Examination of the Reactions of Hexahydropyrrolo[3,2,1-*jk*]carbazole and of Pyrrolo[3,2,1-*hi*]indoles with Arenesulphonyl Azides in Non-polar and Polar Solvents

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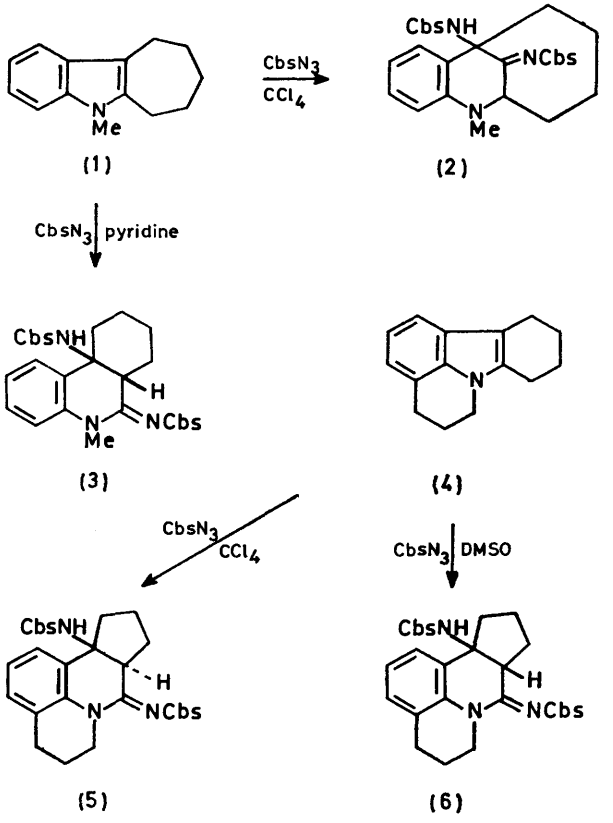
4,5,7,8,9,10-Hexahydropyrrolo[3,2,1-*jk*]carbazole reacts with arenesulphonyl azides in chloroform solution forming derivatives of *trans*-octahydrocyclopenta[*c*]pyrrolo[3,2,1-*ij*]quinoline, whilst in dimethyl sulphoxide solution the *cis*-compounds are obtained. The reactions of 1,2-dihydro-4,5-dimethylpyrrolo[3,2,1-*hi*]indole with azides afford indole derivatives whilst 4-ethyl-5-methylpyrrolo[3,2,1-*hi*]indole yields derivatives of quinoline.

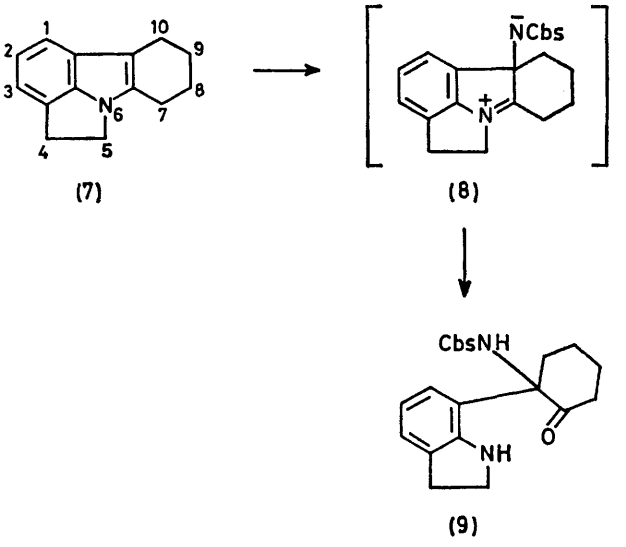
We have shown recently [1,2] that the types of products obtained from the reactions of substituted indoles with arenesulphonyl azides are influenced by the solvent [*e.g.* (1) ⟶ (2) or (3); (4) ⟶ (5) or (6)]. It was



therefore decided to re-examine the reactions with azides of one of the most reactive indoles (7) so far studied.[3,†] The original reactions were performed in polar solvents and one of the major products (9) arose by the addition of water to the intermediate (8); we hoped to minimise the formation of (9) by working with anhydrous solvents.

When compound (7) was mixed with tosyl azide in dry chloroform solution a 1 : 2 adduct was obtained to which we assign the *trans*-structure (10; Z = Ts); the isomeric compound obtained in the original [3] work is assigned the *cis*-configuration (11; Z = Ts) (see later). Treatment of compound (7) with *p*-chlorobenzenesulphonyl azide ($CbsN_3$) in chloroform solution afforded the *trans*-compound (10; Z = Cbs). Small quantities of (9) were also obtained and a trace of a compound (13) whose spectral properties were in close agreement with those of compounds (14) [4] and (15).[5] The reaction between compound (7) and $CbsN_3$ was then examined in chloroform saturated with hydrogen sulphide in an attempt to add H_2S across the $N^+{=}C$ bond of the intermediate (8). The products isolated were (9), (10), and, in trace amounts, the sulphonamide (16). An authentic sample of (16) was prepared by heating [1] compound (9). When heating was prolonged the carbazole (17) was produced, presumably formed *via* (16) by the loss of $CbsNH_2$ followed by oxidation.[6]

