Reactions of 5,6,8,9,10,11-Hexahydro-4*H*-pyrido[3,2,1-*jk*]carbazole and of 5,6,9,10,11,12-Hexahydro-4*H*,8*H*-cyclohepta[4,5]pyrrolo[3,2,1-*ij*]quinoline with Arenesulphonyl Azides

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The title hexahydropyridocarbazole reacts with arenesulphonyl azides giving either *cis*- or *trans*-11a-arylsulphonylamino-8-arylsulphonylimino-octahydrocyclopenta[4.5]pyrido[3,2,1-*ij*]quinoline [(4) or (6)], depending on the solvent. The hexahydrocycloheptapyrroloquinoline yields either a phenanthridine (13) or a 2,4-butanoquinoline (16) under the same conditions.

We have previously investigated the reactions of the pyrroloindoles (1; $n = 4$ or 5) with arenesulphonyl azides and the chemistry of the products.[1] This work has now been extended to the reactions of the pyridoindoles (2; $n = 4$ or 5) to see whether these compounds behaved like (1) or like the *N*-methylated compounds (3; $n = 4$ or 5).[2,3]

Compound (2; $n = 4$) reacted smoothly with *p*-chlorobenzenesulphonyl azide ($CbsN_3$) in chloroform and in carbon tetrachloride yielding a product (4) to which we ascribe the *trans*-configuration. When compound (4) was dissolved in trifluoroacetic acid (TFA) the elimination product (5) was formed. Compound (5) was also obtained when $CbsN_3$ reacted with (2; $n = 4$) in pyridine solution; also from this reaction compound (6), isomeric with (4) was isolated. Compound (6) was the only product obtained when the reaction was run in dry dimethyl sulphoxide. Boiling the indole (2; $n = 4$) with $CbsN_3$ in methanol gave a complex mixture from which a small quantity of the orange spiro-compound (7) was isolated. Treatment of (2; $n = 4$) with $CbsN_3$ in acetic acid in an attempt [2] to make (8) gave an intractable tar; none of the spiro-compound (9) [the product expected from the reaction of (8) with a second molecule of azide] [2,4] was isolated, nor was there any sign of the ring-opened compound (10) [*cf.* the reaction of (1; $n = 4$) with azides [1]].

This is the first time during this work that we have obtained two isomers of structural types (4) and (6); we have examined the relative ease of elimination of $CbsNH_2$ from these two compounds. The acid-catalysed (TFA) elimination of $CbsNH_2$ from compound (4) was very fast. In the time (8—10 min) taken to prepare the solution and run the n.m.r. spectrum (probe temp. 35 °C) elimination was complete; when the solution (TFA) was made up at 0 °C and the n.m.r. spectrum immediately run at 0 °C the signal at τ 4.88 [CH_2N in compound (5)] was already present and after 15 min at 0 °C elimination appeared to be complete. In contrast the n.m.r. spectrum (35 °C) of compound (6) in TFA contained no signal at τ 4.88; after 60 min at 35 °C 50% of the elimination product had been formed (intensity of signal at 4.8). The u.v. spectrum of compound (4) (1 mg in 15 ml of EtOH; 1 cm cell) was recorded and 1 drop of 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) was then added to the solution. The spectrum was re-run immediately and the triple peak at *ca.* 350 nm (see Figure 1 in ref. 2) characteristic of the chromophore in compound (5) was observed; the intensity of this band did not change during 60 min, showing that the elimination was complete in less than 1 min. When the experiment was repeated with triethylamine (1 drop) in place of DBN, elimination was 50% complete in 5 min at 22 °C. When this experiment was performed with compound (6) and triethylamine no elimination occurred during 3 days at room temperature. The solution was then boiled for 4 h; the

[1] A. S. Bailey, P. A. Hill, and J. F. Seager, *J.C.S. Perkin I*, 1974, 967; A. S. Bailey, P. A. Baldry, J. M. Peach, S. R. Critchley, K. Prout, and E. White, *ibid.*, 1976, 2254.

[2] A. S. Bailey, R. Scattergood, and W. A. Warr, *J. Chem. Soc.* (*C*), 1971, 2479.

