Reactions of 1,3,4,5-Tetrahydro-5-methylthiopyrano[4,3-*b*]indole, of 1,2,6,7,8,9-Hexahydropyrrolo[3,2,1-*jk*]carbazole, and of 1,2,7,8,9,10-Hexhydro-6*H*-cyclohepta[*b*]pyrrolo[3,2,1-*hi*]indole with Arenesulphonyl Azides

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Arenesulphonyl azides react with *N*-methyltetrahydrothiopyrano[4,3-*b*]indole yielding derivatives of 3-iminoindoline-2-spirothiacyclopentane and of 2-iminoindoline-3-spirothiacyclopentane in poor yield. With hexahydropyrrolo[3,2,1-*jk*]carbazole the azides gave 2-arylsulphonylamino-2-(indolin-7-yl)cyclohexanones, arylsulphonyliminotetrahydropyrrolo[3,2,1-*hi*]indolespirocyclopentanes, and derivatives of cyclopenta[*c*]pyrrolo[3,2,1-*ij*]quinoline. Hexahydro-6*H*-cyclohepta[*b*]pyrrolo[3,2,1-*hi*]indole afforded derivatives of pyrrolo[3,2,1-*de*]phenanthridine and, in good yield, 6-arylsulphonylamino-5-arylsulphonylimino-1,2,5,6-tetrahydro-4,6-butano-4*H*-pyrrolo[3,2,1-*ij*]quinolines. The chemistry of these last-named compounds has been examined.

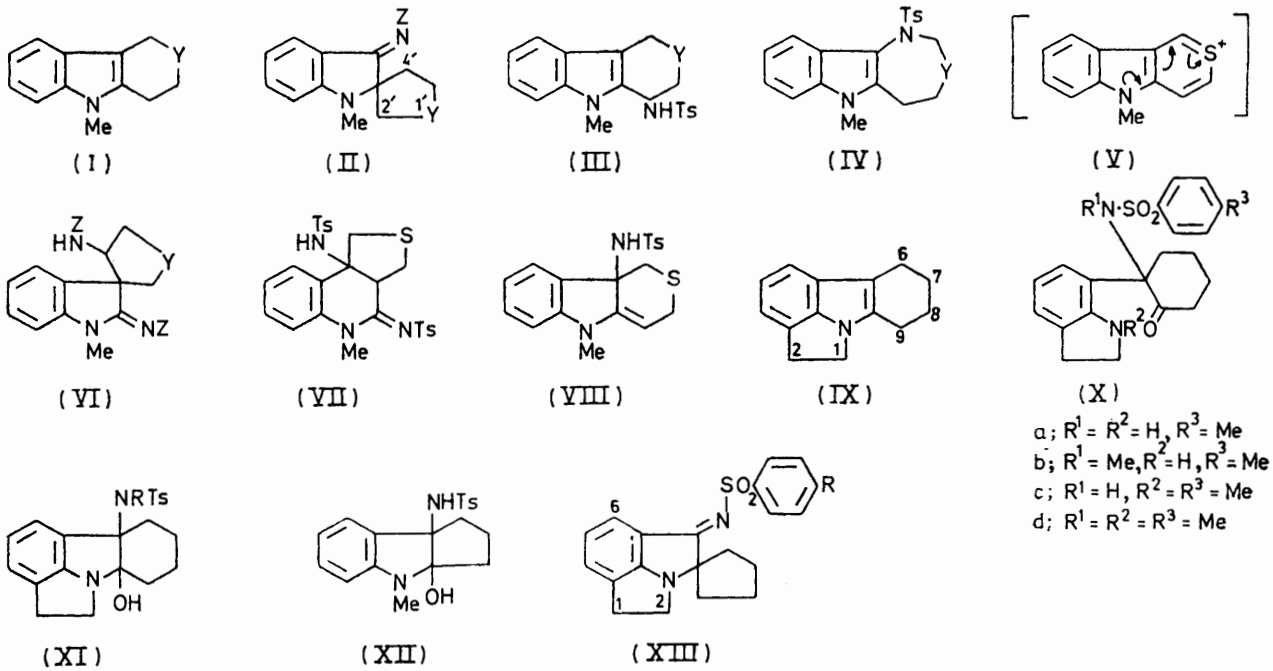
FROM the reaction between *N*-methyltetrahydrocarbazole (I; Y = CH_2) and tosyl azide (TsN_3), five products have been isolated of which two [(II; Y = CH_2, Z = Ts) and (III; Y = CH_2)] are 1 : 1 reaction products.[1] However, the γ-carboline (I; Y = NMe) yields the ring-expanded compound (IV; Y = NMe).[2] We have now examined the reactions of 1,3,4,5-tetrahydro-5-methylthiopyrano[4,3-*b*]indole (I; Y = S) with tosyl azide and with *p*-chlorobenzenesulphonyl azide ($CbsN_3$) to see whether the compound behaves like *N*-methyltetrahydrocarbazole or like the γ-carboline.

The reaction was carried out under a variety of conditions but in all cases the mixtures or solutions became dark red and then black in colour and t.l.c. showed the presence of a great deal of base-line material. From the reaction a small quantity of the orange spiro-compound (II; Y = S, Z = Ts) was isolated. This material is stable in boiling ethanol showing that the tar obtained in the azide reaction is not formed *via* (II; Y = S, Z = Ts). At its m.p., compound (II; Y = CH_2, Z = Ts) loses its colour forming (III; Y = CH_2) in high yield but at the m.p. compound (II; Y = S, Z = Ts) forms a tar which contains several constituents and from which nothing

[1] A. S. Bailey, R. Scattergood, and W. A. Warr, *J. Chem. Soc.* (*C*), 1971, 2479; A. S. Bailey, A. J. Buckley, and J. F. Seager, *J.C.S. Perkin I*, 1973, 1809.