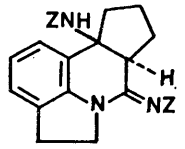
The reaction between compound (7) and $CbsN_3$ in the polar aprotic solvent dimethyl sulphoxide (DMSO) was then examined. In DMSO dried over molecular sieves the only products isolated were the ketone (9) (75%) and a small quantity of the spiran (18). A solution of



$CbsN_3$ in DMSO containing 10% acetic anhydride was kept for 3 days to remove traces of water and then the indole (9) (dried in high vacuum) was added. The products were the *cis*-compound (11; Z = Cbs) (yield 35%), the elimination product (12; Z = Cbs) (45%), and the imine (13) (6%). The pure *cis*- (11; Z = Cbs) and *trans*- (10; Z = Cbs) isomers were dissolved separately in DMSO containing acetic anhydride; after 24 h at room temperature the *trans*-isomer had been transformed into

† The numbering system used in ref. 3 is different from that used in the present paper; the one used here is the correct one.

the elimination product (12; Z = Cbs) (n.m.r.) whilst the *cis*-isomer was unchanged after 6 days. When the *trans*-isomer was kept for 24 h in pure DMSO elimination still occurred, showing that traces of acetic acid were not catalysing the elimination. These results show that the formation of (12; Z = Cbs) in the reaction of (7) with



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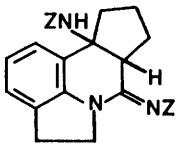

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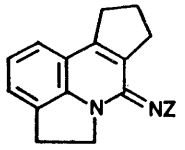

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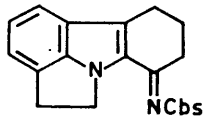

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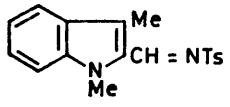

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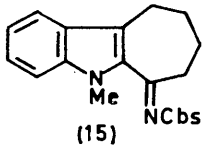

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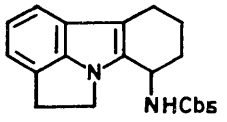

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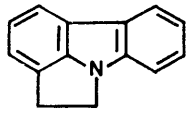

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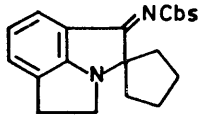
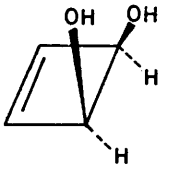


(18)

$CbsN_3$ occurs *via* (10) and not *via* (11), suggesting that in DMSO the attack of azide in (7) is not as selective as the attack of azide on (4), the indole (7) being far more reactive than (4). A similar effect has been observed by De Micheli [7] in the addition of trimethylbenzonitrile oxide to the diol (19); in benzene the *syn* : *anti* product ratio was 9 : 1 and in methanol 1 : 1.

The stereochemistry of compounds (10) and (11) was established by the following observations. The *trans*-isomers (10) have dual m.p.s (loss of sulphonamide) and show no molecular ions in their mass spectra. The *cis*-isomers melt sharply and their mass spectra contain the molecular ions. When the *trans*-isomers were dissolved in trifluoroacetic acid at room temperature elimination occurred before the n.m.r. spectra of the solutions could be measured. In contrast (11; Z = Ts) took 6 days and (11; Z = Cbs) 10 days under the same conditions for elimination to be complete. Further, the *trans*-compound (10; Z = Cbs) rapidly lost $CbsNH_2$ under basic conditions whereas elimination from (11; Z = Cbs) was very slow (see Experimental section). This slow elimination of $CbsNH_2$ has been observed in compound (20) (of known structure).[8]

We next examined the reactions of the indoles (21; R = Me) and (21; R = Et) with azides. The dimethyl compound (21; R = Me) [9] was treated with 1 equiv. of TsN_3. Starting material (40%) was recovered and two products isolated; one (30%) was the expected compound (23; Z = Ts) formed by the loss of diazomethane from (22) (*cf.* reaction of 1,2,3-trimethylindole [4]). The minor product had a u.v. spectrum very similar to that of (23; Z = Ts) but the analytical data and the mass spectrum indicated the presence of an extra CH_2 group in the molecule. There was no NH group (i.r., n.m.r.) and the n.m.r. spectrum showed the presence of an *N*-methyl group. This product is assigned structure (24; Z = Ts) and may arise by methylation of the NH group of (23) by the diazomethane formed in the reaction; it may also arise directly from (22) by intramolecular methylation. A sample of (24; Z = Ts) was prepared by methylation (Me_2SO_4–NaOH) of (23; Z = Ts). Further, a solution of (23; Z = Ts) in chloroform containing diazomethane slowly formed (24; Z = Ts).



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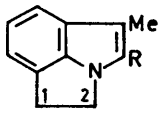

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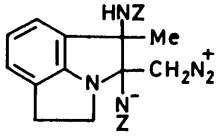

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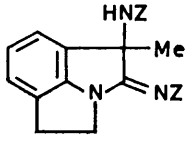

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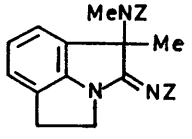
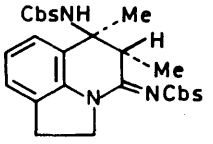


(24)

Treatment of compound (21; R = Me) with $CbsN_3$ afforded (23 and 24; Z = Cbs) but no ring-opened compound corresponding to (9) was obtained even with methanol as solvent.

