The Reactions of Four Derivatives of Pyrrolo[1,2-*a*]indole with Arenesulphonyl Azides

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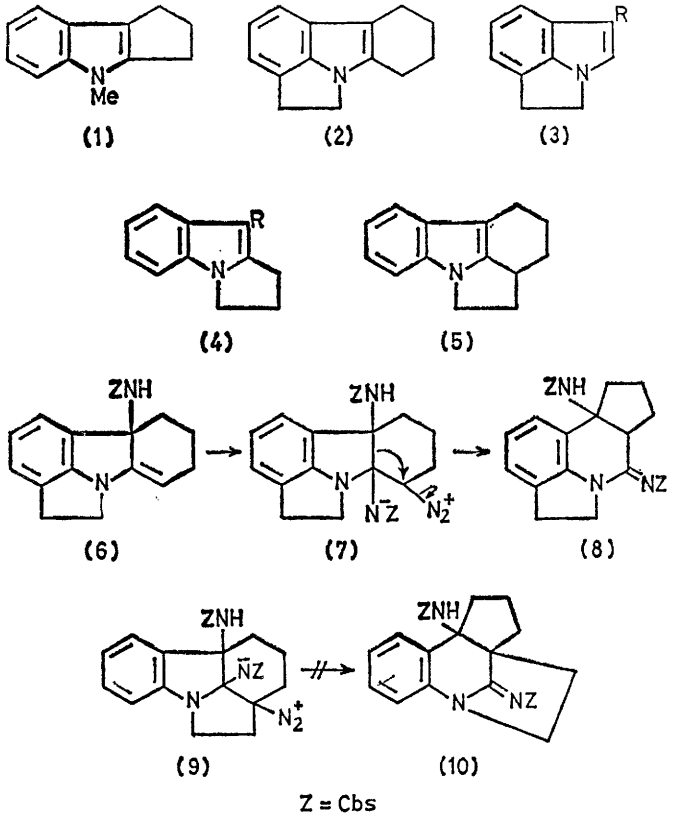
The reactions of arenesulphonyl azides with 2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole, with 2,3-dihydro-9-methyl-1*H*-pyrrolo[1,2-*a*]indole, with 1,2,2a,3,4,5-hexahydropyrrolo[3,2,1-*jk*]carbazole, and with 1,2,4,5-tetrahydro-2a-methyl-3-oxa-10-azacyclopenta[*jk*]fluorene in various solvents have been investigated and structures assigned to the reaction products.

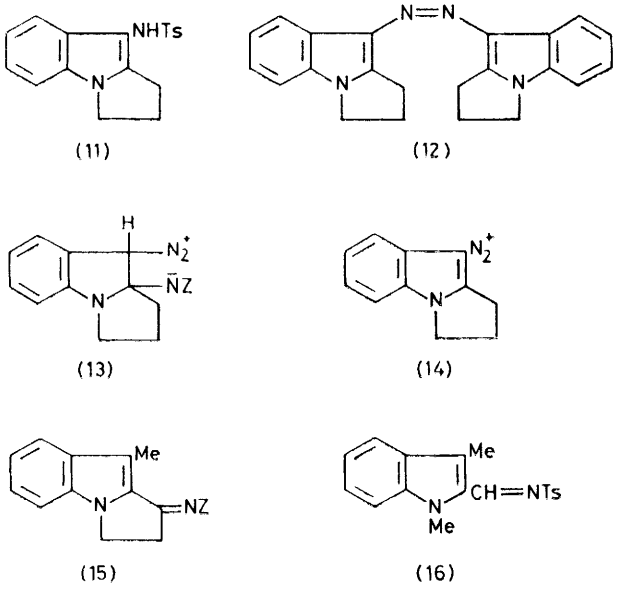
In previous papers we have described the reactions of the 'strained' indoles (1), (2), and (3) with arenesulphonyl azides.[1,2] Indoles containing fused 5-membered rings are much more reactive towards azides than indoles containing fused six-membered rings, *e.g.* (1) is more reactive than *N*-methyltetrahydrocarbazole. We have now extended these observations by an examination of the reactions of azides with (4; R = H), (4; R = Me), and (5). In the reactions of indoles with azides we have frequently observed [2] a ring-enlargement reaction to form quinoline derivatives [*e.g.* (2)→(6)→(7)→(8)] as a



(1) (2) (3) (4) (5) (6) (7) (8) (9) (10)

major reaction pathway. This pathway seemed unlikely to occur in compounds (4; R = Me) and (5), *e.g.* [(9)↛(10)].

Compound (4; R = H) reacted smoothly with tosyl azide, the reaction between the neat reagents being essentially complete in 2.5 days. The major product was the tolylsulphonylaminoindole (11) (yield 60%); and the azo-compound (12) was obtained in 12% yield. These compounds are analogous to those obtained from the reaction of 1,2-dimethylindole with tosyl azide.[3] In ethyl acetate solution the reaction was incomplete after 5 days but the product ratio remained unchanged; however in methanol the reaction was complete after 4 days and only traces of the azo-compound (12) were detected by t.l.c., the product being almost entirely (11). The effect of changing the solvent on the reaction between tosyl azide and 1,4-dihydro-1-methylquinoline-4-carbonitrile has been reported.[4]



