on standing at room temperature dehydration occurred. The



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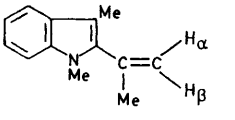

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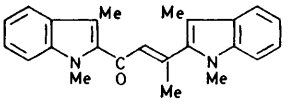

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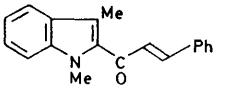

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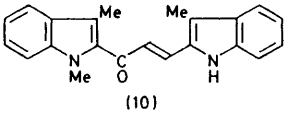
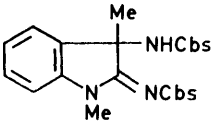


(10)

primary alcohol (5) was produced by the reduction of methyl 1,3-dimethylindole-2-carboxylate; [2] this alcohol



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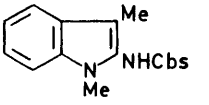

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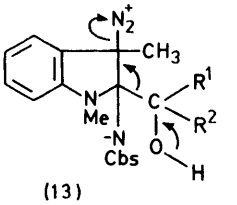

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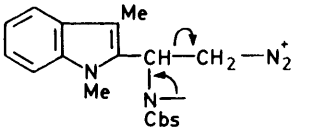

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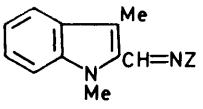


(15)

$-H_2O$ ↑ $+CbsN_3$

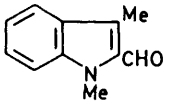
(3)

$CbsN_3$ ↑

(3)

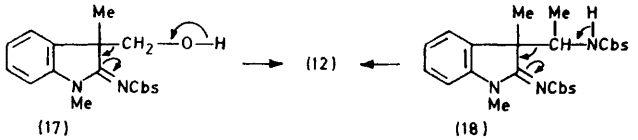
had been obtained previously [3] but not characterised. 1,3-Dimethyl-2-vinylindole (6) was prepared from 1,2,3-trimethylindole *via* the Mannich reaction.[4] Chromatography of the mother-liquors obtained in the preparation of compound (4) afforded a 1% yield of (8), the self-condensation product of 2-acetyl-1,3-dimethylindole; compound (8) was obtained in very small yield by boiling 2-acetyl-1,3-dimethylindole in xylene containing aluminium t-butoxide. The compound is assigned the *trans* configuration by analogy with the formation of *trans*-chalcones by this type of condensation.[5] The two 'model' compounds (9) and (10) were prepared by the reaction of 2-acetyl-1,3-dimethylindole with benzaldehyde and with 2-formyl-3-methylindole.

In preliminary experiments a strong smell of acetaldehyde was noted when compound (3) was warmed with *p*-chlorobenzenesulphonyl azide ($CbsN_3$); therefore a mixture of the alcohol and azide was warmed gently in a stream of nitrogen. The gases were passed through Brady's reagent yielding acetaldehyde DNP. The major products of the reaction were the known [3,6] mono- (12) (yield 75%) and di- (11) (yield 14%) adducts. A 3% yield of the imine (15; Z = Cbs) was also obtained. The structure of (15; Z = Cbs) was established by a comparison of its properties with the known [3] compound (15; Z = Ts). Compound (12) probably arises *via* the intermediate (13) by the loss of acetaldehyde and (12) then reacts with more azide to form (11). The formation of (15) from (3) involves the loss of a carbon atom and we suggest that this occurs by loss of water from the alcohol to form small quantities of the olefin which then adds $CbsN_3$ to yield (14), which loses diazomethane to form (15; Z = Cbs) [*cf.* the reactions of the cyclic olefin (26)]. Loss of water after the addition of $CbsN_3$ to (3) forming (13) could not lead to (15). Treatment of the tertiary alcohol (4) with $CbsN_3$ afforded acetone and the adducts (11) (7% yield) and (12) (59% yield). The reactions of the primary alcohol (5) were different from those of the secondary and tertiary alcohols. No

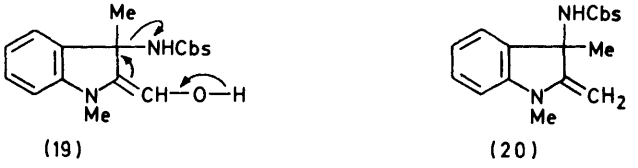


(16)

formaldehyde was detected in the gas evolved. The yield of the aminoindole (12) was only 11% and none of the 2 : 1 adduct (11) was obtained. The imine (15) (yield 4%) was found and also the aldehyde (16) (22%) which was not an impurity in the starting material. The main product was a gum, a mixture of $CbsNH_2$ and an unstable material. Recrystallisation afforded $CbsNH_2$ and compound (12). The n.m.r. spectrum of the crude mixture suggested that the unstable component was (17), formed by migration of the CH_2OH group; (17) then breaks down to form (12) [*cf.* the formation [7] of (12) from (18)]. The aldehyde (16) probably arises by the loss of $CbsNH_2$ from the intermediate (19) [*cf.* the reaction [3] of 1,2,3-trimethylindole which involves (20) as an intermediate]. However the formation of (15) from (5) does not involve the loss of a carbon atom but a molecule of water and we suggest that formation of (15) involves a shift of the N–Cbs group as shown [(21) ⟶ (22)]. Any reaction sequence involving the loss of water as the first step seems unlikely since an intermediate of type (23) would react with $CbsN_3$ at the $N–C=CH_2$ group with the loss of diazomethane.[3]



(17) (12) (18)



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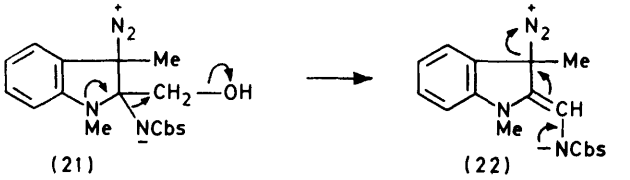

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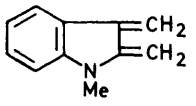
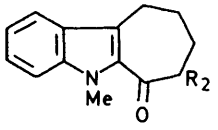


(23)

The reactions of the two olefins with $CbsN_3$ was very complex. Dark polymeric tars were produced and neither p.l.c. nor column chromatography afforded any pure materials.

The reactions of a cyclic alcohol and of the corresponding olefin were also examined. Compounds (25; $R^1 = R^2 = H$) and (26; $R^1 = R^2 = H$) were selected since we know [8] that *N*-methylhexahydrocyclohepta[*b*]-indole reacts faster with azides than does *N*-methyl-



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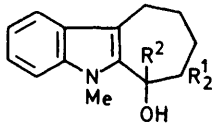

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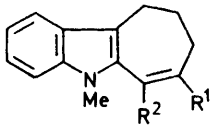

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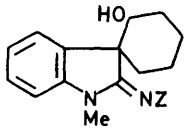
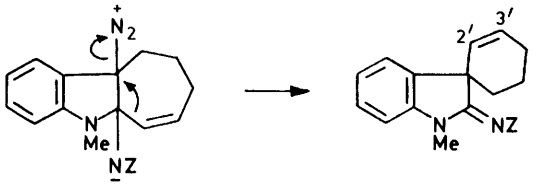


(27)

tetrahydrocarbazole; further, derivatives of 1-hydroxy-tetrahydrocarbazole readily form dihydrocarbazoles

which undergo disproportionation or polymerisation.[9] Hexahydrocyclohept[*b*]indol-6-one [10] was methylated [10] forming the hexahydro-5-methylcyclohept[*b*]indol-6-one (24; R = H). This ketone did not react with azides under a variety of conditions; reduction of the ketone afforded the corresponding alcohol (25; $R^1 = R^2 = H$). Preliminary experiments showed that the alcohol did react with $CbsN_3$ but complications arose since in chloroform solution in daylight the reaction (25) ⟶ (26) rapidly occurred. Therefore all reactions involving (25) and (26) were done as far as possible in the dark.