Treatment of the indole (21; R = Et) with 1 equiv. of $CbsN_3$ in chloroform solution afforded a mixture of *cis*- (25) and *trans*- (26) isomers. The mass spectrum of the *trans*-isomer contained no molecular ion and base-catalysed elimination of $CbsNH_2$ was much faster with

(26) than with (25).[10] No ring-opened product corresponding to (9) was obtained with methanol as solvent. The chemical shifts of the CMe protons in (25) and (26) are summarised in the Table, along with the values[11] for the corresponding *N*-methyl derivatives. The signals of the Me protons A [C(3), quinoline numbering] all fall in the range τ 8.9—9.2 for both *cis*- and *trans*-isomers. In contrast for Me(B) [C(4), quinoline numbering] of the *cis*-isomers the signals appear in the range



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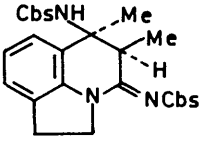

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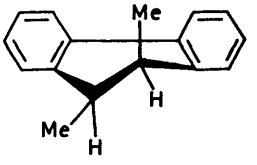

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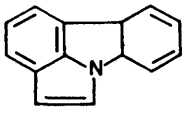

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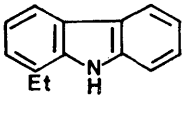


(29)

8.1—8.3 and for the *trans* at 8.75—8.9. This suggests that in both *cis*- and *trans*-isomers the Me(A) groups have the same conformation in both configurations. *X*-Ray crystallographic determinations[12] have shown that in this class of compound the $ArSO_2N{=}C$ group is *anti* to the R–N(indole) group. In the conformation shown (Figure 1) for the *trans*-isomer the proton at C(5) is equatorial and close to the SO_2 grouping. In the alternative conformation for this isomer the C(5)Me group is equatorial and very close to the SO_2 group. The conformation shown in Figure 1 places the C(6)Me grouping pseudoaxial. For the *cis*-compound (Figure 2) the C(5)Me group is also placed axial and away from the sulphonylimino grouping. This places the C(6)Me group pseudoequatorial. Hence the C(5)Me groups have the same chemical shifts in both isomers and the equatorial Me signal (*cis*-isomer) is 0.6 p.p.m. downfield from that of the *trans* C(6)Me signal. In a series of halogenated dihydroanthracene derivatives the equatorial Me signals are 0.4—0.5 p.p.m. downfield of the axial ones,[13] and in

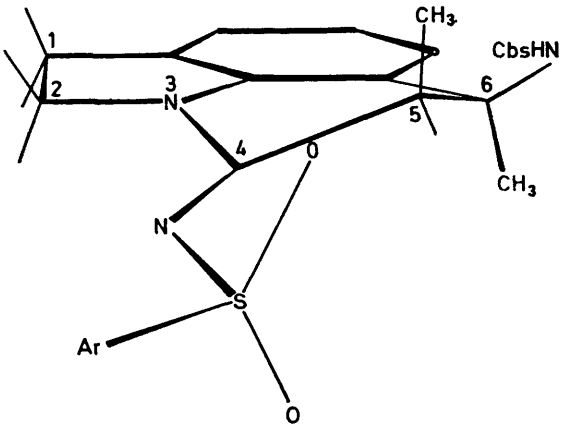


FIGURE 1

the dihydrophenanthrene (27) the chemical shift difference between the Me groups is 1.1 p.p.m. (at −80 °C).[14]

An authentic sample of the carbazole (17) was needed for comparison with the product obtained by heating

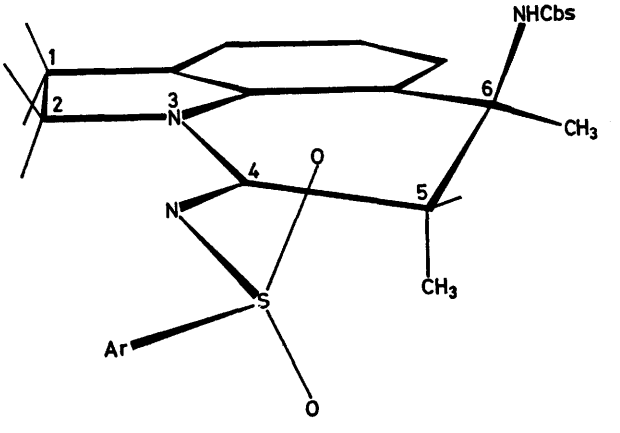
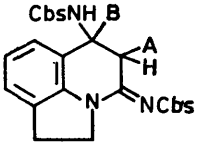
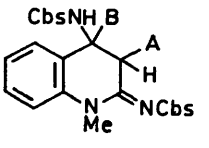
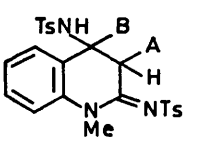


FIGURE 2

compound (9). This was obtained by palladium-catalysed dehydrogenation of (7). The maximum yield of (17) was 50%; attempts to improve the yield afforded the fully aromatic compound (28) and 1-ethylcarbazole (29).