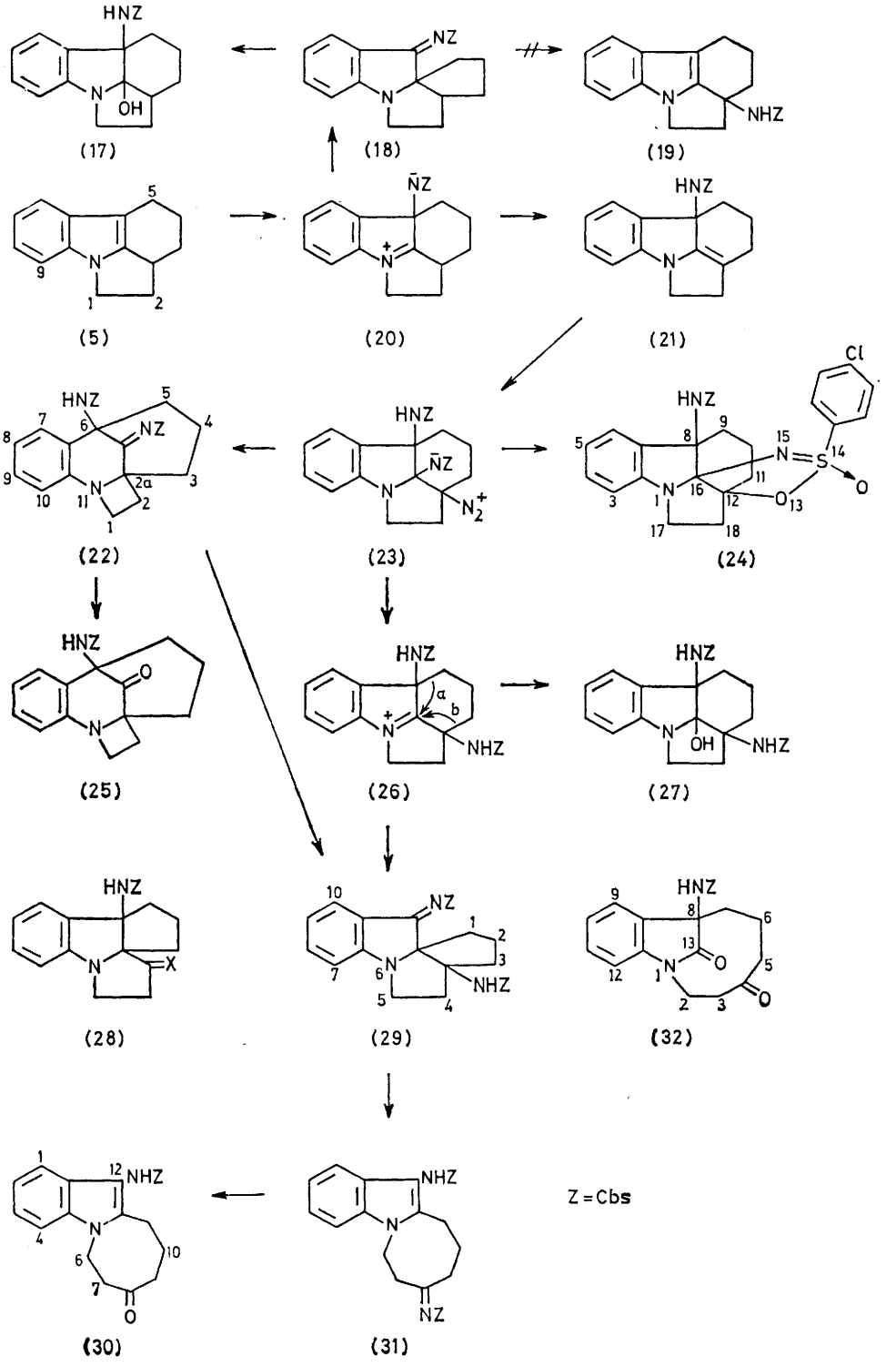
(11) (12) (13) (14) (15) (16)

The reaction between picryl azide and compound (4; R = H) was complete after 16 h; the only product isolated was the charge-transfer complex of picramide and the azo-compound (12), the remainder being an intractable tar. In an attempt to obtain the picramidoindole (11; NH-picryl replacing NH-tosyl) the reaction between (4; R = He) and 2 equivalents of picryl azide was examined but only (12) was isolated as its charge-transfer complex. Having established that the use of methanol as solvent increases the proportion of (11) relative to (12) the reaction between (4; R = H) and

picryl azide was examined in methanol solution. Reaction was complete after only 4 h but the only product isolated was (12) as its charge-transfer complex. These results indicate that in the intermediate (13; Z = Ts) the major reaction involves migration of NZ forming (11) whilst in (13; Z = picryl) loss of picramide forming the diazonium cation (14) is favoured.

The reaction between compound (4; R = Me) and tosyl azide gave a tar from which compound (15; Z = Ts) was isolated in 1% yield as the only crystalline material. The structure of this compound was established by a comparison of its physical properties with those of compound (16).[1b] Treatment of (4; R = Me) with *p*-chlorobenzenesulphonyl azide ($CbsN_3$) afforded only a small quantity of (15; Z = Cbs).

In marked contrast to the reactions of (4; R = Me)

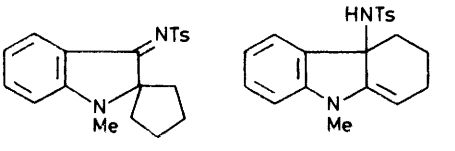


compound (5) reacted very smoothly with *p*-chlorobenzenesulphonyl azide giving a mixture of products; no darkening or tar formation was observed. The structures of four of the products obtained in these reactions have been established by *X*-ray crystallography.[5]

Compound (5) reacted rapidly with $CbsN_3$ in carbon tetrachloride solution giving an unstable 1 : 2 adduct as the major product. The characteristic u.v. spectrum and fluorescence [1b] of the compound suggest the spiro-structure (29) and the reactions of the compound (see later) support this. A small quantity of the hydrate (27) was also obtained. This arises by the addition of water to (26) [*cf.* the reaction of (1) with azides [1]]. Finally a small quantity of the bright yellow 1 : 1 adduct (18) was isolated. The isolation of (18) in small quantity suggests that loss of a proton from (20) forming (21) occurs much faster than ring-contraction to give (18). We have shown [1,6] that enamines of type (21) are intermediates in these reactions and we attempted the preparation of (21) by dissolving (18) in trifluoroacetic acid and treating the resulting salt with base, a route used [1] to convert (33) into (34). The product we obtained was the hydrated compound (17). Further compound (33) rapidly rearranges [1] at its melting point to form (35). In contrast compound (18) was unchanged after being heated for 30 min, and, upon melting, the hydrated compound (17) formed (18) and not (21); these results indicate the reluctance of compounds of types (18) and (29) to revert to the strained indole system.

The reaction between (5) and $CbsN_3$ was repeated using carbon tetrachloride which had been purified by passage down a type H alumina column. From this reaction were isolated the yellow compounds (18) and (29) along with two colourless compounds. The first of these had a molecular formula $C_{26}H_{23}Cl_2N_3O_4S_2$; the u.v. spectrum proved that the compound was not an indole and other spectral data were uninformative. An *X*-ray crystal structure determination [5] shows that the compound has structure (24) and contains an oxathiazole ring. This compound arises by the attack of one of the sulphonamide oxygen atoms on the carbonium ion formed by loss of nitrogen from (23) and provides strong evidence for the intermediacy of (21) and (23) in these reactions. Regitz [7] has suggested the formation of such a structure (37) as an intermediate in the transformation of (36) into (38), and recently L'abbé has obtained an oxathiazole [8] derivative from the reaction between ketenimines and methanesulphonyl azide. The second colourless compound to be isolated had a molecular formula $C_{20}H_{19}ClN_2O_3S$; the u.v. spectrum was that of an indole and the i.r. spectrum showed the presence of HN and CO (1 700 cm^{-1}) groups. The n.m.r. spectra (^1H and ^{13}C) proved that the compound contained six CH_2 groups and structure (30) was assigned to this material. This structure has been confirmed by *X*-ray crystallography.[5]

Compound (30) does not arise directly from the reaction between the indole and azide but is a transformation product of compound (29). The latter is thermally unstable and on being boiled in chlorobenzene solution for a few minutes it isomerises to the indole (31). In $CDCl_3$ solution the n.m.r. spectrum of (31) showed only the presence of aliphatic protons (apart from aromatic and NH), but in $(CD_3)_2SO$ solution a signal appeared at $\tau = 4.48$ characteristic of C*H*=CNTs. Enamines have