Reaction of the alcohol (25; $R^1 = R^2 = H$) with $CbsN_3$ afforded the spiro-alcohol (27; Z = Cbs) (yield 53%) (when the reaction was run in the presence of an anti-oxidant the yield was slightly improved). This structure was supported by its characteristic mass spectrum [3,8]. On carrying out the reaction in acetic anhydride solution small quantities of the spiro-olefin (29; Z = Cbs) were isolated. This is believed to arise *via* (26) rather than by dehydration of (27), since (27; Z = Cbs) melted without decomposition, was stable in chloroform solution in daylight, and dissolving (27; Z = Cbs) in trifluoroacetic acid (TFA) afforded the



(28) (29)

corresponding ester and not the olefin (29; Z = Cbs). Oxidation of (27; Z = Cbs) afforded the corresponding ketone, confirming the presence of a CHOH group.

From the reaction between $CbsN_3$ and the olefin (26; $R^1 = R^2 = H$) three products have been isolated, two of which were easily identified. The spiro-olefin (29; Z = Cbs) [formed *via* (28)] had the expected i.r. and u.v. spectra but the n.m.r. spectrum of the compound [and that of (29; Z = *p*-nitrophenylsulphonyl)] showed unusual features. For the *p*-nitro-derivative, the multiplet at τ 3.8 was assigned to C(3')H, the doublet (*J* 10 Hz) for C(2')H appearing at the 'normal' olefinic CH position. Dreiding models indicate that the favoured conformation is as shown in the Figure; any other half-chair arrangements bring the oxygen atoms of the SO_2 group into contact with the H atoms of the cyclohexene ring. This structure assumes that the C=N–SO_2Ar group is *anti* to the indole *N*-methyl group.[3,11] In this conformation the C(3')H atom and one of the H atoms on C(6') are very close to the SO_2 group. Decoupling experiments gave the assignments indicated in the Figure. The ^{13}C spectrum showed the presence of three CH_2 groups and one quaternary aliphatic C (53.8 p.p.m.). The signals of the two vinylic carbon atoms were in the same region as the eight aromatic (CH) signals. The olefin was characterised as the epoxide (30); bromination afforded the tribromo-derivative (31). Under the same conditions the 'model' compound (32; R = H) gave (32; R = Br) [*cf.* the bromination of (33; R = H) giving (33; R = Br) and of oxindole derivatives [12]]. The second product obtained from

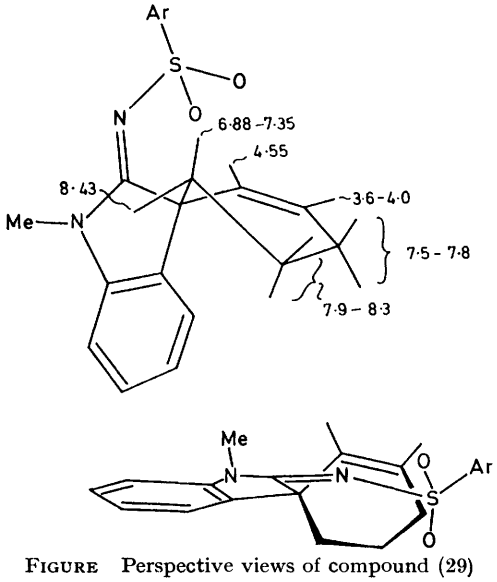
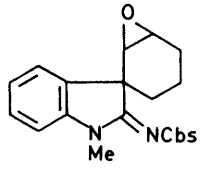


FIGURE Perspective views of compound (29)

(26; $R^1 = R^2 = H$) was the imine (35; $R^1 = R^2 = H$); the u.v. spectrum of the material showed that the C=NCbs group was conjugated with the indole nucleus. Since



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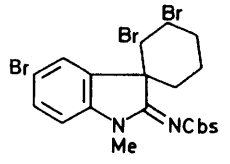

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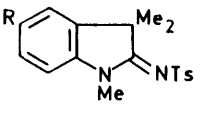

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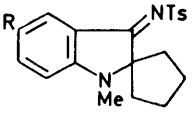

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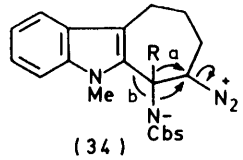

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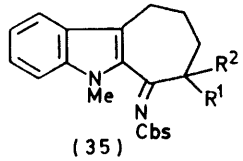

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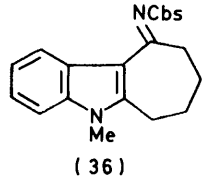
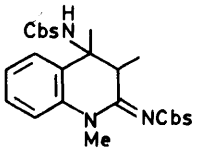


(36)

the compound was not the known imine (36) [8] we assigned the structure (35; $R^1 = R^2 = H$); this was confirmed by hydrolysis [(35; $R^1 = R^2 = H$) ⟶ (24; R = H)].

We assume that (35) arises *via* (34; R = H) by a proton shift (route a).



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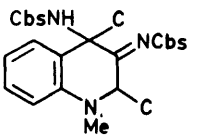

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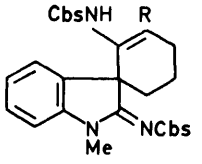

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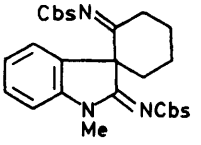

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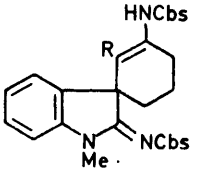
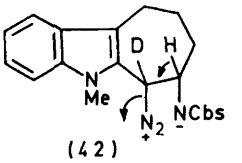


(41)