Chemical shifts (τ) of CMe protons in $CDCl_3$ or * in $(CD_3)_2SO$

				
		CbsNH B A H N NCbs	CbsNH B A H N NCbs Me	TsNH B A H N NTs Me
Me (A)	*cis*	9.01	9.2 *	9.12
	trans	8.90, 9.01 *	9.11 *	9.02, 9.11 *
Me (B)	*cis*	8.12	8.31 *	8.12
	trans	8.75, 8.91 *	8.89 *	8.72, 8.91 *

EXPERIMENTAL

General details and instruments used have been reported.[15] 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. Column and thin-layer chromatography were carried out on silica using chloroform as eluant unless otherwise stated.

Reaction of 4,5,7,8,9,10-*Hexahydropyrrolo*[3,2,1-jk]*carbazole* (7) *with Azides*.—Compound (7) had m.p. 156—158 °C (lit.,[3] 157—158 °C), the value reported [3] (τ 8.83) for the chemical shift of C(9)H_2 [incorrectly numbered C(7)H_2 in ref. 3] and C(8)H_2 was a misprint; the correct value is τ 8.13. A solution of (7) (1 g, dried 110 °C) and $CbsN_3$ (1.1 g) in dry $CHCl_3$ (15 ml) was kept for 7 days and the solid then collected (0.72 g). trans-10a-p-*Chlorophenylsulphonylamino*-7-p-*chlorophenylsulphonylimino*-4,5,7,7a,8,9,10,10a-*octahydrocyclopenta*[c]*pyrrolo*[3,2,1-ij]*quinoline* (10; Z = Cbs) formed rods, m.p. 160—170 and 270—271 °C (from $CHCl_3$–MeOH) (Found: C, 54.4; H, 3.75; N, 7.1. $C_{26}H_{23}Cl_2N_3O_4S_2$ requires C, 54.2; H, 4.0; N, 7.3%); $\lambda_{max.}$ 227, 273, 285, and 310 nm (ε 32 300, 12 200, 13 300, and 16 300); $\nu_{max.}$ 1 610 and 3 280 cm^{-1}; τ 2.06 (2 H, d, *J* 9 Hz), 2.58 (2 H, d, *J* 9 Hz), 2.65—3.1 (7 H, m), 4.82 (1 H, s, exchanged with D_2O), 5.3—6.2 [2 H, m, C(5)H_2], and 6.7—8.3 (9 H, m); *m/e* (M^+ not detected) 384 (6%), 209 (70), and 111 (100). The mother-liquors were concentrated and triturated with MeOH and the solid so obtained washed with hot EtOH giving more (10; Z = Cbs) (0.25 g).

All the mother-liquors were combined and the residue was chromatographed giving (starting material) (0.3 g) and a mixture of two compounds which were separated (p.l.c.) into the ketone (9) (250 mg; m.p. 215—217 °C) [3] and the imine (13) (3 mg). 7-p-*Chlorophenylsulphonylimino*-4,5,7,8,9,10-*hexahydropyrrolo*[3,2,1-jk]*carbazole* (13) formed yellow prisms, m.p. 140—141 °C (from $CHCl_3$–MeOH) (Found: C, 62.3; H, 4.5; N, 7.2. $C_{20}H_{17}ClN_2O_2S$ requires C, 62.5; H, 4.4; N, 7.3%); $\lambda_{max.}$ 255sh and 352 nm (ε 31 100 and 56 500); $\nu_{max.}$ ($CHCl_3$) 1 550 cm^{-1}; τ (Brucker WH90; FT) 1.99 (2 H, d, *J* 9 Hz), 2.47 (2 H, d, *J* 9 Hz), 2.6—3.05 (3 H, m), 5.50 [2 H, t(br), *J* 7 Hz, C(5)H_2], 6.32 [2 H, t(br), *J* 7 Hz, C(4)H_2], 6.66 [2 H, t(br), *J* 7 Hz, C(10)H_2], 6.99 [2 H, t(br), *J* 7 Hz, C(8)H_2], and 7.6—8.0 [2 H, m, C(9)H_2]; *m/e* 384 (M^+, 26%), 320 ($M - SO_2$, 3, *m** 266.6), 209 (100), 207 (12), and 181 (209 − C_2H_4, 24).

Samples of the indole (7) (1 g) and $CbsN_3$ (1.1 g) were dissolved in dry $CHCl_3$ (15 ml) that had been saturated with H_2S. After 6 days the $CbsNH_2$ (0.5 g) (m.p. 140—142°) which had separated was collected (*cf.* the reduction of RN_3 to RNH_2 by H_2S [16]). The solvent was removed. Trituration of the residue with MeOH gave starting material (0.5 g) followed by the ketone (9) (0.3 g). P.l.c. of the non-crystalline residues gave (10; Z = Cbs) (0.25 g) and 7-p-*chlorophenylsulphonylamino*-4,5,7,8,9,10-*hexahydropyrrolo*-[3,2,1-jk]*carbazole* (16) (5 mg), prisms, m.p. 198—199 °C (Found: C, 62.3; H, 5.0; Cl, 9.2; N, 6.9. $C_{20}H_{19}ClN_2O_2S$ requires C, 62.2; H, 4.9; Cl, 9.1; N, 7.2%); $\lambda_{max.}$ 233, 282, and 308sh nm (ε 40 600, 8 500, and 5 000); $\nu_{max.}$ ($CHCl_3$) 1 590w, 3 290br, and 3 390 cm^{-1}; τ 2.10 (2 H, d, *J* 9 Hz), 2.45 (2 H, d, *J* 9 Hz), 2.65—3.15 (3 H, m), 5.50 [2 H, s(br), 1 H exchanged with D_2O, NH and C(7)H]; 5.67 [2 H, t(br), *J* 7 Hz, C(5)H_2], 6.32 [2 H, t(br), *J* 7 Hz, C(4)H_2], 7.2—7.4 [2 H, m, C(10)H_2], and 8.08—8.35 [4 H, m, C(9)H_2 and C(8)H_2]; *m/e* 386 (M^+, 61%), 211 (49), 210 (40), and 196 (100).