(33)

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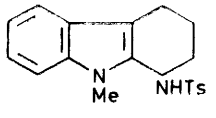

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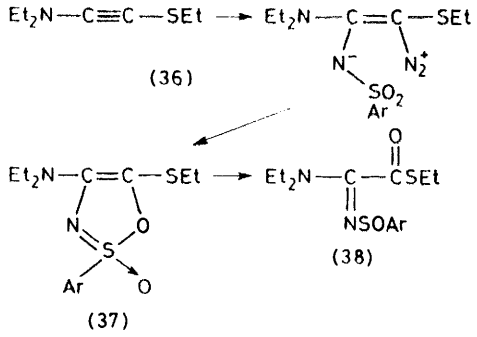
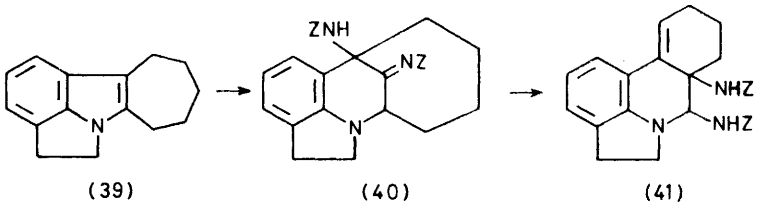


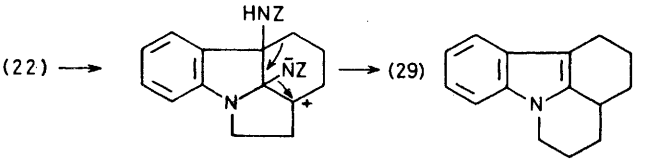
been detected (n.m.r.) in solutions of arenesulphonylimines and such imines are readily hydrolysed.[9,10] Hydrolysis of (31) occurred readily and afforded compound (30); hence it seems likely that (30) is produced during work-up of the reaction mixture.

The indole (5) reacted with $CbsN_3$ in benzene solution to form compounds (18) and (29) and a further 1 : 2 adduct. This material was unstable and difficult to recrystallise. The i.r. spectrum of the compound contained bands at 1 630 (C=N) and 3 260 cm^{-1} (NH) and the u.v. spectrum showed that the indoline-3-imine type of structure [*e.g.* (18)] was absent. On boiling the compound in ethanol it was rapidly hydrolysed, forming a compound $C_{20}H_{19}ClN_2O_3S$ which contained a carbonyl group (1 730 cm^{-1}). We originally assigned structure (28; X = O) to this compound, and considered that it arose by the hydrolysis of (28; X = NCbs), this imine being formed from (26) by ring-contraction ' b ', contraction ' a ' giving the isomer (29). The ^{13}C n.m.r. spectrum of the ketone indicated the presence of five CH_2 groups, supporting structure (28; X = O). However, the ketone failed to exchange hydrogen atoms when treated with D_2O and did not condense with benzaldehyde. These failures threw doubt on structure (28; X = O). *X*-Ray crystallography [5] has shown that the

molecule has the bridged-structure (25) and the product from the indole–azide reaction therefore has structure (22), hydrolysis of (22) giving (25). We had rejected this type of structure since derivatives of tetrahydrocarbazole do not produce this type of molecule but this type of structure is found in the products of the reactions of cycloheptindoles with azides, *e.g.* (39)→(40);[1,2]



(39) (40) (41)



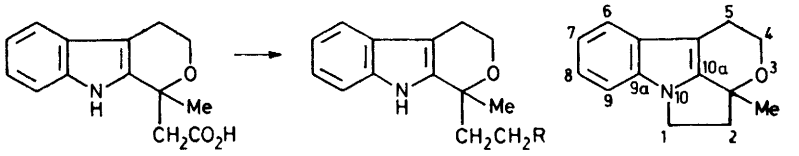
(42) (43)

Z = Cbs

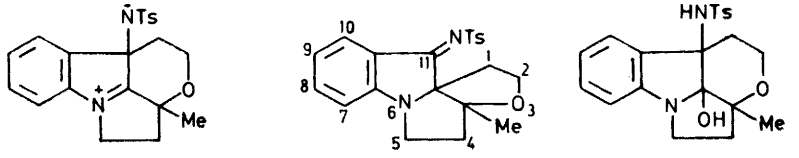
further, structure (22) contains a strained four-membered ring. Compound (22) when heated for a few minutes rearranges to (29), presumably *via* the ion (42). In contrast compound (40) rearranges when heated to form (41).[2,11]

The reaction between (5) and $CbsN_3$ was next examined in methanolic acetic acid solution in the hope[1] of obtaining compounds of type (19). The major product was a colourless crystalline solid of formula $C_{20}H_{19}ClN_2O_4S$; the compound was not an indole (u.v.). The i.r. spectrum showed the presence of an NH group, an aliphatic carbonyl group (1 725), and an amide carbonyl (1 680 cm^{-1}) group. The n.m.r. spectrum indicated the absence of olefinic protons and the compound has been shown by *X*-ray crystallography analysis[5] of the corresponding oxime to have structure (32). The only other crystalline material isolated from this reaction was the 1 : 1 adduct (18). The route for the formation of compound (32) is uncertain. It may be regarded as an oxidation product of (27) (followed by hydrolysis) or it could arise from (30) by oxidation and rearrangement but neither (27) nor (30) were detected in this reaction and (32) was not detected as a product of the reaction between (5) and $CbsN_3$ in non-polar solvents. Examples of oxidation occurring during azide–enamine reactions have been reported.[4]

In sharp contrast to the reactions of (5) compound (43) reacted with $CbsN_3$ to give $CbsNH_2$ as the only crystalline material, along with an intractable tar.



(44) (45) (46)



(47) (48) (49)

Finally, in this series the reactions of compound (46) with TsN_3 was examined; the expected intermediate (47) cannot lose a proton to form an enamine. Compound (46) was prepared by reduction of the acid (44)[12] to the alcohol (45; R = OH). Treatment of the tosylate (45; R = OTs) with $KOBu^t$ afforded (46) [*cf.* the preparation of (5)[13]].

The indole (46) reacted smoothly with TsN_3 giving a good yield of the yellow spiran (48); a small quantity of the hydrated compound (49) was also isolated. When

the reaction between (46) and TsN_3 was carried out in wet chloroform solution compound (49) was the main product. At its m.p. (49) lost water giving (48) and treatment of (49) with tosyl chloride in pyridine solution also afforded (48).

EXPERIMENTAL

I.r. spectra were obtained with either a Perkin-Elmer 257 or a Unicam S.P. 1000 instrument for Nujol mulls; u.v. spectra were measured for solutions in ethanol unless otherwise stated using a Cary 14M spectrometer. N.m.r. spectra were measured for solutions in $CDCl_3$ unless otherwise stated using either Perkin-Elmer R14, R32, or Brucker WH90 instruments. Assignments of the ^{13}C signals were made using data summarised by Joule.[14] Mass spectra were recorded with either a Varian MAT CH7 or an A.E.I. MS9 instrument.