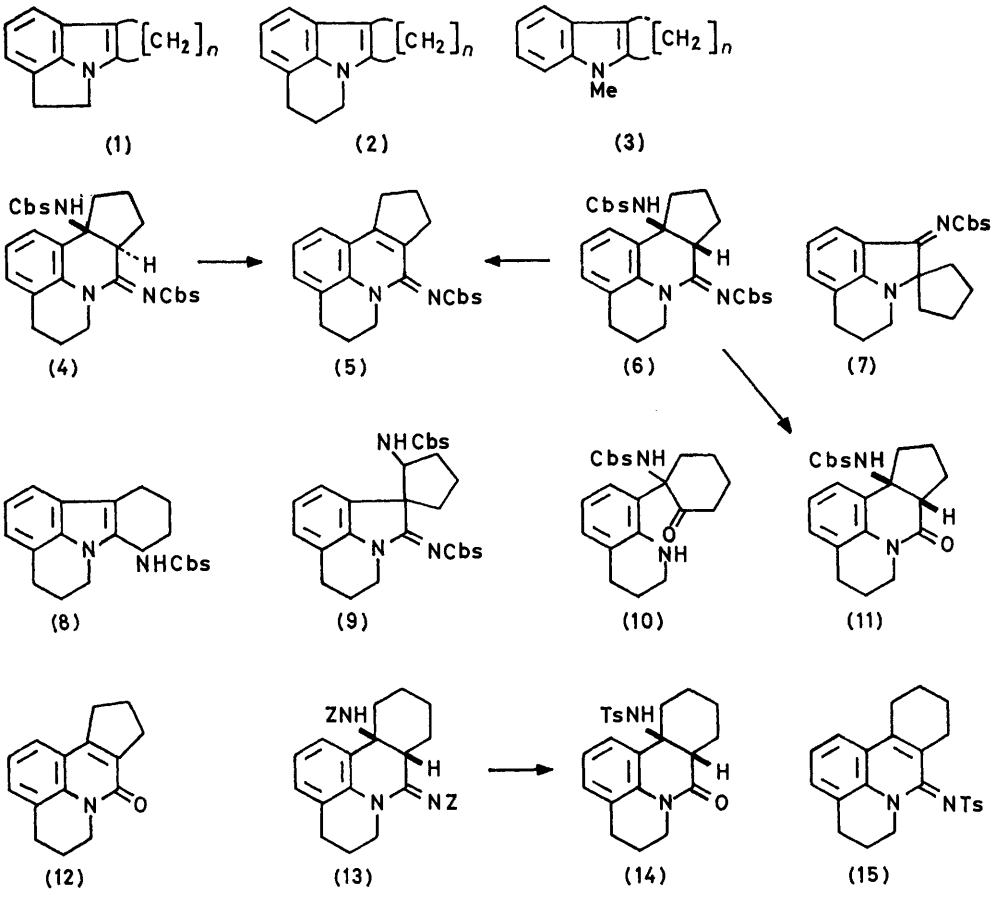
[3] A. S. Bailey and J. F. Seager, *J.C.S. Perkin I*, 1974, 763.

[4] A. S. Bailey, A. J. Buckley, and J. F. Seager, *J.C.S. Perkin I*, 1973, 1809.

spectrum remained unchanged and compound (6) was reisolated. In solution in ethanol containing DBN compound (6) slowly eliminated $CbsNH_2$ at room temperature; the reaction was incomplete after 3 days and was completed by boiling. Heating compound (6) with sodium hydroxide solution afforded the amide (11).

The cycloheptindole (2; $n = 5$) has now been prepared; it reacts with azides more slowly than does (1; $n = 5$). Reaction of (2; $n = 5$) with tosyl azide in chloroform solution yielded the *cis*-fused product (13; Z = Ts). The *cis*-structure is assigned from the similarity in chemical and spectroscopic properties to the compound obtained by the action of TsN_3 on hexahydro-*N*-methylcyclohept[*b*]indole,[3] the structure of which has been determined by *X*-ray crystallography.[5] Hydrolysis of this material afforded (14), and acid-catalysed elimination of $TsNH_2$ yielded (15). The reaction of (2; $n = 5$) with $CbsN_3$ in chloroform solution afforded (13; Z = Cbs); in carbon tetrachloride solution a mixture containing (13; Z = Cbs) and (16) was obtained. When compound (16) was melted, (17) was produced in high yield; the same transformation occurred on dissolving (16) in TFA. Structures (16) and (17) were assigned from a comparison of spectroscopic and chemical properties with compounds obtained in the *N*-methyl series.[3,6] In these reactions (16) resembles (18) rather than (19).[6]

The isomeric compounds (4) and (6) are formed by attack of a molecule of azide on opposite faces of the intermediate (20).[6] Addition of the azide molecule *cis* to the NHZ group in (20) leads to compound (4); *trans*-addition gives (6). The effect of solvents on the stereochemistry of these addition reactions is similar to their effect on the addition of azides to hexahydro-*N*-methylcyclohept[*b*] indole; this has been discussed in an earlier paper.[6]



It is interesting that the reaction of $CbsN_3$ with (2; $n = 4$) in carbon tetrachloride does not give rise to the bridged compound (16; $[CH_2]_3$ replacing $[CH_2]_4$). Increased strain in the '*meta*' bridging now favours shift *a* rather than shift *b* in the intermediate (21).