The ketone (9) (0.5 g) was heated (220 °C; 3 min); the melt was cooled and triturated with MeCN. Recrystallisation (MeCN) of the solid so obtained gave the sulphonamide (16) (0.2 g), identical (m.p., i.r.) with the sample described above. The ketone (9) (1.0 g) was heated (210—215 °C; 15 min), then cooled, and $CHCl_3$ (1 ml) was added. $CbsNH_2$ (0.3 g) separated; chromatography of the mother liquors yielded 4,5-*dihydropyrrolo*[3,2,1-jk]*carbazole* (17) (0.2 g), identical [t.l.c., i.r., u.v.) with the sample described later.

A solution of (7) (1.8 g) in dry $CHCl_3$ (20 ml) containing TsN_3 (3.6 g) was kept for 2 days and then half the solvent was removed. The resulting solid was collected and recrystallised (MeCN) (yield 0.85 g). trans-4,5,7,7a,8,9,10,-10a-*Octahydro*-10a-p-*tolylsulphonylamino*-7-p-*tolylsulphonyliminocyclopenta*[c]*pyrrolo*[3,2,1-ij]*quinoline* (10; Z = Ts) formed needles, m.p. 155—160 and 200—215 °C (Found: C, 63.1; H, 5.5; N, 7.8. $C_{28}H_{29}N_3O_4S_2$ requires C, 62.8; H, 5.5; N, 7.9%); $\lambda_{max.}$ 272, 304, and 308 nm (ε 12 600, 12 100, and 14 700); $\nu_{max.}$ 1 600 and 3 350 cm^{-1}; τ 2.09 (2 H, d, *J* 8 Hz), 2.6—3.15 (9 H, m), 5.1 (1 H, s, exchanged with D_2O), 5.5—6.2 [2 H, m, C(5)H_2], 7.56 (3 H, s, TsMe), 7.68 (3 H, s, TsMe), and 6.7—8.2 (9 H, m); *m/e* 364 (M − $TsNH_2$, 22%), 299 (12), and 209 (100).

A solution of the tetrahydrocarbazole (7) (1 g) in DMSO (20 ml) containing $CbsN_3$ (2.2 g) was kept for 15 h, then diluted with water and extracted with benzene. The organic extract afforded compound (9) (yield 75%) and t.l.c. of the residues showed traces of (18).

$CbsN_3$ (2.2 g) was dissolved in DMSO (20 ml) containing Ac_2O (2 ml). After 3 days compound (7) (1 g; dried at 100 °C for 4 h) was added. Next day the solid which had separated (0.62 g) was collected and washed with MeOH (solid A). Water was then added to the DMSO and the mixture extracted (Et_2O, 2 × 50 ml). The extracts contained an insoluble solid (0.65 g; solid B). Chromatography of the ether-soluble fraction gave starting material (0.2 g), compound (13) (0.11 g), and the elimination product (12; Z = Cbs) (0.15 g), m.p. 268—270 °C (lit.,[3] 268—271 °C). Chromatography of solid A gave (13) (10 mg) and (12; Z = Cbs) (0.4 g). Chromatography of solid B gave (13), (12), and (eluted by $CHCl_3$–1% MeOH) the *cis*-compound (11; Z = Cbs) (0.5 g), m.p. 238—239 °C (lit.,[3] 229—231 °C) (Found: C, 54.5; H, 4.2%); *m/e* 575 (M^+, 1%), 384 (9), 210 (18), 209 (100), and 111 (30).

Formation of Compound (12).—(*a*) Compound (10; Z = Cbs) was heated (5 min; 180—200 °C) and the product recrystallised affording (12; Z = Cbs),[3] m.p. 269—271 °C.

(*b*) Compounds (10; Z = Cbs) and (10; Z = Ts) were dissolved separately in trifluoroacetic acid and the n.m.r. spectra were recorded; in the time (*ca.* 10 min) required for the measurements elimination was complete. Under the same conditions elimination from (11; Z = Cbs) took 10 days and from (11; Z = Ts) 6 days. The n.m.r. spectrum of a solution of (10; Z = Cbs) in pyridine indicated that elimination was complete after 1 h whilst a solution of (11; Z = Cbs) in pyridine was unchanged after 3 days.

(*c*) A solution of (10; Z = Cbs) in EtOH (50 ml; 5×10^{-5}M) was treated with 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) (1 drop) and the u.v. spectrum recorded; the spectrum was that of the quinoline (12; Z = Cbs).

The *cis*-isomer (11; Z = Cbs) (5 mg) was dissolved in EtOH (50 ml) and DBN (1 drop) added. The solution was

boiled under reflux; samples were removed every 12 h and their u.v. spectra recorded (after dilution). Elimination was complete in 96 h.