Thin layer chromatography was carried out using silica-gel H.F. 254—366 plates and column chromatography using silica 80—200 mesh with chloroform as solvent unless otherwise stated.

The preparations of the indoles (4; R = H), (4; R = Me), (5), and (43) have been described.[13]

Reaction of 2,3-*Dihydro*-1H-*pyrrolo*[1,2-a]*indole with Azides*.—(*a*) A mixture of the indole (4; R = H) (0.78 g) and tosyl azide (1.08 g) was kept at room temperature for 60 h. Chromatography of the product gave 9,9′-*azobis*(2,3-*dihydro*-1H-*pyrrolo*[1,2-a]*indole*) (12) (0.2 g) as a yellow powder, m.p. >340 °C (Found: C, 77.5; H, 6.0; N, 16.5. $C_{22}H_{20}N_4$ requires C, 77.6; H, 5.9; N, 16.5%); $\lambda_{max.}$ ($CHCl_3$) 282, 380, 410sh, and 426 nm (ε 13 300, 17 700, 23 700, and 25 900); $\nu_{max.}$ 1 555 and 1 610 cm^{-1}; n.m.r. (F.-t.) τ 1.4—1.6 (2 H, m), 2.6—2.85 (6 H, m), 5.81 (4 H, t, *J* 7 Hz), 6.53 (4 H, t, *J* 7 Hz), and 7.1—7.35 (4 H, m); *m/e* 340 (M^+, 77%), 312 (4%), 171 (100%), 156 (32%), and 142 (61%). Further elution yielded 2,3-*dihydro*-9-p-*tolylsulphonylamino*-1H-*pyrrolo*[1,2-a]*indole* (11) (1.1 g) as pale yellow rods (from MeOH), m.p. 189 °C (Found: C, 66.7; H, 5.8; N, 8.4. $C_{18}H_{18}N_2O_2S$ requires C, 66.3; H, 5.5; N, 8.6%); $\lambda_{max.}$ 222, 276sh, 283, and 290sh nm (ε 48 000, 7 300, 7 700, and 6 800); $\nu_{max.}$ 1 597 and 3 245 cm^{-1}; τ 2.38 (2 H, d, *J* 8 Hz), 2.7—3.3 (6 H, m), 3.83 (1 H, s exchanged with D_2O), 6.0br (2 H, t, *J* 7 Hz, 3-H_2), and 7.0—8.0 (4 H, m, 2-H_2 + 1-H_2); *m/e* 326 (M^+, 4%), 171 (100%), 170 (5%), 155 (9%), 154 (9%), and 129 (9%).

(*b*) A solution of the indole (0.078 g) in EtOAc (2 ml) containing tosyl azide (0.1 g) was left for 5 days and the sulphonamidoindole (11) (0.06 g) was then collected. T.l.c. of the mother-liquors showed the presence of compounds (11) and (12).

(*c*) The above experiment was repeated using MeOH as solvent. After 4 days compound (11) (0.064 g) was collected. T.l.c. of the mother liquors showed that only a trace of the azo-compound had been formed.

A solution of the indole (4; R = H) (0.8 g) and picryl azide (1.25 g) in EtOAc (20 ml) was kept at room temperature for 16 h and the complex of (12) with picramide was then collected (65% yield) as blue-black needles, m.p. >340 °C (Found: C, 59.2; H, 4.3; N, 19.5. $C_{28}H_{24}N_8O_6$ requires C, 59.2; H, 4.2; N, 19.7%); $\nu_{max.}$ 1 583, 1 630, 3 340, and 3 450 cm^{-1}; τ (F.-t.) 0.64 (2 H, s), 0.84—1.29br (2 H, s, NH_2), 1.44—1.67 (2 H, m), 2.52—3.0 (6 H, m), 5.83 (4 H, t, *J* 7 Hz), 6.58 (4 H, t, *J* 7 Hz), and 7.0—7.5 (4 H, m). The complex when boiled in dioxan [3] gave the free azo-compound (12). Evaporation of the mother-liquors gave a glassy black solid which did not separate on t.l.c. The reaction was repeated using 2 equivalents of picryl azide; only the charge-transfer complex of (12) was isolated. In MeOH solution the reaction was complete in 4 h.

Reaction of 2,3-*Dihydro*-9-*methylpyrrolo*[1,2-a]*indole with Azides*.—(*a*) A mixture of (4; R = Me) (0.85 g) and TsN_3 (1.0 g) was left at room temperature for 2 weeks. The gum was triturated with MeOH and the insoluble residue kept under EtOH for 3 days. The solid was collected and recrystallised ($CHCl_3$–MeOH) to give the *imine* (15; Z = Ts) as yellow needles (2 mg), m.p. 256—262 °C (Found: M^+, 338.108 8. $C_{19}H_{18}N_2O_2S$ requires M^+, 338.108 9); $\lambda_{max.}$ ($CHCl_3$) 255 and 350 nm (ε 23 000 and 27 000); $\nu_{max.}$ ($CHCl_3$) 1 598 and 1 620 cm^{-1}; τ (F.-t.) 2.05 (2 H, d, *J* 9 Hz), 2.33—3.0 (6 H, m), 5.55—5.8 (2 H, m, 3-H_2), 5.95—6.2 (2 H, m, 2-H_2), 7.48 (3 H, s, 9-Me), and 7.56 (3 H, s, TsMe); *m/e* 338 (M^+, 37%), 183 (100%), 155 (22%), 154 (15%), and 128 (17%). Chromatography gave complex mixtures and baseline material; nothing crystalline could be isolated.

(*b*) A mixture of the indole (0.425 g) and $CbsN_3$ (0.55 g) gave a tar after 10 min. Chloroform was added and after one week p.l.c. afforded a yellow solid (30 mg). 1-p-*Chlorophenylsulphonylimino*-2,3-*dihydro*-9-*methyl*-1H-*pyrrolo*[1,2-a]*indole* (15; Z = Cbs) formed fine needles (from $CHCl_3$–MeOH), m.p. 227—229 °C (Found: C, 60.6; H, 4.3; N, 7.5. $C_{18}H_{15}ClN_2O_2S$ requires C, 60.3; H, 4.2; N, 7.8%); $\lambda_{max.}$ 243, 255, and 350 nm (ε 16 900, 17 600, and 20 800); $\nu_{max.}$ ($CHCl_3$) 1 570, 1 595, and 1 618 cm^{-1}; τ (F.-t.) 1.97 (2 H, d, *J* 9 Hz), 2.29br (1 H, d, *J* 8 Hz), 2.46 (2 H, d, *J* 9 Hz), 2.55—3.0 (3 H, m), 5.5—5.75 (2 H, m), 5.9—6.15 (2 H, m), and 7.46 (3 H, s); *m/e* 358 (M^+, 24%), 183 (100%), 182 (13%), 155 (21%), 154 (14%), and 128 (19%). When the reaction was run in Me_2SO solution (4 days) compound (15; Z = Cbs) was obtained in 7% yield.