To complete this series of experiments the reaction between *N*-methyltetrahydrocarbazole (3; $n = 4$) and $CbsN_3$ in dimethyl sulphoxide was examined. A 70% yield of the spiro-compound (22) was obtained. The structure was established by the characteristic mass spectrometric fragmentation pattern.[2,7] The isolation of (22) shows that under these conditions the 1,3-shift [4] of the CbsNH group in (23) occurs more quickly than the

[5] S. R. Critchley, K. Prout, D. J. Watkin, A. S. Bailey, and J. M. Peach, *J.C.S. Perkin II*, 1977, in press.

[6] A. S. Bailey and P. A. Wilkinson, *J.C.S. Perkin I*, 1976, 481.

[7] J. Tickle and C. K. Prout, *J. Chem. Soc.* (*C*), 1971, 3401.

addition of a second molecule of azide to (23), whereas in (20) addition of a second molecule of azide occurs more quickly than the 1,3-shift of Cbs-NH.

EXPERIMENTAL

General details and instruments used have been reported.[8] 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.

trans-11a-p-*Chlorophenylsulphonylamino*-8-p-*chlorophenyl sulphonylimino*-5,6,8,8a,9,10,11,11a-*octahydro*-4H-*cyclopenta*[4,5]*pyrido*[3,2,1-ij]*quinoline* (4).—(*a*) 5,6,8,9,10,11-Hexa-4*H*-pyrido[3,2,1-*jk*]carbazole[1 g; m.p. 67—68° (lit.,[9] 65—66°] was dissolved in chloroform (5 ml, purified over alumina) and $CbsN_3$ (2.1 g) was added; after 5 days the solvent was removed and MeOH (2 ml) added. The solid was collected and recrystallised from propan-1-ol (yield 0.63 g).

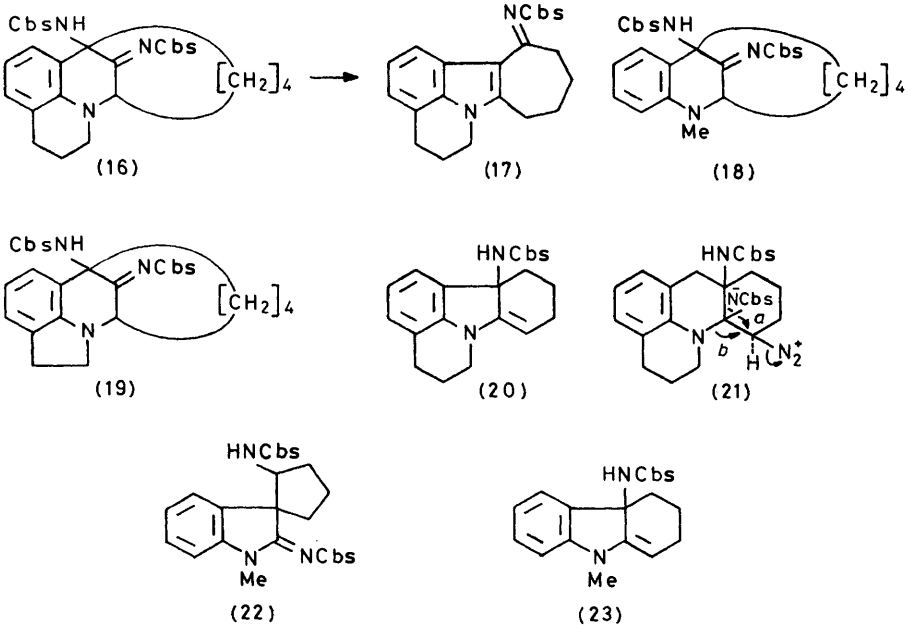
(*b*) The indole (1 g) and the azide (2.1 g) were dissolved in dry carbon tetrachloride (5 ml). After 3 days the solid (2.8 g) was collected and recrystallised from MeCN (25 ml). The solid which separated (0.85 g) was collected and the mother-liquor concentrated to 15 ml yielding further material (0.6 g). The CCl_4 and the MeCN mother-liquors were mixed and evaporated. The residue was chromatographed (silica gel; $CHCl_3$) yielding azide (0.3 g) and (4) (0.21 g). *Compound* (4) formed tiny prisms from propan-1-ol, m.p. 118° (decomp.) (Found: C, 54.7; H, 4.4; N, 6.9; S, 10.5. $C_{27}H_{25}Cl_2N_3O_4S_2$ requires C, 55.0; H, 4.2; N, 7.1; S, 10.8%); $\lambda_{max.}$ 228, 288sh, and 302 nm (ε 34 200, 14 200, and 16 200); $\nu_{max.}$ 1 540 (C=N) and 3 260 cm^{-1} (NH); τ 2.03 (2 H, d, *J* 8 Hz), 2.4—2.9 (9 H, m), 4.58 (1 H, s, NH, exchanged in D_2O), 5.8—6.3 (1 H, m), and 6.5—8.7 (12 H, m); *m/e* 398 (M − $CbsNH_2$, 1%) and 223 (M − Cbs − $CbsNH_2$, 100%). Compound (4) formed tiny prisms, m.p. 129—131°, from MeCN, and these retained solvent after drying at 100 °C *in vacuo* [τ 8.0(s)]. Recrystallisation from $CHCl_3$–CCl_4 gave a sample free from MeCN (absence of signal at τ 8.0) (Found: N, 6.9%).