To an ethanolic solution of the *trans*-compound (10; Z = Cbs) (5×10^{-5}M) was added 1 drop of triethylamine. The solution was kept at 27 °C and the elimination followed by the change in the u.v. spectrum; $t_{\frac{1}{2}} = 33 \pm 3$ min (three determinations). The *cis*-isomer was unaffected under these conditions.

Reactions of 1,2-*Dihydro*-4,5-*dimethylpyrrolo*[3,2,1-hi]*indole* (21; R = Me) *with Azides*.—1-Aminoindoline (13 g) was heated (0.5 h; 100 °C) with butanone (7 g) containing HOAc (1 drop). Sulphuric acid (100 ml; 0.5M) was added and the mixture boiled (75 min). The solid indole was collected and recrystallised (EtOH). The *indole* (21; R = Me) formed needles (yield 40%), m.p. 118—120 °C (Found: C, 84.1; H, 7.6; N, 8.2. $C_{12}H_{13}N$ requires C, 84.2; H, 7.6; N, 8.2%); $\lambda_{max.}$ 207, 233, and 292 nm (ε 20 000, 30 700, and 8 000); τ 2.8—3.3 (3 H, m), 5.78 (2 H, t, *J* 7 Hz), 6.39 (2 H, t, *J* 7 Hz), and 7.5 [6 H, s(br), 2 × Me]; *m/e* 171 (M^+, 90%), 170 (100), 143 (4), and 128 (10). The only data recorded for this compound are mass spectral [9]).

A solution of the indole (0.85 g) in $CHCl_3$ (10 ml) containing TsN_3 (1.0 g) was kept for 5 weeks. The solvent was removed and MeOH added. The solid was collected and recrystallised from $CHCl_3$–MeOH yielding 1,2,4,5-*tetrahydro*-5-*methyl*-5-p-*tolylsulphonylamino*-4-p-*tolylsulphonyliminopyrrolo*[3,2,1-hi]*indole* (23; Z = Ts) (yield 30%), prisms, m.p. 245—250 °C (decomp.) (Found: C, 60.8; H, 5.0; N, 8.3. $C_{25}H_{25}N_3O_4S_2$ requires C, 60.6; H, 5.0; N, 8.5%); $\lambda_{max.}$ 224, 271, 280, and 312 nm (ε 36 300, 17 400, 15 500, and 10 000); $\nu_{max.}$ 1 590, 1 615, 1 645w, and 3 270 cm^{-1}; τ 2.12 (2 H, d, *J* 8 Hz), 2.6—3.2 (9 H, m), 4.4 (1 H, s, exchanged with D_2O), 5.4—6.1 (2 H, m), 6.4—6.74 (2 H, m), 7.55 and 7.60 (each 3 H, s), and 8.42 (3 H, s); *m/e* 495 (M^+, 10%), 340 (88), 185 (55), 171 (35), and 91 (100). The $CHCl_3$–MeOH mother-liquors were concentrated yielding starting material (0.3 g). The reaction mother-liquors were concentrated and the residue chromatographed giving starting material (0.08 g) and a brown gum. Trituration of this gum with MeOH gave 1,2,3,4,5-*tetrahydro*-5-*methyl*-5-(N-*methyl*-p-*tolylsulphonylamino*)-4-p-*tolylsulphonyliminopyrrolo*[3,2,1-hi]*indole* (24; Z = Ts) (20 mg), prisms, m.p. 235—238 °C.

Compound (23; Z = Ts) (0.9 g) and Me_2SO_4 (0.4 ml) were dissolved in Me_2CO (25 ml) and sodium hydroxide solution (2 ml; 25%) was added. Next day water was added and the product (24; Z = Ts) (yield 75%) collected and recrystallised ($CHCl_3$-MeOH); m.p. 238—239 °C; it was identical with the sample described above (Found: C, 61.35; H, 5.4; N, 8.1. $C_{26}H_{27}N_3O_4S_2$ requires C, 61.3; H, 5.3; N, 8.2%); $\lambda_{max.}$ 225, 271, 281, and 312 nm (ε 28 800, 12 900, 11 700, and 7 100); $\nu_{max.}$ ($CHCl_3$) 1 585 cm^{-1}; τ 2.09 (2 H, d, *J* 8 Hz), 2.34 (2 H, d, *J* 8 Hz), 2.55—3.05 (7 H, m), 5.33 (2 H, t, *J* 8 Hz), 6.42 (2 H, t, *J* 8 Hz), 7.08 (3 H, s, NMe), and 7.54, 7.63, and 8.32 each 3 H, s, CMe); *m/e* 354 (*M* — Ts, 100%), 326 (4), 199 (26), 171 (18), and 91 (60).

To a solution of compound (23; Z = Ts) (0.1 g) in $CHCl_3$ (50 ml) was added diazomethane [from *N*-nitrosomethylurea (1 g)] and the solution was kept at 0 °C for 60 days. The solvent was removed giving (24; Z = Ts) (yield 50%), m.p. 238 °C.