The Reactions of 1,2,2a,3,4,5-*Hexahydropyrrolo*[3,2,1-jk]-*carbazole with* $CbsN_3$.—A solution of (5) (2.9 g) in CCl_4 (10 ml) was added in three equal portions to $CbsN_3$ (6.5 g) in CCl_4 (10 ml). A vigorous reaction ensued and the mixture was cooled (25 °C). After 3 days the solid was collected and recrystallised from benzene–light petroleum (b.p. 60—80 °C). 3a-p-*Chlorophenylsulphonylamino*-11-p-*chlorophenylsulphonylimino*-1,2,3,3a,4,5-*hexahydro*-11H-*cyclopenta*[2,3]*pyrrolo*[1,2-a]*indole* (29) formed yellow prisms (3.7 g), m.p. 164—166 °C (decomp.) (Found: C, 54.4; H, 4.1; Cl, 12.3; N, 7.3; S, 11.2. $C_{26}H_{23}Cl_2N_3O_4S_2$ requires C, 54.3; H, 4.0; Cl, 12.3; N, 7.3; S, 11.1%); $\lambda_{max.}$ ($CHCl_3$) 288 and 432 nm (ε 11 200 and 6 100); $\nu_{max.}$ 1 550 and 3 310 cm^{-1}; τ 1.50 (1 H, d, *J* 9 Hz, 10-H), 2.0 (2 H, d, *J* 9 Hz), 2.3—3.3 (9 H, m), 4.2 (1 H, s, exchanged with D_2O), 6.52 (2 H, m, 5-H_2), and 7.6—8.5 (8 H, m); *m/e* 402 ($C_{20}H_{19}ClN_2O_3S$, 3%), 227 (12%), 193 (33%), and 191 (100%). The recrystallisation mother-liquors were concentrated to small volume and light petroleum was added to yield 2a,5a-*bis*-(p-*chlorophenylsulphonylamino*)-1,2,2a,3,4,5,5a,10a-*octahydropyrrolo*[3,2,1-jk]*carbazol*-10a-*ol* (27) (0.7 g), prisms, m.p. 113—114 °C (Found: C, 52.8; H, 4.0; Cl, 12.1; N, 6.9; S, 10.9. $C_{26}H_{25}Cl_2N_3O_5S_2$ requires C, 52.6; H, 4.2; Cl, 11.8; N, 7.1; S, 10.8%); $\lambda_{max.}$ 226, 255sh, and 292 nm (ε 28 000, 8 100, and 1 500); $\nu_{max.}$ 3 240, 3 290, and 3 500 cm^{-1}; τ 2.12 (2 H, d, *J* 9 Hz), 2.15 (2 H, d, *J* 9 Hz), 2.3—3.8 (8 H, m), 3.1, 4.3, and 6.0 (each 1 H, s, exchanged with D_2O), and 6.2—8.7 (10 H, m); *m/e* 593 (M^+, 1%), 402 (12%), 227 (25%), 199 (100%), 182 (10%), and 175 (23%).

The CCl_4 reaction mother-liquors were concentrated and

chromatographed to afford unchanged azide (1.2 g) and a bright orange-coloured gum (0.685 g). Trituration with MeOH and recrystallisation of the resulting solid from MeOH gave 11-p-*chlorophenylsulphonylimino*-1,2,3,3a,4,5-*hexahydro*-11H-*cyclopenta*[2,3]*pyrrolo*[1,2-a]*indole* (18) (0.612 g) as orange prisms, m.p. 123—124 °C (Found: C, 62.1; H, 5.2; Cl, 9.3; N, 7.2; S, 8.4. $C_{20}H_{19}ClN_2O_2S$ requires C, 62.2; H, 4.9; Cl, 9.1; N, 7.3; S, 8.3%); $\lambda_{max.}$ 228, 242sh, 281, and 420 nm (ε 25 300, 22 200, 10 100, and 6 300); $\nu_{max.}$ 1 590 cm^{-1}; τ 1.55 (1 H, d, *J* 8 Hz, 10-H), 2.01 (2 H, d, *J* 8 Hz), 2.35—2.6 (3 H, m), 2.95—3.2 (2 H, m), 6.35—6.6 (2 H, m, 5-H_2), 7.15—7.45 (1 H, m, 3a-H), and 7.7—8.6 (8 H, m); *m/e* 386 (M^+, 4%), 211 (100%), 183 (4%), and 169 (3%). Further elution gave a brown gum which did not crystallise and could not be separated by p.l.c.

The reaction between compound (5) and $CbsN_3$ was carried out in CCl_4 which had been passed down an alumina (type H) column. After 3 days the solid which had separated (2.4 g) was collected and shown (t.l.c.) to be a mixture. Chromatography of this solid gave unchanged azide (0.160 g), (18) (0.56 g), followed by a gum (1.3 g). Trituration (MeOH) of this gave a solid (0.79 g). Recrystallisation (MeCN) afforded 14-p-*chlorophenyl*-8-p-*chlorophenylsulphonylamino*-13-*oxa*-14-*thia*-1,15-*diazapentacyclo*-[10.4.2.$0^{2,7}$.$0^{8,16}$.$0^{12,16}$]*octadeca*-2,4,6,14-*tetraene* S-*oxide* (24) as colourless rods, m.p. 170—171 °C (Found: C, 54.4; H, 4.1; Cl, 12.3; N, 7.3; S, 11.1. $C_{26}H_{23}Cl_2N_3O_4S_2$ requires C, 54.3; H, 4.0; Cl, 12.3; N, 7.3; S, 11.1%); $\lambda_{max.}$ 235 nm (ε 34 600); $\nu_{max.}$ 3 240 cm^{-1}; τ 2.0 (2 H, d, *J* 8 Hz), 2.41 (2 H, d, *J* 8 Hz), 2.55—3.65 (8 H, m), 6.3—7.0 (2 H, m), and 7.7—8.8 (9 H, m); *m/e* 402 (4%), 227 (61%), 191 (58%), and 111 (100%). The MeOH mother-liquors from the trituration were concentrated to small volume and benzene (5 ml) was added. The solid which separated was recrystallised (benzene–light petroleum) (yield 0.234 g). 12-p-*Chlorophenylsulphonylamino*-6,7,10,11-*tetrahydroazocino*-[1,2-a]*indol*-8(9H)-one (30) formed needles, m.p. 229—230 °C (Found: C, 59.8; H, 5.0; Cl, 8.7; N, 6.9; S, 7.8. $C_{20}H_{19}ClN_2O_3S$ requires C, 59.7; H, 4.7; Cl, 8.7; N, 7.0; S, 8.0%); $\lambda_{max.}$ 224 and 282 nm (ε 40 800 and 9 200); $\nu_{max.}$ 1 700 and 3 260 cm^{-1}; τ [$(CD_3)_2SO$]1.0 (1 H, s, exchanged with D_2O, NH), 2.4 (2 H, d, *J* 8 Hz), 2.55—3.3 (6 H, m), 5.41 (2 H, t, *J* 6 Hz, 6-H_2), 6.9—7.6 (6 H, m), and 7.95—8.3 (2 H, m); δ (^{13}C) [$(CD_3)_2SO$] p.p.m. from $SiMe_4$, 22.5 (10-C), 28.2 (11-C), 37.7 (9-C), 39.5 (7-C), 46.0 (6-C), 107.7 (12-C), 109.4 (4-C), 117.0 (1-C), 119.0 (3-C), 121.0 (2-C), 124.7 (11a-C), 133.3 (12a-C), 137.5 (4a-C), and 212 (8-C) (the signals from the Cbs group have been omitted); *m/e* 402 (M^+, 4%), 227 (100%), 185 (5%), 169 (8%), and 168 (8%).