[2] A. S. Bailey, A. G. Holton, and J. F. Seager, *J.C.S. Perkin I*, 1972, 1003.

crystalline could be obtained. The mass spectrum of (II; Y = CH_2, Z = Ts) [1] contains only two intense fragment ions, (M − Ts, 100%) and (M − $TsNH_2$, 11%); in contrast the mass spectrum of (II; Y = S, Z = Ts) contains a very strong (M − $TsNH_2$) signal and the base peak is *m/e* 200, probably the ion (V). This ready loss of $TsNH_2$ may explain the formation of tar on melting compound (II; Y = S, Z = Ts). The only other product isolated from these reactions was the spiro-compound (VI; Y = S, Z = Ts). This compound was stable to cold trifluoroacetic acid (TFA) thus eliminating structure (VII); 1-methyl-2′-*p*-tolylsulphonylamino-2-*p*-tolylsulphonyliminoindoline-3-spirocyclohexane [3] is also stable to cold TFA. The mass spectrum of (VI; Y = S, Z = Ts) was different from



that of (VI; Y = CH_2, Z = Ts); [1] no molecular ion was observed and that of highest mass, *m/e* 336, corresponded to the loss of ($TsNH_2$ + H_2S). There was no sign of the formation of compound (VII) or its elimination (−$TsNH_2$) product even when pyridine was used as solvent. This suggests that elimination of $TsNH_2$ from (III) or (VIII) is an important feature of these reactions and this is supported by the behaviour of (II; Y = S, Z = Ts) on melting and in the mass spectrometer. When these reactions were repeated with $CbsN_3$ only compounds (II; Y = S, Z = Cbs) and (VI; Y = S, Z = Cbs) were obtained, in small quantity.

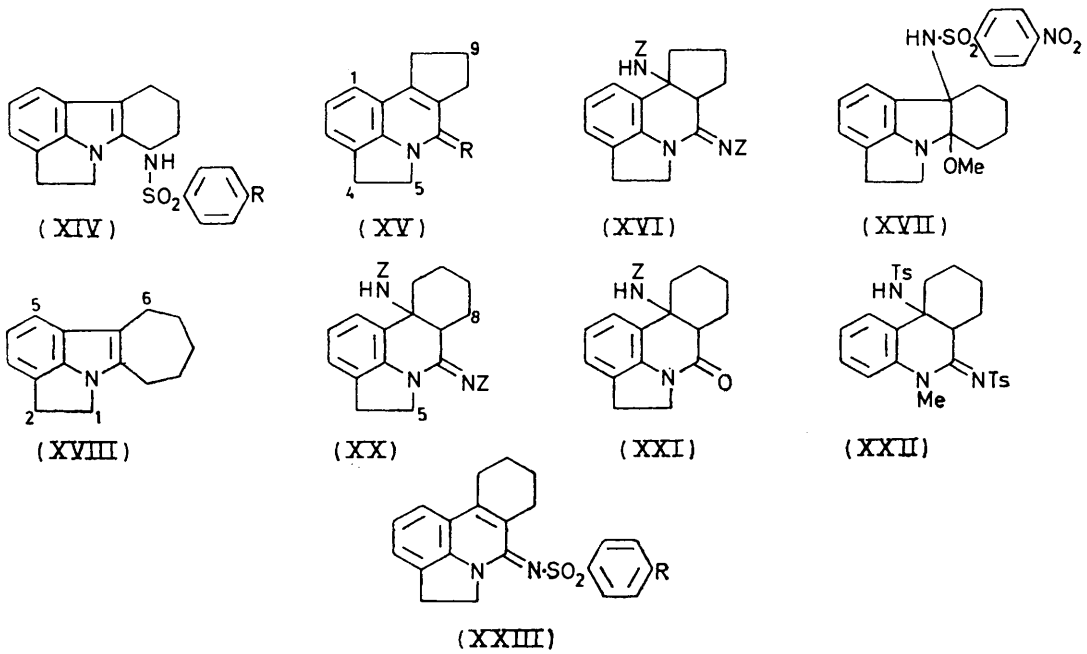
Rapoport [4] has drawn attention to the increased reactivity of indoles when positions 1 and 7 are bridged by an ethano-group and has exploited this feature in a synthesis of apo-β-erythroidine. We have examined the effect of such bridging on the reactions of indoles with azides. We first examined the reactions of the pyrrolocarbazole (IX).[5] With tosyl azide in methanol, (IX) gave a good yield of the ketone (Xa); the i.r. spectrum of the product showed clearly that it was in the ring-opened form (X) rather than the cyclic form (XI) [*cf.* compound (XII), obtained from *N*-methyltetrahydrocyclopentindole and tosyl azide].[6] Methylation of (Xa) with dimethyl sulphate and alkali gave mainly (Xb) plus a little (Xd), whilst treatment with methyl iodide afforded (Xc); a combination of the two methods gave (Xd) in good yield. The n.m.r. data for these four compounds are summarised in the Table (the signals from the aliphatic CH_2 groups are omitted); for comparison NCH_3Ts signals appear at τ 7·33 [1,7] and $PhN(CH_3)_2$ signals at 7·15.[8] The spectra of (Xa) and (Xc) contain only one aromatic proton signal at low field and

N.m.r. spectra (τ values)

Compd.	Aromatic protons	NH	Methyl groups
(Xa)	2·70 (1H, d, *J* 8 Hz)	3·72	7·74 (tosyl Me)
	2·8—3·4 (6H, m)	6·99	
(Xb)	2·06 (2H, d, *J* 8 Hz, Ts)	4·74	7·57
	2·6—3·1 (4H, m)		7·57
	3·37 (1H, t, *J* 8 Hz)		
(Xc)	2·34 (1H, d, *J* 8 Hz)	3·60	8·15 (NMe)
	2·7—3·2 (6H, m)		7·73 (tosyl Me)
(Xd)	2·13 (2H, d, *J* 8 Hz, Ts)		7·38
	2·6—3·3 (5H, m)		7·53
			7·60

[3] A. S. Bailey and J. F. Seager, *J.C.S. Perkin I*, 1974, 763.
[4] J. Blake, J. R. Tretter, G. J. Juhasz, W. Bonthrone, and H. Rapoport, *J. Amer. Chem. Soc.*, 1966, **88**, 4061.
[5] A. N. Kost, L. G. Yudin, Yu. A. Berlin, and A. P. Terent'ev, *Zhur. obshchei. Khim.*, 1959, **28**, 3280 (Eng. trans., p. 3782).
[6] A. S. Bailey, R. Scattergood, and W. A. Warr, *J. Chem. Soc.* (*C*), 1971, 3769.
[7] R. M. Moriarty, *J. Org. Chem.*, 1965, **30**, 600.
[8] J. C. N. Ma and E. W. Warnhoff, *Canad. J. Chem.*, 1965, **43**, 1849.