A solution of the indole (21; R = Me) (0.85 g) and $CbsN_3$ (1.1 g) in dry $CHCl_3$ (10 ml) was kept for 8 weeks. Chromatography afforded starting material (0.5 g) and a gum (1.0 g). Trituration of this gum and recrystallisation of the solid from methanol gave 5-p-*chlorophenylsulphonylamino*-4-p-*chlorophenylsulphonylimino*-1,2,4,5-*tetrahydro*-5-*methylpyrrolo*[3,2,1-hi]*indole* (23; Z = Cbs), prisms (0.4 g), m.p. 191—193 °C (Found: C, 51.8; H, 3.4; N, 7.7. $C_{23}H_{19}Cl_2N_3O_4S_2$ requires C, 51.6; H, 3.5; N, 7.8%); $\lambda_{max.}$ 228, 272, 280, and 314 nm (ε 49 000, 20 400, 18 200, and 12 000); $\nu_{max.}$ ($CHCl_3$) 1 575, 1 590, 1 608, and 3 335 cm^{-1}; τ 1.85 (1 H, s, NH), 2.03 (2 H, d, *J* 9 Hz), 2.53 (2 H, d, *J* 9 Hz), 2.4—3.5 (7 H, m), 5.3—5.9 (2 H, m), 6.35—6.55 (2 H, m), and 8.42 (3 H, s); *m/e* 535 (M^+, 5%), 360 (*M* — Cbs, 60), 296 (8), 185 (70), 183 (75), and 111 (100). The methanolic mother-liquors were concentrated and p.l.c. (10% EtOH–PhH) gave starting material (0.08 g) and an oil (0.2 g). Recrystallisation (MeOH) gave 4-p-*chlorophenylsulphonylimino*-5-(N-*methyl*-p-*chlorophenylsulphonylamino*)-1,2,4,5-*tetrahydro*-5-*methylpyrrolo*[3,2,1-hi]*indole* (24; Z = Cbs) (yield 100 mg), prisms, m.p. 205—207 °C (Found: C, 52.6; H, 4.0; N, 7.6. $C_{24}H_{21}Cl_2N_3O_4S_2$ requires C, 52.4; H, 3.8; N, 7.6%); $\lambda_{max.}$ 226, 272, 282, and 312 nm (ε 39 800, 17 000, 15 800, and 11 200); $\nu_{max.}$ ($CHCl_3$) 1 588 cm^{-1}; τ 2.08 (2 H, d, *J* 9 Hz), 2.31—3.03 (9 H, m), 5.33 [2 H, t(br), *J* 8 Hz], 6.40 (2 H, t, *J* 8 Hz), 7.04 (3 H, s, NMe) and 8.32 (3 H, s, CMe); *m/e* 549 (M^+, 3%), 274 (*M* — Cbs, 100, *m** 254.8), 199 (41), 198 (44), and 111 (31).

Reaction of the indole (0.85 g) with $CbsN_3$ (2.2 g) in MeOH gave (chromatography) starting material (0.1 g), $CbsN_3$ (0.2 g), $CbsNH_2$ (80 mg), and (23; Z = Cbs) (0.8 g) but no sign of any ketonic material corresponding to (9).

Reactions of 1,2-*Dihydro*-4-*ethyl*-5-*methylpyrrolo*[3,2-1-hi]-*indole* (21; R = Et) *with Azides*.—1-Aminoindoline and pentan-3-one gave the *indole* (21; R = Et), needles (EtOH) (yield 30%), m.p. 84—85 °C (Found: C, 84.3; H, 8.2; N, 7.5. $C_{13}H_{15}N$ requires C, 84.3; H, 8.2; N, 7.6%); $\lambda_{max.}$ 233 and 290 nm (ε 33 300 and 8 500); τ 2.75—3.3 (3 H, m), 5.70 (2 H, t, *J* 8 Hz), 6.37 (2 H, t, *J* 8 Hz), 7.32 (2 H, q, *J* 8 Hz), 7.76 (3 H, s), and 8.80 (3 H, t, *J* 8 Hz); *m/e* 185 (M^+, 73%), 170 (100%, *m** 156.2), 156 (11), 143 (4), and 128 (6).

A solution of the indole (0.92 g) and $CbsN_3$ (1.1 g) in MeOH (10 ml) was kept for 24 h. trans-6-p-*Chlorophenylsulphonylamino*-4-p-*chlorophenylsulphonylimino*-1,2,5,6-*tetrahydro*-5,6-*dimethyl*-4H-*pyrrolo*[3,2,1-ij]*quinoline* (26) formed needles (0.3 g), decomp. from 180 °C, m.p. 240—250 °C (Found: C, 53.3; H, 4.4; Cl, 12.3; N, 7.2. $C_{25}N_{23}Cl_2N_3O_4S_2$ requires C, 53.3; H, 4.1; Cl, 12.4; N, 7.4%); $\lambda_{max.}$ 277sh, 286, and 310 nm (ε 13 800, 17 000, and 18 600); $\nu_{max.}$ 1 535 and 3 280 cm^{-1}; τ[$(CD_3)_2SO$] 1.50 (1 H, s, NH), 2.0—2.45 and 2.7—3.05 (11 H, m), 5.85—6.2 [2 H, m, C(2)H_2], 6.5—7.0 [3 H, m, C(1)H_2 + C(5)H]; *m/e* 372 (*M* — Cbs, 6), 308 (7), 197 (100), 191 (8), and 111 (18).