8-p-*Chlorophenylsulphonylimino*-5,6,8,9,10,11-*hexahydro*-4H-*cyclopenta*[4,5]*pyrido*[3,2,1-ij]*quinoline* (5).—(*a*) A solution of compound (4) (1.3 g) in Pr-OH (4 ml) was boiled for 30 min; on cooling the solid product (5) (0.7 g) (pure by t.l.c.) separated.

(*b*) A solution of (4) (200 mg) in TFA (2 ml) was kept at at 20 °C for 10 min. The solvent was then removed *in vacuo* and MeOH (1 ml) added (yield 75%).

(*c*) A solution of the *cis*-isomer (6) (see later) (200 mg) in TFA was kept at room temperature for 4 h (yield 75%).

(*d*) To a solution of compound (4) (100 mg) in EtOH (5 ml) was added DBN (0.1 ml). After 10 min the solvent was removed *in vacuo* and MeOH (1 ml) added (yield 52%); this reaction was repeated using Et_3N (0.5 ml; 2 h).



(*e*) Compound (6) (100 mg) was boiled (4 h) with DBN (0.3 ml) in EtOH (5 ml) (yield 71%). *Compound* (5) formed prisms, m.p. 198—200° (from MeCN) (Found: C, 62.9; H, 4.9; N, 6.8; S, 8.0. $C_{21}H_{19}ClN_2O_2S$ requires C, 63.2; H, 4.8; N, 7.0; S, 8.0%); $\lambda_{max.}$ 218, 230sh, 260sh, 264, 300sh, 338, and 363 nm (ε 33 600, 23 300, 27 200, 29 600, 6 000, 12 100, and 11 600); $\nu_{max.}$ 1 520 cm^{-1}; τ 2.08 (2 H, d, *J* 9 Hz), 2.6—2.9 (5 H, m), 5.82 (2 H, t, *J* 7 Hz), 6.33 (2 H, t, *J* 8 Hz), 6.80 (2 H, t, *J* 8 Hz), 7.03 (2 H, t, *J* 7 Hz), and 7.5—8.0 (4 H, m); τ (TFA) 1.9—2.4 (7 H, m), 4.88 (2 H, t, *J* 6 Hz), 6.3—6.7 (4 H, m), 7.1—7.35 (2 H, t, *J* 8 Hz), and 7.4—7.9 (4 H, m); *m/e* 398 (M^+, 13%), and 223 (100%).

cis-11a-p-*Chlorophenylsulphonylamino*-8-p-*chlorophenyl-sulphonylimino*-5,6,8,8a,9,10,11,11a-*octahydro*-4H-*cyclopenta*[4,5]*pyrido*[3,2,1-ij]*quinoline* (6).—(*a*) A solution of (2; n = 4) (1 g) and $CbsN_3$ (2.1 g) in pyridine (1 ml) was kept at room temperature for 12 days. MeOH (5 ml) was added and the solid collected Recrystallisation from MeCN yielded (5) (m.p., i.r., n.m.r., t.l.c.) (450 mg). The MeCN mother-liquors were evaporated to small volume yielding compound (6) (240 mg), m.p. 132—135°.