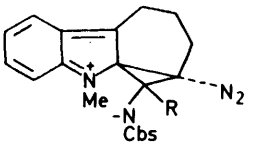
The third product was a 1 : 2 adduct which contained NHCbs and C=NCbs groups (i.r.); the u.v. and mass spectra indicated that the compound was not a quinoline derivative based on structures (37) and (38).[3,13] The n.m.r. spectrum contained a signal (τ 3.65, d, J 10 Hz, NH) coupled to a single olefinic proton (4.25, d, J 10 Hz); on addition of D_2O the signal at 4.25 collapsed to a singlet. A split NH signal has rarely been encountered in the course of this azide–indole work. To accommodate these facts structure (39; R = H) was considered. This structure does not explain why the =CH group shows no coupling to the neighbouring CH_2 group; the magnitude of the HN–C=CH coupling constant is much larger than those reported for an ' allylic ' system.[14] Further, all compounds of this general type encountered in these researches have been of the ' imine ' (40) type [*e.g.* (35), (36), (38)]. However in compounds (35) and (36) the C=N group is conjugated with the indole nucleus and in structures of type (38) the ' *meta* ' bridging and the *N*-methyl group may favour the C=N structure. Indeed, *N*-acyl derivatives of vinylamines prefer the enamine to the imine form.[15] A structure of type (39) would arise by the addition of a further molecule of azide to either (29) or (35), but these were shown not to be intermediates in the formation of the 1 : 2 adduct. This would imply that a second molecule of $CbsN_3$ had added to (34) before (34) had lost nitrogen. Further information was sought by deuterium labelling. The deuteriated ketone (24; R = D) was reduced to (25; R^1 = D, R^2 = H) and dehydration afforded (26; R^1 = D, R^2 = H). This olefin reacted with $CbsN_3$ to give a mixture of the imine (35; R^1 = D, R^2 = H) [*via* (34), route a, R = H] and the 1 : 2 adduct. This material did not contain deuterium and could not be (39; R = D). The adduct was treated with MeOD to show that exchange had not occurred during isolation. Reduction of the ketone (24; R = H) with $LiAlD_4$ followed by dehydration afforded the isomeric olefin (26; R^1 = H, R^2 = D). Treatment of this olefin afforded the imine (35; R^1 = D, R^2 = H) by a D shift in (34; R = D) and the 1 : 2 adduct which now contained a D atom. If the structure involves a six-membered ring this implies an ' abnormal ' addition of $CbsN_3$ to give (42), loss of nitrogen and further reaction giving



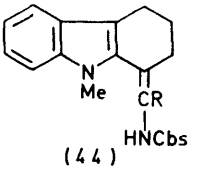
(42)

(41)

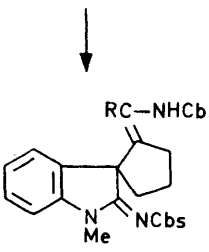
(41; R = D). A second type of structure (44) may be formed from (34) by route b involving C(2) of the indole nucleus. Vinyl groups are known[16] to undergo such a type of migration and anchimeric assistance by the NMe group (43) may occur (ref. 12, p. 109). This would



(43)



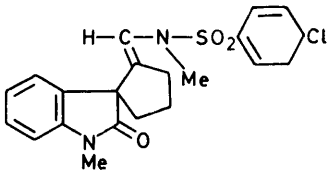
(44)



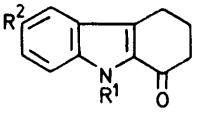
(45)

lead to a type of ring-contraction so far unobserved in this series. Attack of a second molecule of azide on (44) followed by ring-contraction then leads to structure (45) for the 1 : 2 adduct. This structure allows an explanation of the magnitude of the NH–CH= coupling for (45; R = H) and also of the retention of deuterium when (26; R^1 = H, R^2 = D) reacts with $CbsN_3$ forming (45; R = D) *via* (43 and 44; R = D). We hoped to distinguish between the three structures [(39), (41), (45)] by *X*-ray crystallography but failed to obtain suitable crystals. Attempted degradations (see Experimental section) gave amorphous materials, but methylation with Me_2SO_4–NaOH afforded an *N*-methyl derivative in which the C=NCbs group had been hydrolysed. This

compound ($C_{21}H_{21}ClN_2O_3S$) gave crystals suitable for *X*-ray crystallography and a structural determination [17] has shown that the material has structure (46), proving that the 1 : 2 adduct is the ring-contracted material (45; R = H).



(46)



(47)

During this work we attempted the preparation of 3,4-dihydrocarbazol-1(2*H*)-one (47; $R^1 = R^2 = H$) by the periodate oxidation of tetrahydrocarbazole.[18,19] At 0 °C the desired compound was obtained but when the reaction mixture was kept at room temperature overnight the 6-iodo-compound (47; $R^1 = H$, $R^2 = I$) was obtained. This structure followed from its synthesis starting with *p*-iodoaniline. Compound (47; $R^1 = R^2 = H$) is not attacked by iodine in HOAc nor by a mixture of periodic acid and potassium iodide. However, treatment of (47; $R^1 = R^2 = H$) with a mixture of periodic acid and iodine yields (47; $R^1 = H$, $R^2 = I$) showing that traces of iodine formed during the periodic acid oxidation of the hydrocarbazole are responsible for the iodination.

EXPERIMENTAL

General details and instruments used have been reported.[20] U.v. spectra were determined for solutions in ethanol and n.m.r. spectra for solutions in $CDCl_3$ unless otherwise stated; i.r. spectra were recorded for Nujol mulls.