The MeOH solution was left for a further 4 weeks; a second crop (0.05 g) of (26) had then separated. The MeOH was then evaporated off and the black residue extracted with cyclohexane (4 × 50 ml). Chromatography of the extracts gave starting material (0.35 g). The cyclohexane-insoluble material was taken up in $CHCl_3$. Chromatography gave an oil which on trituration gave cis-6-p-*chlorophenylsulphonylamino*-4-p-*chlorophenylsulphonylimino*-1,2,5,6-*tetrahydro*-5,6-*dimethyl*-4H-*pyrrolo*[3,2,1-ij]-*quinoline* (25) (0.15 g), prisms, m.p. 133—135 °C (Found: C, 53.3; H, 4.1; N, 7.5. $C_{25}H_{23}Cl_2N_3O_4S_2$ requires C, 53.3; H, 4.1; N, 7.4%); $\lambda_{max.}$ 274, 283, and 312 nm (ε

14 400, 15 800, and 18 600); $\nu_{max.}$ 1 538, 1 548, and 3 540 cm^{-1}; τ 1.9—3.05 (11 H, m), 4.5 (1 H, s, NH), 5.9—6.25 [2 H, m, C(2)H_2], 6.4—6.7 [2 H, m, C(1)H_2], and 7.3—7.7 [1 H, m, C(5)H]; *m/e* 563 (M^+, 4%), 372 (5), 308 (10), 107 (100), 175 (22), and 111 (61). The remaining material eluted was black and polymeric.

In chloroform solution the indole (0.92 g) + $CbsN_3$ (1.1 g) gave (25) (0.2 g) and (26) (0.2 g) as the only crystalline materials [and starting material (0.55 g)]. A solution of the *trans*-compound (0.1 g) in 2-methoxythanol (75 ml) containing DBN (2 drops) was boiled (1 h) and the solution concentrated *in vacuo* to *ca.* 3 ml. The elimination product 4-p-*chlorophenylsulphonylimino*-1,2-*dihydro*-5,6-*dimethyl*-4H-*pyrrolo*[3,2,1-ij]*quinoline* formed needles (0.042 g), m.p. 218 °C (Found: C, 60.8; H, 4.4; N, 7.2. $C_{19}H_{17}ClN_2O_2S$ requires C, 61.2; H, 4.6; N, 7.5%); $\nu_{max.}$ 1 586 cm^{-1}; τ 2.06 (2 H, d, *J* 8 Hz), 2.41 (2 H, d, *J* 8 Hz), 2.0—2.6 (3 H, m), 5.04 [2 H, t(br), *J* 9 Hz, C(2)H_2], 6.48 [2 H, t(br), *J* 9 Hz, C(1)H_2], and 7.45 and 7.73 (each 3 H, s); *m/e* 372 (M^+, 7%), 308 ($M - SO_2$, 10, *m** 255), 197 (100), and 111 (6).

A solution of the *cis*-compound in ethanol containing DBN was boiled under reflux; elimination of $CbsNH_2$ was followed by the change in the u.v. spectrum of the solution and by t.l.c. Elimination was complete after 72 h.

1,2-*Dihydro*[3,2,1-jk]*carbazole* (17).—A mixture of (7) (0.5 g) and Pd–C (0.25 g, 5%) was heated (260 °C) for 20 min, cooled, and extracted with boiling EtOH. The extracts were concentrated, and the solid (yield 50%) collected and recrystallised (EtOH). The *carbazole* (17) formed pale yellow prisms, m.p. 94.5—95.5 °C (Found: C, 86.9; H, 5.7; N, 7.3. $C_{14}H_{11}N$ requires C, 87.0; H, 5.7; N, 7.3%); $\lambda_{max.}$ 238, 262, 281sh, 286sh, 296, 339, and 355 nm (ε 50 900, 25 300, 9 800, 10 900, 19 300, 4 700, and 4 000); τ 1.85—3.0 (7 H, m), 5.54 (2 H, t, *J* 7 Hz), and 6.20 (2 H, t, *J* 7 Hz); *m/e* 193 (M^+, 100%), 192 (51), 191 (30), 166 (4), and 165 (9). When the reaction mixture was heated (190 °C) for 16 h 1-ethylcarbazole (29) (yield 60%) sublimed out. Recrystallisation afforded plates, m.p. 74.5—76 °C (lit.,[17] 74 °C); τ 1.9—2.9 (8 H, m, Ar + NH, exchanged with D_2O), 7.12 (2 H, q, *J* 8 Hz), and 8.63 (3 H, t, *J* 8 Hz). Use of 10% Pd–C (180 °C; 4 h) and chromatographing the product (silica; 5% benzene–cyclohexane) gave *pyrrolo*[3,2,1-jk]*carbazole* (28) (yield 8%), m.p. 84—88 °C (Found: C, 87.5; H, 5.1; N, 7.1. $C_{14}H_9N$ requires C, 87.9; H, 4.7; N, 7.3%); $\lambda_{max.}$ 234sh, 256sh, 267, 273, 278, 303infl., 314infl., 326infl., and 333 nm (ε 36 200, 40 000, 62 100, 62 500, 60 900, 9 400, 14 500, 17 000, and 19 200); τ 1.9—2.85 (8 H, m), and 3.19 (1 H, d, *J* 3 Hz), *m/e* 191 (M^+, 100%), 190 (16), 164 (7, *m** 140.8), and 163 (9).

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