(*b*) Compound (2; n = 4) (1 g) and $CbsN_3$ (2.1 g) were dissolved in Me_2SO (4 ml; dried by azeotropic removal of

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

[9] A. N. Kost, L. G. Yudin, and A. P. Terent'ev, *Zhur. Obshchei Khim.*, 1959, **29**, 1949; *Chem. Abs.*, 1960, **54**, 8817.

water with benzene and over molecular sieves). The solution became viscous and after 5 days water (10 ml) was added. The solid was collected, suspended in water (50 ml) for 24 h to remove the absorbed Me_2SO, and dried (yield 2.8 g). Recrystallisation from MeCN (8 ml) afforded needles (0.84 g). Further crops (totalling 510 mg) were obtained by concentrating the mother liquors. These were coloured yellow by traces of the spiro-compound (7). Compound (7) (3 mg) was isolated by p.l.c. (silica; PhH–EtOAc, 9 : 1); column chromatography of the MeCN residues gave $CbsN_3$ (186 mg). The *sulphonylimine* (6) formed needles, m.p. 132—135°, containing MeCN (Found: C, 55.4; H, 4.9; N, 8.2, 8.5. $C_{27}H_{25}Cl_2N_3O_4S_2$ requires C, 55.0; H, 4.2; N, 7.1. $C_{27}H_{25}Cl_2N_3O_4S_2 \cdot CH_3CN$ requires C, 55.1; H, 4.4; N, 8.9%); $\lambda_{max.}$ 228, 276sh, 285, and 301 nm (ε 37 500, 16 500, 18 900, and 16 800); $\nu_{max.}$ 1 530 (C=N), 2 250 (MeCN), and 3 200 cm^{-1} (NH): τ 2.07 (2 H, d, *J* 8 Hz), 2.6—3.3 (9 H, m), 4.25 (1 H, NH, exchanged in D_2O), 5.5—6.0 (2 H, m), 6.4—6.6 (1 H, m), 7.1—7.4 (4 H, m), 7.99 (s, CH_3CN), and 8.0—8.8 (6 H, m); τ (TFA) 1.87 (2 H, d, *J* 9 Hz), 2.3 (2 H, d, *J* 9 Hz), 2.6—3.1 (7 H, m), 5.4—5.7 (1 H, m), 5.8—6.2 (2 H, m), 6.9—7.4 (4 H, m), 7.6—8.8 (6 H, m), and 7.9 (s, CH_2CN); during the time taken to make up and run the spectrum in TFA no elimination occurred; *m/e* 589 (M^+, 2%), 414 (*M* − Cbs, 15%), 398 (*M* − $CbsNH_2$, 2%), and 223 (100%).

cis-11a-p-*Chlorophenylsulphonylamino*-5,6,9,10,11,11a-*hexahydro*-4H-*cyclopenta*[4,5]*pyrido*[3,2,1-ij]*quinolin*-8(8a-H)-*one* (11).—A solution of compound (6) (1 g) in EtOH (25 ml) containing NaOH (0.5 g) was boiled for 6 h. Water was added and the mixture extracted with $CHCl_3$; the solution was dried ($MgSO_4$), the solvent removed, and the residue (300 mg) recrystallised from MeOH. *Compound* (11) formed prisms, m.p. 120—121° (Found: C, 60.4; H, 5.3; N, 6.6. $C_{21}H_{21}ClN_2O_3S$ requires C, 60.5; H, 5.0; N, 6.7%); $\lambda_{max.}$ 217, 232sh, 251sh, 267, 278sh, 289sh, 327, and 340sh nm (ε 29 000, 24 000, 12 000, 6 000, 4 000, 3 800, 2 100, and 1 500); $\nu_{max.}$ 1 580, 1 640, 3 240, and 3 340 cm^{-1}; τ 2.1 (2 H, d, *J* 8 Hz), 2.44—3.0 (5 H, m), 4.77 (1 H, s, NH), 5.77 (2 H, t, *J* 6 Hz, CH_2N), 6.66—7.17 (7 H, m), and 7.56—8.11 (4 H, m); *m/e* 416 (M^+, 2%), 225 (*M* − $CbsNH_2$, 14%), 191 (32%), 175 (34%), and 111 (100%). Alkaline hydrolysis of (5) afforded 5,6,9,10-*tetrahydro*-4H-*cyclopenta*[4,5]*pyrido*[3,2,1-ij]*quinoline*-8(11H)-*one* (12) (71%), needles from light petroleum, m.p. 113—115° (Found: C, 79.7; H, 6.8; N, 6.2. $C_{15}H_{15}NO$ requires C, 80.0; H, 6.7; N, 6.2%); $\lambda_{max.}$ 215sh, 235, 250, 267sh, 278, 289sh, 312sh, 326, and 340sh nm (ε 20 300, 30 500, 15 400, 4 700, 6 500, 6 000, 4 200, 5 700, and 4 200); $\nu_{max.}$ 1 585 and 1 650 cm^{-1}; τ 2.6—3.05 (3 H, m), 5.80 (2 H, t, *J* 7 Hz), 6.8—7.15 (6 H, m), and 7.6—8.05 (4 H, m); *m/e* 225 (M^+, 100%), 210 (70%), and 196 (12%).