The carbon tetrachloride mother-liquors from the reaction were chromatographed (eluant CH_2Cl_2) to give the azide (1.8 g), (18) (0.53 g), and 29 (0.29 g). Elution with MeOH (2%)–CH_2Cl_2 yielded (30) (2.04 g).

12-p-*Chlorophenylsulphonylamino*-8-*p-chlorophenylsulphonylimino*-6,7,8,9,10,11-*hexhydroazocino*[1,2-a]*indole* (31). —A solution of compound (29) (1 g) in chlorobenzene (5 ml) was boiled (5 min), cooled, and light petroleum was added. The solid which separated was collected and recrystallised from MeCN. The *imine* (31) (0.65 g) formed prisms, m.p. 212—213 °C (Found: C, 54.6; H, 4.2; Cl, 12.1; N, 7.2; S, 11.0. $C_{26}H_{23}Cl_2N_3O_4S_2$ requires C, 54.3; H, 4.0; Cl, 12.2; N, 7.3; S, 11.1%); $\lambda_{max.}$ 225 and 282 nm (ε 53 800 and 9 200); $\nu_{max.}$ 1 620 and 3 230 cm^{-1}; τ 2.25—3.6 (12 H, m), 3.81 (1 H, s, exchanged with D_2O, NH), 5.3—5.6 (2 H, m), and 6.3—8.3 (8 H, m); in [$(CD_3)_2SO$] solution a signal at 4.48 appeared (C*H*=C–NHCbs); *m/e* 402 (2%), 227 (33%), 191 (63%), 175 (49%), and 111 (100%). Compound (31) was obtained when (29) was boiled (10 min) in ethanol or kept at its m.p. for 5 min. The imine (31) (0.3 g) was boiled (10 min) in HOAc (4 ml) containing conc. HCl (5 drops). The solution was evaporated to dryness and MeOH added to yield the ketone (30), identical (m.p., i.r., n.m.r.) with the material described earlier. The dinitrophenylhydrazone formed yellow prisms, m.p. 256—257 °C (from EtOH) (Found: C, 53.5; H, 3.9; Cl, 6.1; N, 14.1; S, 5.6. $C_{26}H_{23}ClN_6O_6S$ requires C, 53.6; H, 3.9; Cl, 6.0; N, 14.4; S, 5.6%); *m/e* 582 (M^+, 6%) and 407 (100%). The ketone (30) was reduced ($LiAlH_4$–THF) to form 12-p-*chlorophenylsulphonylamino*-6,7,8,9,10,11-*hexahydroazocino*-[1,2-a]*indol*-8-*ol* as prisms (benzene–light petroleum), m.p. 187—188 °C (Found: C, 59.6; H, 5.4; Cl, 8.4; N, 6.8; S, 7.9. $C_{20}H_{21}ClN_2O_3S$ requires C, 59.4; H, 5.2; Cl, 8.7; N, 6.9; S, 7.9%); $\lambda_{max.}$ ($CHCl_3$) 235 and 285 nm (ε 15 800 and 8 600); $\nu_{max.}$ 3 280 and 3 380 cm^{-1}; τ [$(CD_3)_2SO$] 0.75 (1 H, s, exchanged with D_2O), 2.2—3.4 (8 H, m), 5.6br (1 H, s), exchanged with D_2O), 5.85 (2 H, m), and 6.9—8.8 (9 H, m).

A solution of $CbsN_3$ (6.0 g) in MeOH–HOAc (6 : 4; 8 ml) was added to a suspension of (5) (3.0 g) in MeOH–HOAc (8 ml) the temperature being maintained in the range 23—25 °C. After 3 days the solid which had separated was collected and recrystallised (MeCN). 8-p-*Chlorophenylsulphonylamino*-1,2,5,6,7,8-*hexahydro*-1,8-*methano*[1]*benzazecine*-4(3H),13-*dione* (32) formed needles (2.18 g), m.p. 233—234 °C (Found: C, 57.6; H, 4.8; Cl, 8.4; N, 6.6; S, 7.5. $C_{20}H_{19}ClN_2O_4S$ requires C, 57.4; H, 4.5; Cl, 8.4; N, 6.7; S, 7.6%); $\lambda_{max.}$ 235 and 265 nm (ε 17 100 and 5 700); $\nu_{max.}$ 1 680, 1 725, and 3 130 cm^{-1}; τ [$(CD_3)_2SO$] 1.28 (1 H, s, exchanged with D_2O), 2.45—3.2 (8 H, m), 5.8—6.2 (2 H, m), and 6.8—8.15 (8 H, m); *m/e* 418 (M^+, 21%), 243 (83%, *m** 141.2), 227 (13%), 215 (26%), and 201 (15%). The *oxime* formed rods, m.p. 299—300 °C (decomp.) from aqueous pyridine. The crystals contained pyridine (see ref. 5) which was not completely removed on drying (Found: C, 56.8; H, 4.8; N, 9.7; M^+, 433.086 7, 435.084 4. $C_{20}H_{20}ClN_3O_4S$ requires C, 55.4; H, 4.6; N, 9.7%; M^+, 433.086 3, 435.083 4); *m/e* 433 (M^+, 35%), 258 (100%), and 79 (C_5H_5N, 30%).

Chromatography of the MeOH–HOAc mother-liquors gave azide (2.14 g) and (18) (0.108 g) followed by a gum (1.4 g) which yielded nothing crystalline on p.l.c.