Starting Materials.—2-Acetyl-1,3-dimethylindole was reduced ($LiAlH_4$) forming 1-(1,3-*dimethylindol*-2-*yl*)*ethanol* (3) (95%), b.p. 100—110° at 0.1 mmHg, rods, m.p. 50—52° (from cyclohexane) (Found: C, 76.3; H, 7.6; N, 7.5. $C_{12}H_{15}NO$ requires C, 76.2; H, 7.9; N, 7.4%); $\lambda_{max.}$ 230, 275sh, and 298 nm (ε 30 500, 6 000, and 6 500); $\nu_{max.}$ ($CHCl_3$) 1 612 and 3 610 cm^{-1}; τ 2.45—2.65 (1 H, m), 2.75—3.2 (3 H, m), 4.95 (1 H, q, *J* 7 Hz), 6.43 (3 H, s), 7.50br (1 H, s, exchanged with D_2O), 7.80 (3 H, s), and 8.57 (3 H, d, *J* 7 Hz); *m/e* 189 (M^+, 97%), 174 (100), 172 (44), 146 (35), and 144 (32). Treatment of 2-acetyl-1,3-dimethyl-2-indole with methylmagnesium iodide (NH_4Cl work-up) afforded 2-(1,3-dimethylindol-2-yl)propan-2-ol (4); $\nu_{max.}$ 3 315 cm^{-1}; τ 2.4—3.0 (4 H, m), 6.13 (3 H, s, NMe), 7.66 [3 H, s, C(3)Me], 8.08 (1 H, s, OH, exchanged with D_2O), and 8.32 (6 H, s, CMe_2). All attempts to purify the alcohol afforded the olefin. P.l.c. (SiO_2, 10% EtOAc in benzene) of the residue from the Grignard reaction afforded trans-1,3-*bis*-(1,3-*dimethylindol*-2-*yl*)*but*-2-*en*-1-*one* (8) (10 mg); $\lambda_{max.}$ 226 and 328 nm (ε 40 900 and 12 900); $\nu_{max.}$ ($CHCl_3$) 1 220, 1 470, 1 623, and 1 650 cm^{-1}; τ(CCl_4) 2.4—3.2 (9 H, m, Ar and HC=), 6.37 (3 H, s, NMe), 6.44 (3 H, s, NMe), 7.37 [3 H, s, C(3)Me], 7.76 (3 H, d, *J* 1.5 Hz, CH_3C=CH), and 7.83 [3 H, s, C(3)Me]; *m/e* 356 (M^+, 100%), 341 (97), 212 (16), 184 (34), 172 (32), and 168 (40). 2-Acetyl-1,3-dimethylindole (1.87 g) was boiled (4 h, stirred) in xylene (40 ml) with aluminium t-butoxide (1.35 g). Water (0.4 ml) was then added to the cold solution. After 60 h the solid was filtered off, the solvent evaporated off, and the residue extracted with pentane. P.l.c. of the insoluble material afforded compound (8) (50 mg). 2-Acetyl-1,3-dimethylindole was condensed with benzaldehyde (EtOH–dil. NaOH), forming 1-(1,3-*dimethylindol*-2-*yl*)-3-*phenylprop*-2-*en*-1-*one* (9) (60%) as yellow prisms, m.p. 66—68° (from EtOH) (Found: C, 82.7; H, 6.2; N, 5.2. $C_{19}H_{17}NO$ requires C, 82.9; H, 6.2; N, 5.1%); $\lambda_{max.}$ 225, 285sh, 315sh, and 340 nm (ε 29 500, 15 000, 19 500, and 20 100); $\nu_{max.}$ ($CHCl_3$) 1 580, 1 595, 1 630, and 1 650 cm^{-1}; τ(CCl_4) 2.5—3.1 (11 H, m, Ar and CH=CH), 6.15 (3 H, s, NMe), and 7.46 (3 H, s, CMe); *m/e* 275 (M^+, 100%), 274 (23), 198 (44), and 184 (32). A similar reaction between 2-acetyl-1,3-dimethylindole and 3-methylindole-2-carbaldehyde gave 1-(1,3-*dimethylindol*-2-*yl*)-3-(3-*methylindol*-2-*yl*)*prop*-2-*en*-1-*one* (10) (yield 20%) as orange needles, m.p. 184° (from EtOH) (Found: C, 80.6; H, 6.0; N, 8.2. $C_{22}H_{20}N_2O$ requires C, 80.5; H, 6.0; N, 8.5%); $\lambda_{max.}$ 268 and 435 nm (ε 12 200 and 31 000); $\nu_{max.}$ ($CHCl_3$) 1 575, 1 640, and 3 480 cm^{-1}; τ 2.16br (1 H, s, exchanged with D_2O, NH), 2.13 (1 H, d, *J* 16 Hz, CH=), 2.30—3.05 (9 H, m, Ar and =CH), 6.20 (3 H, s, NMe), 7.49 (3 H, s, CMe), and 7.62 (3 H, s, CMe); *m/e* 328 (M^+, 100%), 187 (50), 172 (50), and 144 (100). Methyl 1,3-dimethylindole-2-carboxylate was reduced ($LiAlH_4$) forming 1,3-dimethyl-2-hydroxymethylindole (5) as prisms (from cyclohexane), m.p. 119—121° (lit.,[3] m.p. 117—118°); $\nu_{max.}$ ($CHCl_3$) 3 420 and 3 608 cm^{-1}; τ 2.4—2.6 (1 H, m), 2.7—3.05 (3 H, m), 5.31 (2 H, s), 6.34 (3 H, s), 7.72 (3 H, s), and 8.38 (1 H, s, exchanged with D_2O); *m/e* 175 (M^+, 95%), 174 (21), 158 (100), and 144 (29). 1,3-Dimethyl-2-vinylindole (6), prepared from 1,2,3-trimethylindole,[4] had b.p. 110—120° at 1 mmHg, m.p. 13—20° (lit.,[4] 10—19°); $\lambda_{max.}$ 235 and 305 305 nm (ε 26 000 and 16 300); $\nu_{max.}$ 1 472 and 1 627 cm^{-1}; τ 2.4—2.65 (1 H, m), 2.75—3.1 (3 H, m), 3.33 (1 H, q, $J_{H_\gamma H_\alpha}$ 18 Hz, $J_{H_\gamma H_\beta}$ 11 Hz, H_γ), 4.51 (1 H, q, $J_{H_\alpha H_\gamma}$ 18 Hz, H_α), 4.70 (1 H, q, $J_{H_\beta H_\gamma}$ 11 Hz, $J_{H_\beta H_\alpha}$ 1 Hz, H_β), 6.50 (3 H, s), and 7.65 (3 H, s); *m/e* 171 (M^+, 100%), 170 (79), 156 (9), 154 (17), and 144 (35). Distillation of the alcohol (4) afforded 2-(1,3-*dimethylindol*-2-*yl*)*propene* (7), b.p. 90° at 0.1 mmHg (Found: C, 84.1; H, 8.0; N, 7.5. $C_{13}H_{15}N$ requires C, 84.3; H, 8.1; N, 7.6%); $\lambda_{max.}$ 229 and 292 nm (ε 30 000 and 9 300); $\nu_{max.}$ 1 478 and 1 640 cm^{-1}; τ(CCl_4) 2.55—3.25 (4 H, m), 4.58 (1 H, q, H_α), 5.0 (1 H, q, H_β), 6.50 (3 H, s), 7.78 (3 H, s), and 7.96 (3 H, d, CH_3C=C); calc. τ values [21] H_α 4.64 and H_β 5.08; decoupling experiments gave the following values, $J_{H_\alpha H_\beta}$ 2.5 Hz, $J_{H_\alpha CMe}$ 1.1, and $J_{H_\beta CMe}$ 0.7 Hz; *m/e* 185 (M^+, 100%), 184 (50), 170 (15), and 144 (30).

Reaction of Compounds (3) *and* (4) *with* p-*Chlorobenzenesulphonyl Azide* (CbsN$_3$).—A mixture of the indole (3) (0.95 g) and the azide (2.2 g) was heated (70 °C, 30 min) whilst a stream of nitrogen was passed over the melt and into Brady's reagent affording acetaldehyde DNP (m.p., t.l.c.). Methanol (5 ml) was added to the melt and after 24 h at 0 °C compound (12) (0.37 g) was collected. Chromatography (SiO_2; $CHCl_3$) of the residue afforded CbsN$_3$ (1 g); 2-p-*chlorophenylsulphonyliminomethyl*)-1,3-*dimethylindole* (15; Z = Cbs) (50 mg) as yellow prisms ($CHCl_3$–MeOH), m.p. 170—171° (Found: C, 58.7; H, 4.5; N, 7.8. $C_{17}H_{15}ClN_2O_2S$ requires C, 58.9; H, 4.3; N, 8.1%); $\lambda_{max.}$ 225, 255sh, and 350 nm (ε 40 300, 25 900, and 21 800); $\nu_{max.}$ ($CHCl_3$) 1 160 and 1 580 cm^{-1}; τ 0.80 (1 H, s, CH=N), 2.05 (2 H, d, *J* 9 Hz), 2.49 (2 H, d, *J* 9 Hz), 2.22—3.0 (4 H, m), 5.98 (3 H, s), and 7.39 (3 H, s); *m/e* 346 (M^+, 9%), 171 (M – Cbs, 100), 170 (8), and 144 (15). Further

elution afforded more (12) (1.15 g) and finally compound (11) (0.37 g). A mixture of the alcohol (4) (1.6 g), $CbsN_3$ (1.8 g), and EtOAc (2 ml) was heated (50 °C, 3 h) in a stream of nitrogen, the effluant affording acetone DNP (t.l.c. and m.p.). Chromatography of the reaction mixture afforded the olefin (7) (0.23 g), $CbsN_3$ (0.1 g), 2-acetyl-1,3-dimethylindole (0.12 g) (12) (1.55 g), and (11) (0.3 g).