the tosyl group signals have moved upfield; the most striking feature of the spectrum of (Xc) is the upfield shift of 1 p.p.m. shown by the signals of the NMe group relative to the NMe signals from dimethylaniline; in the case of the dimethylated compound (Xd) this does not happen. These results suggest that in (Xa) and (Xc) the NHTs group is hydrogen-bonded to the C=O group and this places the bulky indoline group axial: mutual shielding [9] by the aryl groups occurs and the indoline NMe group is placed in the shielding region of the C=O group: long-range shielding by tosyl groups is also known.[10] In contrast, in the spectra of (Xb) and (Xd) the low-field tosyl signals appear near their normal positions. In the mass spectrometer compounds (Xa) and (Xb) show similar behaviour, both losing water and also giving the same intense ions, *m/e* 213 (*M* — TsNHR) and 185 (213 — CO). The mass spectral behaviour of



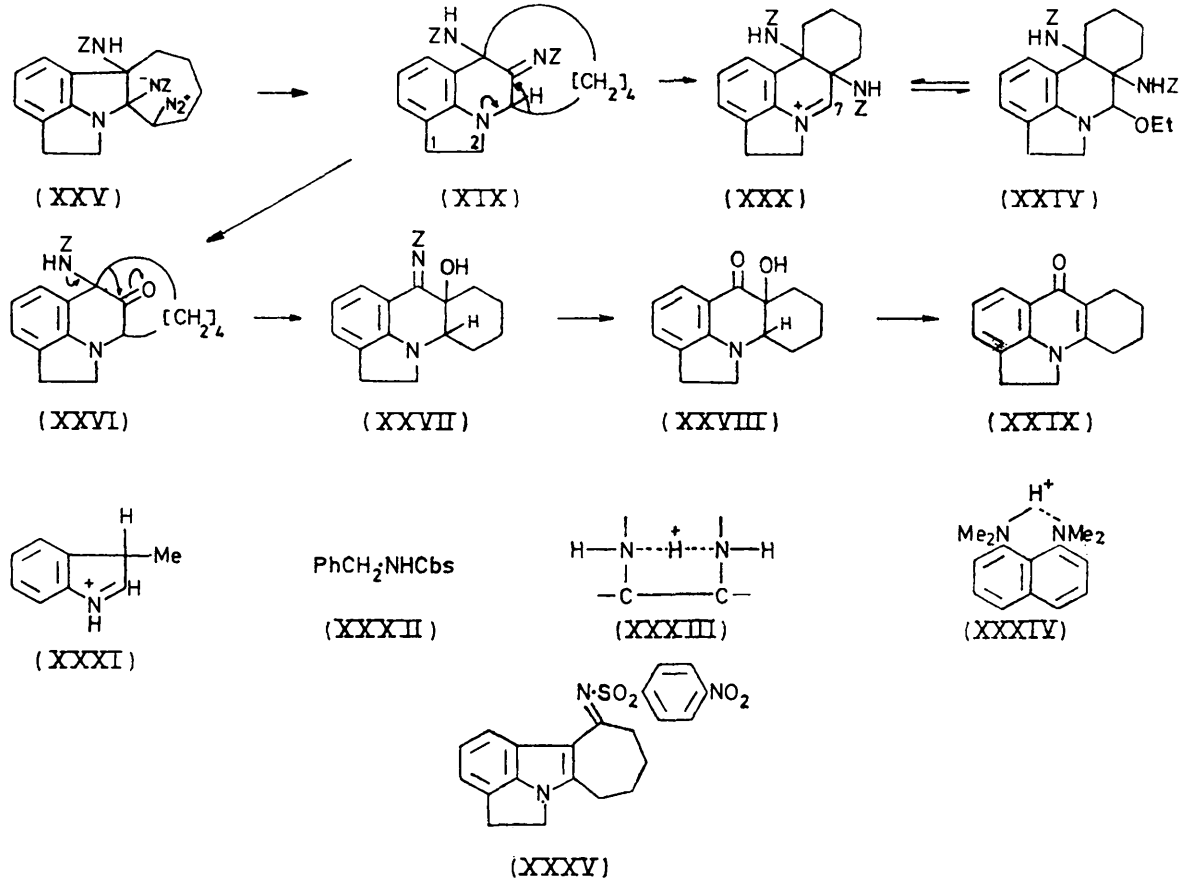
(Xc) and (Xd) is different; both give strong peaks corresponding to (*M* — Ts — CO) and (*M* — TsNR — CO).

Two other compounds were isolated from the reaction of (IX) with tosyl azide. The orange fluorescent material (XIII; R = Me) was isolated in 3% yield; the product was similar to that (II; Y = CH_2, Z = Ts) isolated from the reaction of *N*-methyltetrahydrocarbazole. In the n.m.r. spectrum of (XIII; R = Me) the signal from C(6)H appears at τ 2·1, shifted upfield from the signal of C(4)H in (II; Y = CH_2, Z = Ts).[1] Finally, the sulphonamide (XIV; R = Me) was isolated in 1% yield. Compound (III; Y = CH_2) is the major product obtained [1] from *N*-methyltetrahydrocarbazole and tosyl azide in acetic acid; however (IX) gave a dark tar under these conditions from which 5% of (XIV; R = Me) was isolated. Compound (Xa) melts with decomposition forming a red liquid and so we examined the effect of heat on (Xa) in an attempt to obtain (XIII; R = Me) in quantity. Although t.l.c. showed traces of (XIII; R = Me) in the melt, the only crystalline material isolated was (XIV; R = Me) in 45% yield. The reaction between (IX) and tosyl azide was next run in dry pyridine; compound (Xa) was obtained (17%) but the main product was the quinoline derivative (XV; R = NTs) whose structure followed from the characteristic u.v. spectrum and hydrolysis to the quinolone (XV; R = O). Also (XVI; Z = Ts), the precursor of (XV; R = NTs), was isolated and was converted into (XV; R = NTs) by treatment with base. Since structures of type (Xa) had not been isolated in our earlier work [1,3] with indoles and azides, the effect of a more reactive azide, *p*-chlorobenzenesulphonyl azide, was investigated, in methanolic solution. From this reaction four compounds were isolated: (X; R^1 = R^2 = H, R^3 = Cl), (XIII; R = Cl), and, in 2% yields, (XV; R = NCbs) and (XVI; Z = Cbs). The yield of (XIII; R = Cl) was 16% as compared with 3% of (XIII; R = Me), and so a still more reactive azide, *p*-nitrobenzenesulphonyl azide, was used. The reaction between this azide and (IX) was complete after 15 min in boiling methanol and the product (XVII) was obtained in high (89%) yield; the i.r. spectrum of the compound did not contain any C=O band, indicating that the material was not (X; R^1 = R^2 = H, R^3 = NO_2) containing methanol of crystallisation. Compound (XVII) was purified by recrystallisation from chloroform–methanol: when recrystallisation from propanol was