Indole (5) (1 g) in benzene (5 ml) was added to a solution of $CbsN_3$ (2.5 g) in benzene (5 ml). After 24 h compound (29) (0.75 g) was collected and the filtrate cooled to 0 °C. Next day the solid (1.2 g) which had separated was collected. A small sample of the material was recrystallised by dissolution in benzene (50 °C) and slow addition of light petroleum to give 6-p-*chlorophenylsulphonylamino*-12-p-*chlorophenylsulphonylimino*-2,2a,3,4,5,6-*hexahydro*-2a,6-*methano*-1H-*azeto*[1,2-a][1]*benzazocine* (22) as an unstable solid, m.p. 110—111 °C (Found: C, 54.6; H, 4.3; Cl, 11.8; N, 7.1; S, 10.7. $C_{26}H_{23}Cl_2N_3O_4S_2$ requires C, 54.3; H, 4.0; Cl, 12.2; N, 7.3; S, 11.1%); $\lambda_{max.}$ 228 and 250 nm (ε 28 900 and 6 200); $\nu_{max.}$ 1 630 and 3 260 cm^{-1}; τ 2.0—3.75 (12 H, m), and 6.2—8.7 (11 H, m); *m/e* 402 (15%), 227 (34%), 199 (100%), 191 (15%), and 175 (16%).

The benzene mother-liquors were chromatographed (CH_2Cl_2) to give $CbsN_3$ (0.56 g), (18) (0.15 g), and (30) (0.14 g).

Compound (22) (0.5 g) was heated (115 °C) for 5 min,

cooled, and light petroleum added to give compound (29) (0.383 g) (m.p., i.r., n.m.r.). Compound (22) (0.5 g) was boiled in EtOH for 2 min; on cooling the solution (25) (0.32 g) separated. 6-p-*Chlorophenylsulphonylamino*-2,2a,3,4,5,6-*hexahydro*-2a,6-*methano*-1H-*azeto*[1,2-a][1]-*benzazocin*-12-*one* (25) formed prisms, m.p. 201—202 °C (Found: C, 59.6; H, 6.0; Cl, 8.8; N, 6.9; S, 8.1. $C_{20}H_{19}ClN_2O_3S$ requires C, 59.7; H, 4.7; Cl, 8.7; N, 7.0; S, 8.0%); $\lambda_{max.}$ 225 and 260 nm (ε 20 700 and 10 100); $\nu_{max.}$ 1 730 and 3 280 cm^{-1}; τ 2.1 (2 H, d, *J* 8 Hz), 2.3—3.53 (6 H, m), 4.1 (1 H, s, exchanged with D_2O), 5.8—6.1 (1 H, m), 6.3—6.62 (1 H, m), and 7.0—8.5 (8 H, m); δ (^{13}C) (C_5D_5N) 18.5 (4-C), 23.3 (2-C), 41.8 (3-C), 42.2 (5-C), 51.8 (1-C), 69.7 (2a-C), 71.7 (6-C), 115.5 (10-C), 121.5 (7-C), 123.7 (8-C), 128.1 (9-C), 144.3 (6a-C), 148.8 (10a-C), and 209.3 (12-C) (Cbs signals have been omitted); *m/e* 402 (M^+, 15%), 227 (25%), 199 (100%), and 182 (8%).

5a-p-*Chlorophenylsulphonylamino*-1,2,2a,3,4,5,5a,10a-*octahydropyrrolo*[3,2,1-jk]*carbazol*-10a-*ol* (17).—Compound (18) (0.5 g) was dissolved in trifluoroacetic acid containing trifluoroacetic anhydride (10%) (2 ml). After 24 h the solvent was removed under nitrogen and the resulting solid recrystallised from benzene–light petroleum. The *trifluoroacetate* formed needles (0.24 g), m.p. 104—105 °C (decomp.) (Found: C, 46.9; H, 3.3; Cl, 5.6; F, 18.9; N, 4.6. $C_{21}H_{21}ClF_6N_2O_6S$ requires C, 46.9; H, 3.4; Cl, 5.6; F, 18.6; N, 4.6%). This compound (1.5 g) was dissolved in MeOH (10 ml) and water (5 ml) was added. The mixture was cooled in ice and sodium carbonate solution was added. The solid which separated was collected and recrystallised (EtOH). The *alcohol* (17) formed needles, m.p. 129—130 °C (yield 0.65 g) (Found: C, 59.4; H, 5.2; Cl, 8.5; N, 6.7; S, 7.7. $C_{20}H_{21}ClN_2O_3S$ requires C, 59.4; H, 5.2; Cl, 8.7; N, 6.9; S, 7.9%); $\lambda_{max.}$ 238 and 300 nm (ε 15 500 and 3 060); $\nu_{max.}$ 3 180 and 3 400 cm^{-1}; τ 2.5—3.9 (8 H, m), 4.38 and 5.90 (each 1 H, s, exchanged with D_2O), 6.2—6.5 (1 H, m), 6.7—7.0 (1 H, m), and 7.3—9.4 (9 H, m); *m/e* 404 (M^+, 1%), 386 (6%), 211 (100%), 195 (9%), and 167 (7%). Compound (17) was kept at its m.p. for 30 min to give (18) and not (21); (18) did not rearrange to (19) when heated.

The reaction of the pyridoindole (43) with $CbsN_3$ in $CHCl_3$ gave $CbsNH_2$ and a tar; similar results were obtained in CCl_4, PhH, and MeOH.

1,2,4,5-*Tetrahydro*-2a-*methyl*-3-*oxa*-10-*azacyclopenta*[jk]-*fluorene* (46).—The acid (44), m.p. 148—151 °C (lit.,[12] 150—152 °C) was reduced ($LiAlH_4$–Et_2O) to form 1-(2-*hydroxyethyl*)-1-*methyl*-3,4-*dihydro*-1H,9H-*pyrano*[3,4-b]*indole* (45; R = OH) (yield 78%), b.p. 190—200 °C/0.1 mmHg (Found: C, 71.7; H, 7.5; N, 6.2. $C_{14}H_{17}NO_2$ requires C, 72.7; H, 7.4; N, 6.1%); $\lambda_{max.}$ 225, 282, and 290sh nm (ε 19 800, 4 600, and 4 100); $\nu_{max.}$ (thin film) 3 100—3 650 cm^{-1}; τ 1.38 (1 H, s, NH), 2.4—3.0 (4 H, m), 5.9—6.1 (2 H, m), 6.2—6.5 (4 H, m), 7.65br (1 H, s, OH), 7.9 (2 H, t, *J* 6.5 Hz), and 8.45 (3 H, s); *m/e* 231 (M^+, 28%) and 186 (100%). The alcohol reacted with tosyl chloride in pyridine solution (0 °C, 24 h). Chromatography (alumina–benzene) afforded the *toluene*-p-*sulphonate* (45; R = OTs) (yield 44%) as an oil which slowly solidified to give prisms, m.p. 107—110 °C (Found: C, 66.1; H, 6.0; N, 3.5; S, 8.2. $C_{21}H_{23}NO_4S$ requires C, 65.5; H, 6.0; N, 3.6; S, 8.3%); $\nu_{max.}$ 3 400 cm^{-1}; *m/e* 385 (M^+, 1%), 261 (44%), 215 (68%), and 188 (100%).