Reaction of 1,3-*Dimethyl*-2-*hydroxymethylindole* (5) *with* $CbsN_3$.—A solution of the alcohol (0.45 g) in EtOAc (20 ml) containing $CbsN_3$ (0.55 g) was heated (50 °C, 50 h) in a stream of nitrogen. Chromatography afforded 1,3-dimethylindole-2-carbaldehyde (0.1 g), the imine (15; Z = Cbs) (0.03 g), (12) (0.1 g), and a yellow gum (0.4 g). T.l.c. (SiO_2; $CHCl_3$) of this material indicated traces of (12), and of $CbsNH_2$; the major component had R_F 0.05. Recrystallisation of the gum from benzene afforded $CbsNH_2$ (0.08 g). P.l.c. of the benzene residues gave the indole (12) but no sign of the material of R_F 0.05. The n.m.r. spectrum of the crude material contained the following signals (omitting those due to $CbsNH_2$): τ 2.0—3.15 (8 H, m), 5.28br [1 H, d, *J* 11 Hz, C(3)C*H*OH], 6.02br [1 H, d, *J* 11 Hz, C(3)C*H*–OH], 6.65 (3 H, s, NMe), 7.30br [1 H, s, exchanged with D_2O], and 8.34 (3 H, s, CMe); $\nu_{max.}$ 1 560 (C=N) and 3 460 (OH) cm^{-1}.

The olefins (6) and (7) were treated with $CbsN_3$ in CCl_4 and in DMSO under a variety of conditions. In all cases dark-coloured tars were obtained; t.l.c. of these showed large numbers of components. P.l.c. and column chromatography failed to give crystalline material.

5-*Methyl*-5,8,9,10-*tetrahydrocyclohept*[b]*indole* (26; $R^1 = R^2$ = H).—2-Hydroxymethylenecycloheptanone [22] was coupled with benzenediazonium chloride [10] and the resulting phenylhydrazone (30 g) cyclised in boiling formic acid (80%, 200 ml, 1 h). Water (100 ml) was then added and the product recrystallised [25 g, m.p. 146—147° (from HOAc): lit.,[10] 145—147°]. Methylation (Me_2SO_4–KOH–H_2O–Me_2CO) afforded (24; $R^1 = R^2$ = H), m.p. 65—66° (lit.,[10] 64.5—65.5°). Reduction of the ketone (20 g) ($LiAlH_4$, Et_2O, room temp.) afforded 5,6,7,8,9,10-*hexahydro*-5-*methylcyclohept*[b]*indol*-6-*ol* (25; $R^1 = R^2$ = H) as needles (17.6 g), m.p. 92—93° (from benzene–light petroleum) (Found: C, 78.3; H, 8.0; N, 6.6. $C_{14}H_{17}NO$ requires C, 78.2; H, 7.9; N, 6.5%); $\lambda_{max.}$ 207, 229, 282sh, 290, and 294 nm (ε 31 500, 55 100, 9 400, 9 800, and 9 700); $\nu_{max.}$ 3 310 cm^{-1}; τ 2.4—3.1 (4 H, m), 4.8—5.0 (1 H, m), 6.29 (3 H, s), 7.0—7.3 (2 H, m), and 7.8—8.6 (7 H, m, one proton exchanged with D_2O); *m/e* 215 (M^+, 100%), 198 (60, *m** 182.4), 197 (48), 171 (41, *m** 136.0), 158 (39), and 144 (51). A solution of the alcohol (10 g) in $CHCl_3$ (300 ml) was kept in daylight for 24 h. Chromatography (SiO_2; $CHCl_3$) gave the olefin. 5-*Methyl*-5,8,9,10-*tetrahydrocyclohept*[b]*indole* (26; $R^1 = R^2$ = H) (8 g) formed plates, m.p. 36—38° (from EtOH) (Found: C, 84.9; H, 7.8; N, 7.1. $C_{14}H_{15}N$ requires C, 85.3; H, 7.6; N, 7.1%); $\lambda_{max.}$ 207, 231, 301sh, and 308 nm (ε 17 300, 24 500, 12 100 and 12 300); $\nu_{max.}$ 1 635 cm^{-1}; τ 2.5—3.0 (4 H, m), 3.55br (1 H, d, *J* 12 Hz), 3.9—4.2 (1 H, m), 6.35 (3 H, s), 6.98 (2 H, t, *J* 7 Hz), 7.45—7.7 (2 H, m), and 7.85—8.15 (2 H, m); *m/e* 197 (M^+, 100%), 196 (83), 182 (34), 168 (23), and 167 (32). The ketone (24; R = H) (8 g) in 1,2-dimethoxyethane (50 ml) was boiled (30 min) with D_2O (15 ml) containing NaOD (from Na, 1 g). The mixture was diluted with water, the partially deuteriated material isolated, and the deuteriation repeated (5 h reflux); the product showed τ 2.45 (1 H, d, *J* 9 Hz), 2.7—3.2 (3 H, m), 6.00 (3 H, s), 6.95br (2 H, t, *J* 6 Hz), 8.0—8.3 (4 H, m). The signal at τ 7.32 ($CO.CH_2$) in the starting material was absent. 7,7-[$^2H_2$]-7,8,9,10-Tetrahydro-5-methylcyclohept[*b*]indol-6(5*H*)-one (24; R = D) (5 g) was reduced and dehydrated forming 7-[^{2}H]-5,8,9,10-tetrahydrocyclohept[*b*]indole (26; R^1 = D, R^2 = H); the n.m.r. spectrum included τ 3.65 [1 H, d, *J* 1.3 Hz, C(6)H] but the signal at τ 3.9—4.2 [C(7)H] was absent; on irradiation at τ 7.52 the doublet at 3.65 collapsed to a singlet. Reduction of the ketone (24; R = H) with $LiAlD_4$ gave the alcohol (25; R^1 = H, R^2 = D) and dehydration yielded 6-[^{2}H]-5,8,9,10-tetrahydrocyclohept[*b*]indole (26; R^1 = H, R^2 = D); the signal at τ 3.65 [C(6)H] was absent.