[9] I. Baxter and D. W. Cameron, *J. Chem. Soc.* (*B*), 1971, 696; see also ref. 2.
[10] R. S. Macomber, *J. Org. Chem.*, 1972, **37**, 1205, 1208.

attempted a red tar was obtained and so boiling was continued until decomposition was complete. From this reaction (XIII; R = NO_2) and (X; $R^1 = R^2 = H$, $R^3 = NO_2$) were isolated. Finally, a sample of (XVII) was melted, yielding a mixture of the spiro-compound (XIII; R = NO_2) and the sulphonamide (XIV; R = NO_2).

We have observed [3] that the reactions of *N*-methylhexahydrocyclohept[*b*]indole with azides are different from those of *N*-methyltetrahydrocarbazole, and it was of interest to prepare compound (XVIII) and study its reactions. 1,2,7,8,9,10-Hexahydro-6*H*-cyclohepta[*b*]-pyrrolo[3,2,1-*hi*]indole (XVIII) is readily obtained from cycloheptanone and 1-aminoindoline. When this material is mixed neat with tosyl azide the mixture explodes and therefore the reaction was run at room temperature in purified chloroform. The major product (60%) was the bridged compound (XIX; Z = Ts); similar compounds had been obtained in small yields [3] from other indoles, *e.g.* the corresponding compound from *N*-methylhexahydrocyclohept[*b*]indole was obtained in 15% yield. From this reaction was also isolated the phenanthridine derivative (XX; Z = Ts). The mass spectrum of (XX; Z = Ts) contained peaks due to loss of Ts and TsNH but not $TsNH_2$, and boiling the compound (XX; Z = Ts) with alkali resulted in the hydrolysis of the tosylimino-group but not in elimination, thus yielding (XXI; Z = Ts); compound (XXIII) shows similar behaviour.[3] When the indole and the azide were mixed in dry pyridine the same two products (XIX and XX; Z = Ts) were isolated, but none of the material (XXIII; R = Me) which would have been formed from (XX) by elimination of $TsNH_2$ under these basic conditions. The reaction of (XVIII) with $CbsN_3$ in chloroform also yielded the bridged compound (XIX; Z = Cbs) in good yield, compound (XX; Z = Cbs), and a new type of structure (XXIV; Z = Cbs) in small yield (see later). The production of structures of type (XIX) in good yield indicates the formation of (XXV) as an intermediate. For the first time in this work we had compounds of structure (XIX) available in quantity and were able to examine their reactions. Compound (XIX; Z = Ts) was boiled with alkali in an attempt to prepare (XXVI). Both tosyl groups were removed and the product (XXVIII) showed the characteristic u.v. behaviour and fluorescence of the *o*-amino-ketone chromophore [*cf.* the properties of the ketone obtained [1] by hydrolysis of (II; Y = CH_2, Z = Ts)]; structure (XXVIII) was also supported by the n.m.r. and i.r. spectra, and treatment of the compound with polyphosphoric acid resulted in loss of water yielding the 4-quinilone derivative (XXIX) whose spectral properties (especially u.v.) completely paralleled those of *N*-methyl-1,2,3,4-tetrahydroacridanone.[3] By hydrolysing compound



(XIX; Z = Cbs) with alkali at room temperature we succeeded in isolating the intermediate (XXVI; Z = Cbs), and heating this caused rearrangement with formation of (XXVII; Z = Cbs), an orange compound with the same chromophore as (II) and (XIII). Since alkali causes rearrangement of (XIX) forming the acridine skeleton, we examined the effect of acid, as elimination reactions have been observed [3] in TFA. Compound (XIX; Z = Cbs) was dissolved in TFA, and after 7 days the acid was removed and the residue recrystallised from ethanol; the mass spectrum and analytical data of the product show that this compound (XXIV; Z = Cbs) is derived from (XIX) by the addition of EtOH, and that the material contains 2NH groups but no C=N. A small quantity of (XXIV; Z = Cbs) had been isolated from the reaction between (XVIII) and $CbsN_3$; we believe it must have been formed in the work-up since the chloroform used as solvent had been freed from ethanol. A sample of (XIX; Z = Cbs) was dissolved in TFA and the n.m.r. spectrum was measured at intervals during 7 days; the spectrum gradually changed and, in particular, three sharp singlets appeared at τ 0·59, 3·26, and 3·62. The signal at lowest field is attributed to C(7)H in (XXX); this agrees with the position of signal reported [11] for C(2)H in the protonated form of skatole (XXXI). From the integration of the n.m.r. spectrum the other two singlets must be assigned to the two NH groups present in (XXX). In the course of our work we have recorded the n.m.r. spectra of several sulphonamides in TFA and never observed any clear signal that we associated with N*H*Ts, neither have we observed any coupling of C*H*·NHTs under these conditions, and we have assumed that either rapid NH exchange or inversion was occurring in this solvent, although NH signals and the coupling C*H*·NH are often observed in chloroform. The n.m.r. spectrum of (XXXII) in TFA contained no signal in the region 3·2—4·0 attributable to NH and the signal of the CH_2 appeared as a sharp singlet (5·75), showing no coupling to NH. To prove that the two signals at τ 3·26 and 3·62 in the spectrum of (XXX; Z = Cbs) were caused by NH groups, compound (XIX; Z = Cbs) was dissolved in CF_3·CO_2D; after 24 h at 40° the spectrum contained a one-proton singlet at τ 0·59, its intensity showing that conversion was complete; but there were no signals at 3·26 and 3·62. Further, these two signals were absent from the spectrum of (XXIV; Z = Cbs) run in CF_3·CO_2D. In the ion (XXX) the two NH groups are *cis* to each other and proton exchange may be slowed by formation of an ion of partial structure (XXXIII). A similar situation arises in (XXXIV); [12] in the n.m.r. spectrum (TFA) of this compound the Me signals appear as a doublet and proton exchange has been estimated [13] as occurring 10^5 times more slowly for this amine than for other amines. The n.m.r. spectrum of (XXX) in TFA has been examined down to τ − 10 to see if we could detect the third proton in structure (XXXIII), but no signal was observed [the NH signal of (XXXIV) in TFA occurs at τ −9·51].