Compound (45; R = OTs) (7 g) was dissolved in dry t-butyl alcohol (100 ml) in which potassium (0.5 g) had been dissolved. The solution was boiled (10 min) and then poured into ice-cold water (200 ml). The mixture was extracted with ether, the dried extracts evaporated, and the residue recrystallised from light petroleum (b.p. 60—80 °C). The indole (46) (yield 3.2 g) formed tiny cubes, m.p. 140—143 °C (Found: C, 79.0; H, 6.9; N, 6.6. $C_{14}H_{15}NO$ requires C, 78.9; H, 7.0; N, 6.6%); $\lambda_{max.}$ 202sh, 230, 276, and 295sh (ε 19 600, 34 800, 6 600, and 4 000); τ 2.4—2.6 (1 H, m), 2.7—3.0 (3 H, m), 5.5—5.9 (3 H, m), 5.9—6.3 (1 H, m), 7.0—7.4 (2 H, m), 7.3—7.6 (2 H, m), and 8.2 (3 H, s); *m/e* 213 (M^+, 88%), 198 (18%), 182 (100%), and 167 (22%).

1,2,4,5-*Tetrahydro*-3a-*methyl*-11-*tosylimino*-11H-*furo*-[2′,3′;2,3]*pyrrolo*[1,2-a]*indole* (48).—A mixture of the indole (46) (1 g) and tosyl azide (1 g) was warmed to 50 °C for 1 min and then kept at room temperature for 3 h. MeOH (5 ml) was added and the solid (1.22 g) collected. The *imine* (48) formed yellow prisms (from MeOH), m.p. 172—174 °C (Found: C, 66.1; H, 5.8; N, 7.3; S, 8.3. $C_{21}H_{22}N_3OS$ requires C, 66.0; H, 5.8; N, 7.3; S, 8.4); $\lambda_{max.}$ 205sh, 229, 247sh, 282, 293sh, 380sh, 420, and 455infl nm (ε 23 500, 32 500, 16 400, 10 200, 7 300, 2 400, 5 000, and 2 400); $\nu_{max.}$ 1 560 cm^{-1}; τ 1.4 (1 H, d, *J* 9 Hz), 2.05 (2 H, d, *J* 10 Hz), 2.3—3.2 (5 H, m), 5.7—6.2 (3 H, m), 6.3—6.5 (1 H, m), 7.1—8.5 (4 H, m), 7.56 (3 H, s), and 8.7 (3 H, s); *m/e* 382 (M^+, 60%), 339 (12%, *m** 300.8), 227 (100%, *m** 134.9), 182 (53%), and 169 (61%). Chromatography of the mother-liquors gave TsN_3 (0.13 g), (48) (0.1 g), and the alcohol (49) (0.028 g), identical with the material described below.

The indole (46) (1 g) was dissolved in chloroform (7 ml) containing water (0.2 ml) and TsN_3 (1 g) was added. The mixture was boiled under reflux (3 h), the solvent removed, and MeCN (5 ml) added. The solid which separated was collected and recrystallised (MeOH). 1,2,4,5,5a,10a-*Hexahydro*-2a-*methyl*-5a-*tosylamino*-3-*oxa*-10-*azacyclopenta*[jk]-*fluoren*-10a-*ol* (49) formed colourless needles, double m.p. 132 and 165—171 °C (Found: C, 62.7; H, 6.2; N, 7.0; S, 8.1. $C_{21}H_{24}N_2O_4S$ requires C, 63.0; H, 6.0; N, 7.0; S, 8.0%); $\lambda_{max.}$ 205, 232, 225sh, and 302 nm (ε 29 700, 14 600, 7 400, and 2 900); $\nu_{max.}$ 3 080—3 300 and 3 430 cm^{-1}; τ 2.6 (2 H, d, *J* 9 Hz), 2.7—3.1 (3 H, m), 3.4—3.8 (3 H, m), 4.35 (1 H, s, exchanged with D_2O), 5.8 (1 H, s, exchanged with D_2O), 6.1—6.5 (2 H, m), 6.6—7.1 (2 H, m), 7.3—8.2 (4 H, m), 7.6 (3 H, s), and 8.5 (3 H, s); *m/e* 400 (M^+, 1%), 382 (54%), 227 (100%), 197 (32%), and 169 (63%).

Chromatography of the combined mother-liquors gave (48) (0.075 g) and (49) (0.10 g). A sample of (49) was kept at 135 °C for 2 min. The melt was cooled and treated with MeOH to give (48) (yield 90%). Treatment of (49) with tosyl chloride in pyridine at 0 °C gave recovered (49) (21%) and the imine (48) (63%).

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REFERENCES

[1] (*a*) A. S. Bailey, P. A. Baldry, and P. W. Scott, *J.C.S. Perkin I*, 1979, 2387; A. S. Bailey, P. A. Hill, and J. F. Seager, *J.C.S. Perkin I*, 1974, 967; (*b*) A. S. Bailey, R. Scattergood, and W. A. Warr, *J. Chem. Soc.* (*C*), 1971, 2479, 3769.

[2] 'New Trends in Heterocyclic Chemistry,' ed. R. B. Mitra, Elsevier, Amsterdam, 1979, p. 56.

[3] A. S. Bailey and J. J. Merer, *J. Chem. Soc.* (*C*), 1966, 1345.

[4] A. S. Bailey, T. Morris, and Z. Rashid, *J.C.S. Perkin I*, 1975, 420.

[5] K. Prout, M. Sims, D. Watkin, C. Couldwell, M. Vandrevala, and A. S. Bailey, *Acta Cryst.*, 1980, **B36**, 1846.

[6] A. S. Bailey, C. M. Birch, D. Illingworth, and J. C. Willmott, *J.C.S. Perkin I*, 1978, 1471.
[7] D. Frank, G. Himbert, and M. Regitz, *Chem. Ber.*, 1978, **111**, 183.
[8] G. L'abbé, Chih-Chou Yu, J. P. Declercq, G. Germain, and M. Van Meerssche, *Angew. Chem. Internat. Edn.*, 1978, **17**, 352.
[9] R. A. Wohl, *J. Org. Chem.*, 1973, **38**, 3862.
[10] R. A. Abramovitch, G. N. Knaus, M. Pavlin, and W. D. Holcomb, *J.C.S. Perkin I*, 1974, 2169.
[11] A. S. Bailey, P. A. Baldry, J. M. Peach, S. R. Critchley, K. Prout, and E. White, *J.C.S. Perkin I*, 1976, 2254.
[12] C. A. Demerson, L. G. Humber, and T. A. Dobson, *J. Medicin. Chem.*, 1975, **18**, 189.
[13] A. S. Bailey, P. M. Scott, and M. H. Vandrevala, *J.C.S. Perkin I*, 1980, 97.
[14] J. A. Joule in 'The Alkaloids,' ed. J. E. Saxton, Specialist Periodical Reports, The Chemical Society, London, 1975, vol. 5, pp. 184—191.