2-p-*Chlorophenylsulphonylimino*-2′-*hydroxy*-1-*methylindoline*-3-*spirocyclohexane* (27; Z = Cbs).—(*a*) A solution of (25; $R^1 = R^2$ = H) (1 g) in CCl_4 (4 ml) containing $CbsN_3$ (2.2 g) was kept at room temperature for 2 weeks and the solid (0.4 g) collected. The mother-liquors contained only polymeric material and $CbsN_3$. (*b*) The alcohol (1.0 g) was dissolved in dry DMSO (4 ml) containing $CbsN_3$ (1.02 g) and 1 crystal of 2,6-di-isopropylphenol was added. After 10 days water was added and the mixture extracted (3 × 30 ml) with benzene. The extracts were washed with water, dried, and the solvent removed. Acetonitrile (5 ml) was added to the residue and the solid (0.8 g) collected; concentration of the mother-liquor gave further material (0.36 g) and chromatography of the residue yielded the olefin (28; Z = Cbs) (23 mg). In the absence of di-isopropylphenol the yield decreased to 53%. The *alcohol* (27; Z = Cbs) formed prisms from MeCN, m.p. 171—172°, which contained MeCN of crystallisation which was not removed upon drying (n.m.r.) (Found: C, 59.6; H, 5.6; Cl, 8.7; N, 8.8; S, 8.0. $C_{20}H_{21}ClN_2O_3S$ requires C, 59.3; H, 5.2; Cl, 8.7; N, 6.9; S, 7.9. $C_{20}H_{21}ClN_2O_3S.CH_3CN$ requires C, 59.2; H, 5.4; Cl, 8.0; N, 9.4; S, 7.2%); $\lambda_{max.}$ 224, 279sh, 284, and 297sh nm (ε 26 000, 16 000, 16 400, and 12 800); $\nu_{max.}$ 1 565 and 3 840br cm^{-1}; τ 2.0 (2 H, d, *J* 9 Hz), 2.2—3.1 (6 H, m), 5.2—5.6br (1 H), 6.45 (3 H, s), 7.7—8.6 (9 H, m, including OH, exchanged D_2O), and 8.0 (s, MeCN); *m/e* 404 (M^+, 11%), 229 (*M* − Cbs, 100), 201 (16), 159 ($C_{10}H_{11}N_2$, 21), and 145 (43). Treatment of the alcohol with TsN_3 in DMSO (room temperature, 4 weeks) gave 2′-*hydroxy*-1-*methyl*-2-p-*tolylsulphonyliminoindoline*-3-*spirocyclohexane* (27; Z = Ts) (40%) as prisms, m.p. 148—150° (from MeCN) (Found: C, 65.6; H, 5.9; N, 7.5. $C_{21}H_{24}N_2O_3S$ requires C, 65.5; H, 6.3; N, 7.3%); $\lambda_{max.}$ 221, 278sh, 283, and 300sh nm (ε 23 500, 13 700, 14 300, and 10 700); $\nu_{max.}$ 1 575, 2 280w (MeCN), and 3 440br (OH) cm^{-1}; the presence of MeCN in the crystals after drying was supported by the signal at τ 8.0 in the n.m.r. spectrum. The alcohol (27; Z = Cbs) was dissolved in trifluoroacetic acid. After 30 min the solution was evaporated to dryness and a little methanol added. The *trifluoroacetate* (53% yield) had m.p. 150—151° (Found: C, 52.9; H, 4.1; F, 11.5. $C_{22}H_{20}ClF_3NO_4S$ requires C, 52.8; H, 4.0; F, 11.1%); $\nu_{max.}$ 1 790 cm^{-1}; τ 2.05 (2 H, d, *J* 10 Hz), 2.2—3.1 (6 H, m), 4.2 (1 H, t, *J* 6.5 Hz), 6.4 (3 H, s), and 7.5—8.7 (8 H, m). The alcohol (0.25 g) in CH_2Cl_2 (10 ml) was oxidized with the chromium pentaoxide–pyridine complex (30 ml).[23] After 12 h Et_2O (200 ml) was added, the solution was filtered, and the solvent removed. Chromatography (SiO_2; benzene–EtOAc) yielded 2-p-*chlorophenylsulphonylimino*-1-*methylindoline*-3-*spirocyclohexan*-2′-*one* (40%), m.p. 194—195° (Found: C, 58.9; H, 5.0; Cl, 8.8; N, 7.0. $C_{20}H_{19}ClN_2SO_3$ requires C, 59.7; H, 4.7; Cl, 8.7; N, 7.0); $\lambda_{max.}$ 225, 287, and 300sh nm (ε 21 500, 18 100, and 12 600); $\nu_{max.}$ 1 700 cm^{-1}; τ 2.1 (2

H, d, *J* 10 Hz), 2.3—3.2 (6 H, m), 6.7 (3 H, s), 6.8—9.1 (8 H, m); *m/e* 402 (M^+, 6%), 227 (*M* − Cbs, 100), 199 (26), 185 (227 − C_2H_2O, 20), and 172 (14).

2-p-*Chlorophenylsulphonylimino*-1-*methylindoline*-3-*spirocyclohex*-2′-*ene* (29; Z = Cbs).—(*a*) A solution of the olefin (26; $R^1 = R^2 = H$) (0.5 g) in dry DMSO (3 ml) containing $CbsN_3$ (1.1 g) was left for 8 weeks and then poured into water. The tar was washed by decantation and MeCN (5 ml) added. After 24 h at 0 °C the solid (0.45 g) was collected and recrystallised (MeCN, yield 0.21 g, two crops). A black polymeric residue was obtained; the yield was not improved by addition of an antioxidant.