1′-p-*Chlorophenylsulphonyliminospiro*[*cyclopentane*-2′(1′-H)-*pyrrolo*[3,2,1-ij]*quinoline*] (7).—A solution of (2; *n* = 4) (0.5 g) in methanol (5 ml) containing $CbsN_3$ (0.5 g) was boiled for 1 h and the solvent removed. The resulting oil was chromatographed on silica. Benzene–ethyl acetate (10 : 1) eluted an oil to which a little methanol was added. Next day the solid was collected and recrystallised from ethanol (yield 40 mg). *Compound* (7) formed orange needles, m.p. 187—188° (Found: C, 62.8; H, 5.6; N, 7.0. $C_{21}H_{21}ClN_2O_2S$ requires C, 63.0; H, 5.3; N, 7.0%); $\lambda_{max.}$ 233, 255sh, 296, and 475 nm (ε 29 200, 13 100, 9 000, and 9 500); $\nu_{max.}$ 1 610 cm^{-1}; *m/e* 400 (M^+, 23%), 225 (*M* − Cbs, 100%), 210 (13%), and 197 (12%).

Reactions of 5,6,9,10,11,12-*Hexahydro*-4H,8H-*cyclohepta*-[4,5]*pyrrolo*[3,2,1-ij]*quinoline* (2; *n* = 5) *with Azides*.—Compound (2; *n* = 5) was prepared from 1-aminotetrahydroquinoline (16.2 g) [8] and cycloheptanone (12.3 g). The resulting hydrazone was heated (1 h) with sulphuric acid (10%; 150 ml). The *indole* (2; *n* = 5) was recrystallised from ethanol (yield 11.8 g); m.p. 96—97° (Found: C, 84.9; H, 8.5; N, 6.2. $C_{16}H_{19}N$ requires C, 85.3; H, 8.5; N, 6.2%); $\lambda_{max.}$ 205, 232, 288, and 293 nm (ε 20 800, 32 600, 7 100, and 7 200); τ 2.73—3.30 (3 H, m), 5.97—6.08 (2 H, t, *J* 6 Hz), 7.0—7.3 (6 H, m), 7.58—7.90 (2 H, m), and 8.16br (6 H, m); *m/e* 225 (M^+, 100%), 196 (58%), and 183 (30%). A solution of (2; *n* = 5) (2 g) and tosyl azide (3.5 g) in chloroform (20 ml) was kept at room temperature for 4 days; the solvent was then removed and methanol added. The solid which separated was collected and recrystallised from acetonitrile. cis-5,6,8a,9,10,11,12,12a-*Octahydro*-12a-p-*tolylsulphonylamino*-8-p-*tolylsulphonylimino*-4H,8H-*pyrido*[3,2,1-de]-*phenanthridine* (13; Z = Ts) formed prisms (1.1 g; a further 300 mg recovered from the mother-liquors), m.p. 261—263°, (decomp.) (Found: C, 64.0; H, 6.0; N, 7.6. $C_{30}H_{33}N_3O_4S_2$ requires C, 64.0; H, 5.9; N, 7.5%); $\lambda_{max.}$ 225, 274sh, 283, and 302 nm (ε 31 000, 14 100, 16 600, and 16 500); $\nu_{max.}$ 1 550 (C=N) and 3 320 (NH) cm^{-1}; τ 2.11 (2 H, d, *J* 8 Hz), 2.55—3.10 (9 H, m), 5.42 (1 H, s), 5.7—6.0 (1 H, m), 6.2—6.35 (1 H, m), 6.7—6.9 (1 H, m), 7.1—7.4 (2 H, m), 7.59 (3H, s), 7.75 (3 H, s), and 8.0—9.2 (10 H, m); *m/e* 563 (M^+, 28%), 408 (*M* − Ts, 52%), and 237 (100%). A solution of (13; Z = Ts) (450 mg) in water (5 ml) and ethanol (5 ml) containing sodium hydroxide (400 mg) was boiled under reflux (4 h, diluted with water, and neutralised (HCl). The solid was collected and recrystallised from ethanol. cis-5,6,8a,9,-10,11,12,12a-*Octahydro*-12a-p-*tolylsulphonylamino*-4H,8H-*pyrido*[3,2,1-de]*phenanthridin*-8-*one* (14) formed prisms, m.p. 262—264° (yield 300 mg) (Found: C, 67.2; H, 6.2; N, 6.9; S, 7.7. $C_{23}H_{26}N_2O_3S$ requires C, 67.4; H, 6.3; N, 6.8; S, 7.8%); $\lambda_{max.}$ 216, 234sh, 255, 263sh, 287, and 298 nm (ε 25 400, 10 900, 9 500, 7 800, 2 700, and 2 500); $\nu_{max.}$ 1 655 (C=O) and 3 220 (NH) cm^{-1}; τ 2.55—3.15 (7 H, m), 4.50 (1 H, s, NH, exchanged D_2O), 5.6—5.9 (1 H, m), 6.6—6.8 (1 H m), 7.1—7.6 (3 H, m), 7.61 (3 H, s), and 8.0—9.0 (10 H, m); *m/e* 410 (M^+, 41%) and 240 (*M* − TsNH, 100%). A solution of (13; Z = Ts) in TFA (1 H; room temp.) gave 5,6,9,10,11,12-*hexahydro*-8-*p*-*tolylsulphonylimino*-4H,8H-*pyrido*[3,2,1-de]*phenanthridine* (15) (79%) as prisms (from ethanol), m.p. 174—175° (Found: C, 70.2; 6.2; N, 7.1. $C_{23}H_{24}N_2O_2S$ requires C, 70.4; H, 6.1; N, 7.1%); $\lambda_{max.}$ 219, 264, and 345 nm (ε 37 000, 31 000, and 12 300); ν_{max} 1 510 (C=N) and 1 610 cm^{-1} (C=C); τ 2.1—2.8 (7 H, m), 5.52 (2 H, t, *J* 8 Hz), 6.95—7.08 (6 H, m), 7.62 (3 H, s), and 7.8—8.4 (6 H, m); *m/e* 392 (M^+, 3%) and 237 (100%).