Finally, the reaction of (XVIII) with the most reactive azide, *p*-nitrobenzenesulphonyl, was investigated. The first product isolated was assigned structure (XX; Z = *p*-O_2N·C_6H_4·SO_2); the material was insoluble in dimethyl sulphoxide and in chloroform so no n.m.r. data could be obtained, and the compound was boiled in suspension in aqueous ethanolic alkali in an attempt to form the hydrolysis product (XXI; Z = *p*-O_2N·C_6H_4·SO_2); however the product obtained was that formed by elimination, (XXIII; R = NO_2), in contrast to the reactions of the compounds obtained by using TsN_3 and $CbsN_3$. It seems to us unlikely that the stereochemical course of the reaction between (XVIII) and *p*-nitrobenzenesulphonyl azide is different from that with tosyl azide and we believe that this result reflects the fact that the *p*-nitrobenzenesulphonamidate anion is a much better leaving group than $TsNH^-$; also the proton at C(7a) in (XX) will be more labile when Z = *p*-O_2N·C_6H_4·SO_2 than when Z = Ts. This is the first example of a structure of general type (XX) we have produced in which Z = *p*-O_2N·C_6H_4·SO_2; we hope to examine this reaction in more detail with simpler indoles.

The other products of this reaction were (*a*) (XIX; Z = *p*-O_2N·C_6H_4·SO_2), (*b*) the imine (XXXV), and (*c*) the phenanthridine derivative (XXIV; Z = *p*-O_2N·C_6H_4·SO_2). Compound (XIX; Z = *p*-O_2N·C_6H_4·SO_2) decomposed on boiling in propanol; when the product from this reaction was recrystallised from ethanol, (XXIV; Z = *p*-O_2N·C_6H_4·SO_2) was isolated.

EXPERIMENTAL

General details and instruments used have been reported.[1-3] 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. In the mass spectral data reported here a dagger (†) indicates that high resolution measurement has been made to support the fragmentation scheme.

1,3,4,5-*Tetrahydro-5-methylthiopyrano*[4,3-b]*indole* (I; Y = S).—(*a*) 1,3,4,5-Tetrahydrothiopyrano[4,3-*b*]indole (m.p. 163—164°; lit.,[14] 159·5—161°) was methylated with sodamide–liquid ammonia–methyl iodide.

(*b*) Tetrahydro-1-thio-4-pyrone was mixed with *N*-methyl-*N*-phenylhydrazine and the resulting hydrazone cyclised with sulphuric acid (1M; 100°; 1 h). The *indole* formed needles, m.p. 95—97° (from ethanol) (Found: C, 71·0; H, 6·4; N, 6·9; S, 15·5. $C_{12}H_{13}NS$ requires C, 71·0; H, 6·4; N, 6·9; S, 15·8%); $\lambda_{max.}$ 226, 285, and 293 nm (ε 36,500, 6300, and 5800); τ 2·5—3·2 (4H, m, Ar), 6·19 [2H, s, C(1)H_2], 6·50 (3H, s, NMe), and 7·06br [4H, s, C(3)H_2 and C(4)H_2], *m/e* 203 (*M*, 82%), 170 (*M* − SH, 24%), 175 (*M* − C_2H_4, 27%), and 157 (*M* − CH_2S, 100%).

[11] R. L. Hinman and E. B. Whipple, *J. Amer. Chem. Soc.*, 1962, **84**, 2534.
[12] R. W. Alder, P. S. Bowman, W. R. S. Steele, and D. R. Winterman, *Chem. Comm.*, 1968, 723.
[13] F. H. Hibbert, *J.C.S. Chem. Comm.*, 1973, 463.
[14] T. E. Young, C. J. Ohnmacht, and C. R. Hamel, *J. Org. Chem.*, 1967, **32**, 3622.

1-*Methyl*-3-p-*tolylsulphonyliminoindoline*-2-*spiro*-3′-*thiacyclopentane* (II; Y = S, Z = Ts).—The indole (2 g) and tosyl azide (3·5 g) were boiled in ethanol (20 ml) for 2 h; the solvent was removed and the material chromatographed on silica. Benzene eluted starting materials (3·5 g); benzene–ethyl acetate (2%) yielded the spiro-compound (0·5 g). The *indoline* (II; Y = S, Z = Ts) formed orange prisms (from benzene), m.p. 194—195° (Found: C, 61·5; H, 5·4; N, 7·5; S, 17·5. $C_{19}H_{20}N_2O_2S_2$ requires C, 61·4; H, 5·4; N, 7·5; S, 17·1%); $\lambda_{max.}$ 230, 287, and 465 nm (ε 28,000, 9500, and 9100); $\nu_{max.}$ 1610 cm^{-1}; τ 1·48 [1H, d, *J* 8 Hz, C(4)H], 2·11 (2H, d, *J* 8 Hz, low-field half of tosyl signal), 2·54 [1H, t, *J* 8 Hz, C(6)H], 2·73 (2H, d, *J* 8 Hz, high-field half of tosyl signal), 3·23 [1H, t, *J* 8 Hz, C(5)H], 3·35 [1H, d, *J* 8 Hz, C(7)H], 6·83 (3H, s, NMe), 6·7—7·2 [4H, m, C(2′)H_2 and C(5′)H_2], 7·60 (3H, s, tosyl Me), and 7·74 [2H, t, *J* 7 Hz, C(4′)H_2]; *m/e* 372 (*M*, 16%), 313 (*M* − C_2H_3S, 21%), 217 (*M* − Ts, 61%), 201 (*M* − $TsNH_2$, 80%), 200 ($C_{12}H_{10}NS$, 100%), and 189 (217 − C_2H_4, 55%). Elution with 10% ethyl acetate–benzene gave a tar (1·5 g) which crystallised on trituration with ethanol (yield 0·63 g). 1-*Methyl*-4′-p-*tolylsulphonylamino*-2-p-*tolylsulphonyliminoindoline*-3-*spiro*-3′-*thiacyclopentane* (VI; Y = S, Z = Ts) formed plates, m.p. 199—200° (from ethanol) (Found: C, 57·3; H, 4·9; N, 7·5; S, 17·1. $C_{26}H_{27}N_3O_4S_3$ requires C, 57·7; H, 5·0; N, 7·8; S, 17·7%); $\lambda_{max.}$ 225, 285, and 300 nm (ε 42,200, 16,600, and 12,200); $\nu_{max.}$ 1620 and 3240 cm^{-1}; τ 2·08 (2H, d, *J* 8 Hz), 2·3—3·2 (10H, m, Ar), 4·5—4·8 [1H, q, collapsing to t on adding D_2O, C(4′)H], 5·88 [1H, d, *J* 11 Hz, C(5′)H], 6·02 (1H, d, *J* 10 Hz, NH, exchanged D_2O), 6·69 (3H, s, NMe), 6·8—7·5 (3H, m), 7·57 (3H, s, tosyl Me), and 7·67 (3H, s, tosyl Me); *m/e* (*M* not observed) 336 (*M* − $TsNH_2$ − H_2S, 3%), 300 (*M* − $TsNC_3H_4S$, 12%), 214 (9%), 182 (8%), 181 (9%), and 91 (100%). When the time of heating the reaction mixture was increased to 6 h, little starting material was recovered but more tarry products were formed. The reaction was also run in ethyl acetate, acetic acid, pyridine, benzene, and chloroform.