(*b*) The alcohol (25; $R^1 = R^2 = H$) reacted with $CbsN_3$ in DMSO–Ac_2O (9 : 1) giving a 10% yield of the olefin. The *olefin* (29; Z = Cbs) formed prisms, m.p. 192—194° (from EtOH) (Found: C, 61.9; H, 4.8; N, 7.4. $C_{20}H_{19}ClN_2O_2S$ requires C, 62.1; H, 4.9; N, 7.2%); $\lambda_{max.}$ 226, 284sh, 288, 297sh nm (ε 30 200, 17 400, 18 000, and 15 200); $\nu_{max.}$ 1 571 cm^{-1}; τ 2.05 (2 H, d, *J* 10 Hz), 2.4—3.1 (6 H, m), 3.65—3.85 [1 H, m, C(3′)H], 5.00br [1 H, d, *J* 10 Hz, C(2′)H], 6.58 (3 H, s), 6.8—7.2 (1 H, m), 7.5—7.8 (2 H, m), 7.9—8.2 (2 H, m), and 8.3—8.7 (1 H, m); *m/e* 386 (M^+, 15%), 211 (*M* − Cbs, 100, *m** 115.3), 183 (211 − C_2H_4, 51), 170 (23), and 146 (15). This compound did not react further with $CbsN_3$ to form (45). The olefin (0.225 g) was oxidised [perbenzoic acid (0.116 g), $CHCl_3$]. The usual work-up gave 2-p-*chlorophenylsulphonylimino*-2′,3′-*epoxy*-1-*methylindoline*-3-*spirocyclohexane* (30) (70%), m.p. 154—155° (from MeOH) (Found: C, 59.6; H, 4.8; N, 6.7. $C_{20}H_{19}ClN_2O_3S$ requires C, 59.7; H, 4.7; N, 7.0%); $\lambda_{max.}$ 205, 225, 280sh, 286, and 300sh nm (ε 25 100, 25 600, 14 500, 16 100, and 13 800); $\nu_{max.}$ 1 560 cm^{-1}; τ 2.05 (2 H, *d*, *J* 9.0 Hz), 2.1—3.2 (6 H, m), 6.5 [1 H, d, *J* 4 Hz, C(2′)H], 6.65 (3 H, s), 7.2—7.65 [1 H, m, C(3′)H], 7.6—8.8 (6 H, m); *m/e* 402 (M^+, 25%), 386 (10), 361 (60), 227 (*M* − Cbs, 100), 199 (45), and 173 ($C_{10}H_9N_2O$, 100). Bromination of the olefin in chloroform (3 h) and chromatography of the product (Al_2O_3; $CHCl_3$) gave the *tribromo*-compound (31) (64%), m.p. 201—203° (Found: C, 38.6; H, 2.9; H, 4.3. $C_{20}H_{18}Br_3ClN_2O_2S$ requires C, 38.6; H, 2.9; H, 4.5%); $\lambda_{max.}$ 225, 287, and 312sh nm (ε 26 500, 19 500, and 9 900); $\nu_{max.}$ 1 570 cm^{-1}; τ 2.01 (2 H, d, *J* 9 Hz), 2.3—2.6 (4 H, m), 3.07 (1 H, d, *J* 10 Hz), 5.0 [1 H, d, *J* 12 Hz, C(2′)H], 5.3—5.8 [1 H, m, C(3′)H], 6.25 (3 H, s), and 7.1—8.5 (6 H, m). Bromination of (32; R = H) afforded (32; R = Br) (80%) as needles, m.p. 220—222° (from MeCN) (Found: C, 53.3; H, 4.7; Br, 19.4; N, 7.0. $C_{18}H_{19}BrN_2O_2S$ requires C, 53.2; H, 4.7; Br, 19.5; 6.9%); $\lambda_{max.}$ 222, 290, and 300sh nm (ε 40 200, 37 300, and 26 500); $\nu_{max.}$ 1 550 cm^{-1}. Alkaline hydrolysis afforded 5-*bromo*-1,3,3-*trimethyloxindole* as needles, m.p. 104—107° (from light petroleum) (Found: C, 52.1; H, 4.7; Br, 31.6; N, 5.4. $C_{11}H_{12}BrNO$ requires C, 52.0; H, 4.7; Br, 31.5; N, 5.5%); $\nu_{max.}$ 1 710 cm^{-1}. The olefin (26; $R^1 = R^2 = H$) was mixed with *p*-nitrobenzenesulphonyl azide in dry DMSO. After 8 weeks the solid was collected and recrystallised (MeCN) yielding 1-*methyl*-2-p-*nitrophenylsulphonyliminoindoline*-3-*spirocyclohex*-2′-*ene* (29; Z = Nbs) as prisms (10%), m.p. 190° (Found: C, 60.5; H, 5.0; N, 10.6; S, 7.8. $C_{20}H_{19}N_3O_4S$ requires C, 60.5; H, 4.8; N, 10.6; S, 8.0%); $\lambda_{max.}$ 216, 270sh, 280, and 287sh nm (ε 22 100, 16 100, 17 900, and 13 400); $\nu_{max.}$ 1 560 cm^{-1}; τ 1.6—1.95 (4 H, m, Nbs), 2.6—3.2 (4 H, m), 3.6—4.0 [1 H, m, C(3′)H] 4.55 [1 H, d, *J* 10 Hz, C(2′)H], 6.6 (3 H, s), 6.88—7.35 [1 H, m, C(6′)H], 7.5—7.8 [4 H, m, C(4′)H_2], 7.9—8.3 [2 H, m, C(5′)H], and 8.43br [1 H, d, *J* 13 Hz, C(6′)H]; on irradiation (*a*) at τ 7.7 the C(3′)H signal collapsed to a doublet, *J* 12 Hz, (*b*) at τ 7.12 the C(6′)H signal at τ 8.43 collapsed into a v.br, singlet, (*c*) at τ 8.43 the C(6′)H signal at 6.9—7.3 collapsed into a distorted triplet, *J* 9.5 Hz; the ^{13}C n.m.r. spectrum included signals from three CH_2 groups (18.4, 23.6, and 29.8 p.p.m.,) C(3) (54.0), and C=N (174.5), the C(2′) and C(3′) signals appearing amongst the Ar–C signals.

2′-p-*Chlorophenylsulphonylaminomethylene*-2-p-*chlorophenylsulphonylimino*-1-*methylindoline*-3-*spirocyclopentane* (45; R = H).—The olefin (26; $R^1 = R^2 = H$) (0.5 g) and $CbsN_3$ (1.1 g) were mixed in CCl_4 (2 ml). Four weeks later the solid was collected and recrystallised (MeOH). The *imine* (45; R = H) formed tiny needles, 0.29 g, m.p. 201° (Found: C, 54.2; H, 4.4; Cl, 12.2; N, 7.3; S, 10.8. $C_{26}H_{23}Cl_2N_3O_4S_2$ requires C, 54.2; H, 4.0; Cl, 12.3; N, 7.3; S, 11.1%); $\lambda_{max.}$ 226, 275, and 303sh nm (ε 49 000, 20 000, and 14 000); $\nu_{max.}$ 1 560br (C=N) and 3 196 (NH) cm^{-1}; τ 2.13 (2 H, d, *J* 9 Hz), 2.35 (2 H, d, *J* 9 Hz), 2.4—3.1 (8 H, m), 3.65 (1 H, d, *J* 10 Hz, exchanged with D_2O, NH), 4.25 (1 H, d, *J* 10 Hz, collapsed to s on D_2O exchange, CH=C), 6.55 (3 H, s), and 6.8—8.5 (8 H, m); *m/e* 575 (M^+, 4%), 400 (*M* − Cbs, 100), 225 (*M* − 2Cbs, 85), 224 (55), 209 (*M* − Cbs − $CbsNH_2$, 68), 197 (225 − CH_2N, 41), and 183 ($C_{11}H_9N_3$, 16). The mother-liquor afforded the imine (35) (see later). Reaction of the olefin with TsN_3 gave the corresponding *tosyl compound* (45, R = H, Ts replacing Cbs) as needles, m.p. 236—239° (from nitromethane) (Found: C, 62.7; H, 5.5; N, 7.4; S, 12.1. $C_{28}H_{29}N_3O_4S_2$ requires C, 62.8; H, 5.4; N, 7.9; S, 12.0%); $\nu_{max.}$ 1 575 and 3 198 cm^{-1}; n.m.r. spectrum included signals at τ ([$^2H_6$]DMSO) 0.57 (1 H, d, *J* 11 Hz, NH) and 4.7 (1 H, d, *J* 11 Hz). Reaction of (26; $R^1 = D$, $R^2 = H$) with $CbsN_3$ in CCl_4 yielded (45; R = H) (17%) and (35; $R^1 = D$, $R^2 = H$) (13%). From the reaction between (26; $R^2 = D$, $R^1 = H$) and $CbsN_3$ the deuteriated *imine* (45; R = D) (yield 19%) and the monodeuteriated compound (35; $R^1 = D$, $R^2 = H$) were isolated [Found: for (45): C, 53.8; H + D, 4.1; Cl, 12.5; N, 7.0; S, 10.9. $C_{26}H_{22}DCl_2N_3O_4S_2$ requires C, 54.1; H + D, 4.2; Cl, 12.1; N, 7.2; S, 11.1%); $\nu_{max.}$ 1 570 and 3 200 cm^{-1}; the n.m.r. spectrum included τ([$^2H_6$]DMSO) 0.4 (1 H, s, NH) but no signal at τ 4.25 (CH=C); *m/e* 576 (M^+, 6%), 401 (100), 226 (70), and 210 (58). We could not obtain crystals of (45) suitable for *X*-ray crystallographic determination and attempts at bromination, hydrolysis, oxidation, and reduction failed. A sample of the compound (45; R = H) (0.22 g) was dissolved in acetone (15 ml) containing NaOH (0.74 g), water (3 ml), and dimethyl sulphate (1 ml). After 18 h stirring the acetone was removed *in vacuo* and water added. Extraction with benzene afforded an oil to which benzene–light petroleum (1 : 1, 2 ml) was added. Next day the solid was collected (0.1 g + 0.04 g in mother-liquor). 2′-p-*Chlorophenylsulphonylaminomethylene*-NN′-*dimethyl*-2-*oxoindole*-3-*spirocyclopentane* (46) formed prisms, m.p. 145° (Found: C, 60.6; H, 5.3; N, 6.8; S, 7.7. $C_{21}H_{21}ClN_2O_3S$ requires C, 60.6; H, 5.1; N, 6.7; S, 7.7%); $\lambda_{max.}$ 210, 230sh, and 260sh nm (ε 37 800, 20 000, and 11 300); $\nu_{max.}$ 1 700 cm^{-1}; τ 2.55 (2 H, d, *J* 9 Hz), 2.6—3.0 (5 H, m), 3.2 [1 H, d, *J* 7 Hz, C(7)H], 5.1 (1 H, s, CH=C), 6.82 (3 H, s, NMe), 7.22 (3 H, s, CH_3NCbs), 7.5—8.3 (6 H, m); *m/e* (*M* not detected) 241 (*M* − Cbs, 100%) and 210 (*M* − CbsNMeH, 13).