The indole (2; *n* = 5) (2 g) and $CbsN_3$ (3.8 g) were dissolved in carbon tetrachloride (20 ml); after 2 days the solvent was removed and methanol added. The solid which separated was recrystallised from acetonitrile. cis-12a-p-*Chlorophenylsulphonylamino*-8-p-*chlorophenylsulphonylimino*-5,6,8a,9,10,11,12,12a-*octahydro*-4H,8H-*pyrido*[3,2,1-de]-*phenanthridine* (13; Z = Cbs) formed tiny prisms (0.75 g), m.p. 134—135° (Found: C, 55.3; H, 4.6; N, 7.0; S, 10.4. $C_{28}H_{27}Cl_2N_3O_4S_2$ requires C, 55.6; H, 4.5; N, 6.9; S, 10.6%); $\lambda_{max.}$ 225, 275sh, 283, and 302 nm (ε 33 500, 14 100, 16 200, and 16 800); $\nu_{max.}$ 1 550 and 3 240 cm^{-1}; τ 2.14 (2 H, d, *J* 8 Hz), 2.52—2.62 (3 H, m), 2.8—3.1 (6 H, m), 4.80 (1 H, s, NH, exchanged D_2O), 5.8—6.2 (2 H, m), 6.72br (1 H, d, *J* 8 Hz), 7.1—7.6 (2 H, m), and 8.0—8.9 (10 H, m); *m/e* 603 (M^+, 4%), 428 (22%), 237 (*M* − Cbs − $CbsNH_2$, 60%), and 225 (100%). The acetonitrile mother liquors from the recrys-