From the reaction between (I; Y = S) and $CbsN_3$, 3-p-*chlorophenylsulphonylimino*-1-*methylindoline*-2-*spiro*-3′-*thiacyclopentane* (II; Y = S, Z = Cbs) was isolated (yield 14%), orange prisms (chloroform–methanol), m.p. 180—182° (Found: C, 54·8; H, 4·4; Cl, 9·2; N, 7·0; S, 16·9. $C_{18}H_{17}ClN_2O_2S_2$ requires C, 55·0; H, 4·3; Cl, 9·1; N, 7·1; S, 16·3%); $\lambda_{max.}$ 203, 232, 286, and 466 nm (ε 21,000, 21,500, 6500, and 6100); $\nu_{max.}$ 1620 cm^{-1}; τ 1·51 [1H, d, *J* 8 Hz, C(4)H], 2·03 (2H, d, *J* 8 Hz, low-field half of Cbs signal), 2·4—2·6 (3H, m), 3·20 [1H, t, *J* 8 Hz, C(5)H], 3·32 [1H, d, *J* 8 Hz, C(7)H], 6·6—7·2 [4H, m, C(2′)H_2 and C(5′)H_2], 6·81 (3H, s, NMe), and 7·73 [2H, t, *J* 7 Hz, C(4′)H_2]. 4′-p-*Chlorophenylsulphonylamino*-2-p-*chlorophenylsulphonylimino*-1-*methylindoline*-3-*spiro*-3′-*thiacyclopentane* (VI; Y = S, Z = Cbs) formed prisms, m.p. 209—210° (from 2-methoxyethanol) (Found: C, 49·3; H, 4·0; Cl, 12·2; N, 6·7; S, 16·5. $C_{24}H_{21}Cl_2N_3O_4S_3$ requires C, 49·5; H, 3·6; Cl, 12·2; N, 7·2; S, 16·5%); $\lambda_{max.}$ 228, 285, and 302 nm (ε 30,700, 10,100, and 8300); $\nu_{max.}$ 1580 and 3260 cm^{-1}; *m/e* [*M* (581) absent] 356 (*M* − $CbsNH_2$ − H_2S, 20%), 320 (*M* − $CbsNC_3H_4S$, 45%), 214 ($C_{12}H_{10}N_2S$ 19%), 196 (65%), 182 (40%), 181 (55%), and 112 (100%).

1,2,6,7,8,9-*Hexahydropyrrolo*[3,2,1-jk]*carbazole* (IX).—1-Nitrosoindoline [5] was reduced ($LiAlH_4$) in ether, forming 1-aminoindoline,[4,5,15] b.p. 60—62° at 0·5 mmHg. The compound was immediately condensed with cyclohexanone (100°; 30 min) and the resulting hydrazone cyclised with sulphuric acid (4% v/v; 10 ml per g of aminoindoline used) at 100° for 1 h (use of 20% sulphuric acid [5] caused charring and gave tar). The compound formed plates, m.p. 157—158° (lit.,[5] 169·5—170°); τ 2·86 [1H, d, *J* 7 Hz, C(5)H], 3·05—3·3 (2H, m), 5·73 [2H, t, *J* 8 Hz, C(1)H_2], 6·33 [2H, t, *J* 8 Hz, C(2)H_2], 7·3br [4H, s, C(6)H_2 and C(9)H_2], and 8·83 [4H, m, C(8)H_2 and C(7)H_2].

2-(*Indolin*-7-*yl*)-2-p-*tolylsulphonylaminocyclohexanone* (Xa).—(*a*) A solution of the indole (IX) (2 g) and TsN_3 (2·1 g) in methanol (20 ml) was boiled for 3 h, then cooled, and the solid was recrystallised from acetonitrile (2·11 g, 55% yield).

(*b*) The indole (2 g) and azide (4 g) were mixed in pyridine (20 ml; distilled from KOH). After 3 days the solution was heated (60°; 4 h), then cooled, and the solid (A) was collected. The liquors were evaporated and the residue chromatographed (silica; benzene–ethyl acetate) (yield 0·67 g, 17%). The *ketone* (Xa) formed prisms, m.p. 222—224° (from acetonitrile) (Found: C, 65·7; H, 6·3; N, 7·3; S, 8·4. $C_{21}H_{24}N_2O_3S$ requires C, 65·6; H, 6·3; N, 7·3; S, 8·3%); $\lambda_{max.}$ 202, 212sh, 227sh, and 312 nm (ε 29,300, 20,600, 14,800, and 1900); $\nu_{max.}$ 1702, 3320, and 3375 cm^{-1}; *m/e* 384 (*M*, 12%), 366 (*M* − H_2O, 5%), 229 (*M* − Ts, 27%, *m** 136·6), 213 (*M* − $TsNH_2$, 10%), 211 (366 − Ts, 15%), and 185† (213 − CO, 100%).