The methanolic mother liquors from the preparation of (45) were concentrated to give 6-p-*chlorophenylsulphonyl*-

imino-5,6,7,8,9,10-*hexahydro*-5-*methyl*-*cyclohept*[b]*indole* (35; $R^1 = R^2 = H$) as pale yellow needles, m.p. 146—149° (from EtOH), (Found: C, 61.6; H, 5.0; N, 7.1. $C_{20}H_{19}ClN_2O_2S$ requires C, 62.1; H, 4.9; N, 7.2%); $\lambda_{max.}$ 201, 251, and 349 nm (ε 38 800, 13 800, and 27 000); $\nu_{max.}$ 1 556 cm^{-1}; τ 2.02 (2 H, d, *J* 10 Hz), 2.2—3.0 (6 H, m), 6.2 (3 H, s), 6.54 [2 H, t, *J* 6.6 Hz, C(7)H_2], 6.95 [2 H, t, *J* 6.6 Hz, C(10)H_2], and 7.7—8.5 (4 H, m); *m/e* 386 (M^+, 20%), 211 (100), 183 (11), and 169 (15). The isomeric compound (36) has [13] m.p. 222°. Alkaline hydrolysis of the imine gave (24; R = H) (m.p., i.r.). The methanolic mother liquors from the reaction of both deuteriated olefins (26; $R^1 = D$, $R^2 = H$) and (26; $R^1 = H$, $R^2 = D$) gave the same monodeuteriated imine, 7-[^{2}H]-6-p-*chlorophenylsulphonylimino*-5,6,7,8,9,10-*hexahydro*-5-*methylcyclohept*[b]*indole* (35; $R^1 = H$, $R^2 = D$) (Found: C, 62.1; H, 4.8; Cl, 9.2; N, 7.3; S, 8.0. $C_{20}H_{18}DClN_2O_2S$ requires C, 62.0; H + D, 5.2; Cl, 9.0; N, 7.2; S, 8.3%); $\nu_{max.}$ 1 550 cm^{-1}; τ 2.05 (2 H, d, *J* 10 Hz), 2.2—3.0 (3 H, m), 6.23 (3 H, s), 6.57 [1 H, t, *J* 6.6 Hz, C(7)H], 6.97 [2 H, t, *J* 6 Hz, C(10)H_2], and 7.8—8.4 (4 H, m); *m/e* 387 (M^+, 20%), 212 (100), and 169 (18).

Action of Periodic Acid on Tetrahydrocarbazole.—Oxidation of tetrahydrocarbazole in methanol at 0 °C followed by work-up after 30 min gave 3,4-dihydrocarbazol-1(2*H*)-one.[18] The reaction mixture was left at room temperature overnight and then poured into water. Extraction (Et_2O) gave an oil which on trituration with ethanol and recrystallisation from acetic acid gave 3,4-*dihydro*-6-*iodocarbazol*-1(2H)-*one* (47; $R^1 = H$, $R^2 = I$) (41%) as prisms, m.p. 213—216° (decomp.) (Found: C, 46.3; K, 3.3; I, 40.4; N, 4.4%); $\lambda_{max.}$ 215, 239, 313, and 346sh nm (ε 29 800, 26 200, 27 600, and 4 900); $\nu_{max.}$ 1 643 and 3 270 cm^{-1}; τ 0.39 (1 H, s, NH), 2.02br (1 H, s), 2.42 (1 H, dd, *J* 8, 2 Hz), and 2.77 (1 H, d, *J* 8 Hz), 7.07 (2 H, t, *J* 6 Hz), 7.34 (2 H, t, *J* 6 Hz), and 7.6—7.9 (2 H, m); *m/e* 311 (M^+, 98%), 283 (45), 269 (29), 255 (100), and 128 (91).

Treatment of compound (47; $R^1 = R^2 = H$) in MeOH with $I_2 + HIO_4$ for 12 h gave (47; $R^1 = H$, $R^2 = I$) (63%). *Cyclohexane*-1,2-*dione* p-*iodophenylhydrazone* was prepared by coupling *p*-iodobenzenediazonium chloride (from *p*-iodoaniline, 18.8 g) with 2-hydroxymethylenecyclohexanone.[10] A small quantity of the crude product (yield 89%) was recrystallised (EtOH), to afford yellow-brown prisms (m.p. 181—183°) (Found: C, 44.1; H, 3.9; N, 8.5. $C_{12}H_{13}IN_2O$ requires C, 43.9; H, 4.0; N, 8.6%); $\nu_{max.}$ 1 600, 1 699, and 3 250 cm^{-1}. Cyclisation of this compound in 80% formic acid afforded a dark tar. This was washed (decantation) with MeOH and recrystallised (HOAc) (yield (34%) affording 3,4-dihydro-6-iodocarbazol-1(2*H*)-one, identical (m.p., i.r., t.l.c.) with the sample obtained above. Methylation (KOH–Me_2CO–Me_2SO_4) of both samples gave 3,4-*dihydro*-6-*iodo*-9-*methylcarbazol*-1(2H)-*one* (47; $R^1 = Me$, $R^2 = I$) as needles, m.p. 134—136° (from light petroleum–benzene) (Found: C, 48.5; H, 3.7; N, 4.3. $C_{13}H_{12}INO$ requires C, 48.0; H, 3.7; N, 4.3%); $\nu_{max.}$ 1 667 cm^{-1}.

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