tallisation of (13; Z = Cbs) were evaporated and methanol (2 ml) was added. The solid was collected and recrystallised from ethanol. 13-p-*Chlorophenylsulphonylamino*-14-p-*chlorophenylsulphonylimino*-5,6,8,9,10,11,12,13-*octahydro*-8,13-*methano*-4H-*azonino*[3,2,1-ij]*quinoline* (16) formed yellow needles (0.85 g), m.p. 144—145° (decomp.) (Found: C, 56.2; H, 4.7; N, 7.0; S, 10.3. $C_{28}H_{27}Cl_2N_3O_4S_2$ requires C, 55.9; H, 4.5; N, 6.9; S, 10.6%); $\lambda_{max.}$ 219, 232, 264, and 315 nm (ε 34 600, 33 200, 9 700, and 2 700); $\nu_{max.}$ 1 650 and 3 280 cm^{-1}; τ 2.05 (2 H, d, *J* 9 Hz), 2.45—3.90 (9 H, m), 4.40 (1 H, NH, exchanged with D_2O), 4.55—4.65 (1 H, m), 6.70 (2 H, t, *J* 6 Hz), 7.2—7.3 (2 H, m), and 7.4—9.0 (10 H, m); *m/e* 412 (*M* − $CbsNH_2$, 14%), 237 (27%), 209 (27%), 195 (24%), and 112 (100%).

12-p-*Chlorophenylsulphonylimino*-5,6,9,10,11,12-*hexahydro*-4H,8H-*cyclohepta*[4,5]*pyrrolo*[3,2,1-ij]*quinoline* (17). —(*a*) Compound (16) was heated at 150 °C for 4 min, methanol added, and the solid recrystallised from ethanol (yield 78%).

(*b*) Compound (16) was boiled for 12 h in ethyl propionate (yield 91%).

(*c*) Compound (16) was dissolved in TFA, the solution evaporated after 12 h, and methanol added to the residue (yield 80%). *Compound* (17) formed needles, m.p. 173—174° (Found: C, 64.3; H, 5.0; N, 6.8; S, 8.1. $C_{22}H_{21}ClN_2O_2S$ requires C, 64.0; H, 5.1; N, 6.8; S, 7.9%); $\nu_{max.}$ 220, 248, 265, 278, and 357 nm (ε 30 000, 10 900, 12 200, 12 500, and 22 500); $\nu_{max.}$ 1 520 cm^{-1} (C=N); τ 2.05 (2 H, d, *J* 8 Hz), 1.15—3.10 (5 H, m), 5.95 (2 H, t, *J* 6 Hz), 6.5—6.6 (2 H, m), 7.0—7.1 (4 H, m), and 7.6—8.2 (6 H, m); τ (TFA) 1.90 (2 H, d, *J* 10 Hz), 2.23—2.63 (5 H, m), 5.63 (2 H, t, *J* 6 Hz), 6.60—6.95 (6 H, m), 7.5—7.7 (2 H, m), and 7.9—8.1 (4 H, m); *m/e* 412 (M^+, 66%), 348 (*M* − SO_2, 29%, *m** 294.1), 237 (M − Cbs, 100%), 209 (237 − C_2H_4, 37%), 195 (237 − C_3H_6, 68%), 181 (14%), and 167 (16%).

2′-p-*Chlorophenylsulphonylimino*-1′-*methyl*-2-p-*chlorophenylsulphonylaminospiro*[*cyclopentane*-3′-*indoline*] (22).—9-Methyltetrahydrocarbazole (3; *n* = 4) (1 g) in dry Me_2SO (2 ml) was mixed with $CbsN_3$ (2 g) in Me_2SO (2 ml). After 2 weeks water (5 ml) was added. Next day the solid was collected and recrystallised from MeCN–$CHCl_3$ (1 : 1) (yield 2.1 g). The *spiro-compound* formed plates (from propan-1-ol), m.p. 228—230° (Found: C, 53.5; H, 4.2; N, 7.8; S, 11.1. $C_{25}H_{23}Cl_2N_3O_4S_2$ requires C, 53.0; H, 4.4; N, 7.4; S, 11.3%); $\nu_{max.}$ 1 565 (C=N) and 3 300 cm^{-1} (NH); τ [$(CD_3)_2SO$] 2.04 (2 H, d, *J* 8 Hz), 2.28—2.9 (10 H, m, ArH), 5.2 (1 H, s, NH), 6.7 (3 H, s, NMe), and 7.8—8.5 (7 H, m); *m/e* 563 (M^+, 10%), 388 (*M* − Cbs, 32%), 334 (*M* − CbsN:CH·CH:CH_2, 16%), 333 (82%), 213 (*M* − 2 Cbs, 30%), 198 (338 − CbsNH, 7%), 197 (23%), 171 (*M* − CbsN:CH·CH_3–Cbs, 22%), 159 (334 − Cbs, 100%), 158 (39%), and 111 (C_6H_4Cl, 61%).

[7/069 *Received*, 13*th January*, 1977]