2-(*Indolin*-7-*yl*)-2-(N-*methyl*-p-*tolylsulphonylamino*)*cyclohexanone* (Xb).—Dimethyl sulphate (2 g) was added slowly to a solution of (Xa) (200 mg) in acetone (5 ml) and KOH solution (50%; 5 ml). After 1 h the product was isolated and purified by chromatography. The *compound* (Xb) formed needles, m.p. 165—166° (from ethanol) (yield 85 mg) (Found: C, 66·4; H, 6·6; N, 7·2; S, 8·3. $C_{22}H_{26}N_2O_3S$ requires C, 66·4; H, 6·5; N, 7·0; S, 8·0%); $\lambda_{max.}$ 201, 223sh, 252sh, 305sh, and 335 nm (26,600, 21,000, 7800, 1600, and 3600); $\nu_{max.}$ 1705 and 3380 cm^{-1}; *m/e* 398 (*M*, 5%), 380 (*M* − H_2O, 1%), 243 (*M* − Ts, 17%, *m** 148·4), 213 (*M* − TsNHMe, 50%), 185 (67%), and 91 (100%).

2-(1-*Methylindolin*-7-*yl*)-2-p-*tolylsulphonylaminocyclohexanone* (Xc).—Compound (Xa) (500 mg) was boiled for 48 h with MeI (2 ml) and acetonitrile (5 ml). The solvent was removed, and the residue treated with sodium carbonate solution. The product was isolated (chloroform) and purified on silica; the *ketone* (Xc) formed prisms, m.p. 133—134° (from methanol) (yield 210 mg) (Found: C, 66·4; H, 6·6; N, 7·2. $C_{22}H_{26}N_2O_3S$ requires C, 66·4; H, 6·5; N, 7·0%); $\lambda_{max.}$ 219, 254sh, and 292 nm (ε 19,000, 4900, and 1850); $\nu_{max.}$ 1710 and 3235 cm^{-1}; *m/e* 398 (*M*, 36%), 370 (22%, *m** 344·0), 243 (*M* − Ts, 21%, *m** 148·4), 215† (*M* − Ts − CO, 100%), and 200† (*M* − TsNH − CO, 100%).

2-(1-*Methylindolin*-7-*yl*)-2-(N-*methyl*-p-*tolylsulphonylamino*)*cyclohexanone* (Xd).—Compound (Xa) (200 mg) was methylated with dimethyl sulphate and the crude product was boiled with MeI in acetonitrile; the dimethylated product was purified on silica. The *ketone* (Xd) formed prisms, m.p. 153—154° (from ethanol) (76 mg) (Found: C, 66·6; H, 6·7; N, 7·0; S, 7·7. $C_{23}H_{28}N_2O_3S$ requires C, 67·0; H, 6·8; N, 6·8; S, 7·8%); $\lambda_{max.}$ 201, 217sh, and 304 nm (ε 26,300, 21,700, and 2600); $\nu_{max.}$ 1724 and 1738 cm^{-1}; *m/e* 412 (*M*, 16%), 384 (3%), 257 (7%), 229 (384 − Ts, 90%), 228 (*M* − TsNMe, 20%), 227 (23%), 213 (34%), 200 (*M* − TsNMe − CO, 90%), and 91 (100%).

[15] D. E. Ames and H. Z. Kucharska, *J. Chem. Soc.*, 1962, 1509.

1,2,4,5-*Tetrahydro*-5-p-*tolylsulphonyliminopyrrolo*[3,2,1-hi]*indole*-4-*spirocyclopentane* (XIII; R = Me).—The methanolic liquors from the preparation of (Xa) [experiment (a)] were evaporated and the residue was chromatographed on silica. The *spiro-compound* formed bright orange plates, m.p. 210—212° (from ethanol) (yield 110 mg) (Found: C, 68·7; H, 6·0; N, 7·6; S, 9·0. $C_{21}H_{22}N_2O_2S$ requires C, 68·9; H, 6·0; N, 7·7; S, 8·7%); $\lambda_{max.}$ 202, 230, 283, and 450 nm (ε 22,300, 22,200, 9300, and 7800); $\nu_{max.}$ 1555 cm^{-1}; τ 2·0—2·2 (3H, m, Ar), 2·76 (high-field half of tosyl signal), 2·91 [1H, d, *J* 8 Hz, C(8)H], 3·41 [1H, t, *J* 8 Hz, C(7)H], 6·35 (2H, t, *J* 7 Hz), 6·75 (2H, t, *J* 7 Hz), 7·62 (3H, s, tosyl Me), and 7·9—8·3 (8H, m); *m/e* 366 (*M*, 11%), 211 (*M* − Ts, 100%, *m** 121·6), 209 (211 − 2H, 8%, *m** 207·0), 194 (6%), and 183 (16%).

1,2,6,7,8,9-*Hexahydro*-9-p-*tolylsulphonylaminopyrrolo*-[3,2,1-jk]*carbazole* (XIV; R = Me).—(*a*) A mixture of equimolar quantities of the indole (IX) and tosyl azide were kept in acetic acid at room temperature for 2 weeks. The neutral black tar was chromatographed on silica (yield 90 mg, 5%).

(*b*) The residues from the preparation of (Xa) in methanol yielded 30 mg (1%).

(*c*) Compound (Xa) (200 mg) was heated (oil-bath) to its m.p. for 30 min. The melt was cooled and triturated with methanol, and the resulting solid was recrystallised from ethanol. The *sulphonamide* (XIV; R = Me) formed prisms (85 mg), m.p. 204—205° (Found: C, 68·7; H, 5·9; N, 7·4; S, 9·0. $C_{21}H_{22}N_2O_2S$ requires C, 68·9; H, 6·0; N, 7·7; S, 8·7%); $\lambda_{max.}$ 203, 233, and 283 nm (ε 23,100, 38,000, and 7400); $\nu_{max.}$ 3240 cm^{-1}; τ 2·23 (2H, d, *J* 8 Hz, low-field half of tosyl signal), 2·6—3·2 (5H, m, Ar), 5·53br (2H, s, NH and CH, intensity of signal diminished 50% on adding D_2O), 5·78 [2H, t, *J* 7 Hz, C(1)H_2], 6·42 [2H, t, *J* 7 Hz, C(2)H_2], 7·2—7·5 (2H, m), 7·58 (3H, s, tosyl Me), and 8·1—8·6 (4H, m); *m/e* 366 (*M*, 69%), 323 (16%), 211 (*M* − Ts, 85%, *m** 121·6), 210 (72%, *m** 209·0), 196 (*M* − TsNH, 100%), and 195 (48%).

4,5,7,8,9,10 *Hexahydro*-7-p-*tolylsulphonyliminocyclopenta*-[c]*pyrrolo*[3,2,1-ij]*quinoline* (XV; R = NTs).—(*a*) The solid (A) obtained during reaction of (IX) with TsN_3 in pyridine was recrystallised from acetonitrile (0·87 g); chromatography of the pyridine mother-liquors yielded more material (0·93 g).

(*b*) The preparation of (Xa) in methanol afforded 91 mg (2% yield) on chromatography. The *quinoline* formed fine needles, m.p. 230—232° (Found: C, 69·5; H, 5·5; N, 7·6; S, 8·6. $C_{21}H_{20}N_2O_2S$ requires C, 69·2; H, 5·5; N, 7·7; S, 8·8%); $\lambda_{max.}$ 220, 269, 310, 340sh, and 350 nm (ε 34,800, 39,300, 4800, 9700, and 11,900); $\nu_{max.}$ 1508 cm^{-1}; τ 2·05 (2H, d, *J* 8 Hz, low-field half of tosyl signal), 2·5—2·9 (5H, m, Ar), 5·50 (2H, t, *J* 8 Hz), 6·3—6·7 (4H, m), 6·88 (2H, t, *J* 8 Hz), 7·61 (3H, s, tosyl Me), and 7·77 (2H, quint, *J* 8 Hz); *m/e* 364 (*M*, 6%), 299 (*M* − SO_2 − H, 5%, *m** 245·6), 209 (*M* − Ts, 100%, *m** 120), and 192 (4%).

4,5,7,7a,8,9,10,10a-*Octahydro*-10a-p-*tolylsulphonylamino*-7-p-*tolylsulphonyliminocyclopenta*[c]*pyrrolo*[3,2,1-ij]*quinoline* (XVI; Z = Ts).—Further chromatography of the mother-liquors from the preparation of (A) above gave the *sulphonylimine* as prisms, m.p. 239—241° (from acetonitrile) (yield 0·97 g, 18%) (Found: C, 62·7; H, 5·5; N, 7·9; S, 12·0. $C_{28}H_{29}N_3O_4S_2$ requires C, 62·8; H, 5·4; N, 7·9; S, 12·0%); $\lambda_{max.}$ 223, 273, 283, and 309 nm (ε 18,300, 9900, 11,200, and 9200); $\nu_{max.}$ 1550 and 3250 cm^{-1}; τ [$(CD_3)_2SO$] 1·64br (1H, s, NH, exchanged D_2O), 2·22 (2H, d, *J* 8 Hz, low-field half of tosyl signal), 2·65 (2H, d, *J* 8 Hz), 2·8—3·5 (7H, m, Ar), 5·73 (1H, t, *J* 9 Hz), 5·9—6·3 (2H, m), 6·8—7·2 (2H, m), 7·65 (3H, s, tosyl Me), 7·75 (3H, s, tosyl Me), and 7·4—9·0 (6H, m); *m/e* 535 (*M*, 4%), 365 (*M* − TsNH, 12%), 364 (12%), 299 (7%), 209 (100%), and 192 (4%). This compound (200 mg) was boiled for 19 h in ethanol (4 ml) containing 1,5-diazabicyclo[4.3.0]non-5-ene. The usual work-up gave compound (XV; R = NTs), needles, m.p. 230—232° (77 mg) (from acetonitrile).

4,5,9,10-*Tetrahydrocyclopenta*[c]*pyrrolo*[3,2,1-ij]*quinolin*-7(8H)-*one* (XV; R = O).—Compound (XV; R = NTs) (200 mg) was boiled in ethanol (5 ml) and sodium hydroxide (2M; 5 ml) for 6 h. Addition of water and extraction with chloroform yielded the *quinolone* (XV; R = O), needles (from benzene), m.p. 171—173° (86 mg) (Found: C, 79·7; H, 6·4; N, 6·9. $C_{14}H_{13}NO$ requires C, 79·6; H, 6·2; N; 6·6%); $\lambda_{max.}$ 205, 220sh, 234, 251, 268, 278, 288, 316sh 327, and 340 nm (ε 31,700, 24,100, 26,800, 18,300, 4100, 5000, 4600, 3800, 5200, and 4000); $\nu_{max.}$ 1640 cm^{-1}; τ 2·6—3·1 (3H, m, Ar), 5·63 (2H, t, *J* 8 Hz), 6·61 (2H, t, *J* 8 Hz), 6·8—7·2 (4H, m), and 7·82 (2H, quint, *J* 8 Hz); *m/e* 211 (*M*, 80%), 210 (100%), and 192 (210 − H_2O, 3%, *m** 175·5).

Reaction of the Indole (IX) *with* p-*Chlorobenzenesulphonyl Azide*.—A solution of the indole (2 g) in methanol (20 ml) containing $CbsN_3$ (3·3 g) was boiled for 2 h, then cooled, and the solid was collected. Recrystallisation from acetonitrile gave 2-p-*chlorophenylsulphonylamino*-2-(*indolin*-7-*yl*)*cyclohexanone* (X; R^1 = R^2 = H, R^3 = Cl), pale yellow prisms, m.p. 230° (decomp.) (370 mg) (Found: C, 59·8; H, 5·5; Cl, 8·8; N, 6·9; S, 7·4. $C_{20}H_{21}ClN_2O_3S$ requires C, 59·3; H, 5·2; Cl, 8·8; N, 6·9; S, 7·9%); $\lambda_{max.}$ 281 and 310 nm (ε 15,500 and 1900); $\nu_{max.}$ 1692, 3315, and 3355 cm^{-1}; τ 2·72 (1H, d, *J* 8 Hz), 2·8—3·4 (6H, m), 3·62 (1H, exchanged D_2O), 6·31 (1H, m), 6·79 (1H, m), 6·96 (1H, m, exchanged D_2O), and 7·1—8·6 (10H, m); *m/e* 404 (*M*, 23%), 386 (2%), 229 (67%, *m** 129·8), 213 (10%), 212 (229 − OH, 20%, *m** 196·3), 211 (16%), 201 (19%), and 185 (100%). The methanolic liquors were evaporated and the residue chromatographed yielding, in order of elution: 5-p-*chlorophenylsulphonylimino*-1,2,4,5-*tetrahydropyrrolo*-[3,2,1-hi]*indole*-4-*spirocyclopentane* (XIII; R = Cl), orange prisms, m.p. 225—227° (from acetonitrile) (630 mg, 16%) (Found: C, 62·1; H, 4·9; Cl, 9·4; N, 7·2; S, 8·3. $C_{20}H_{19}ClN_2O_2S$ requires C, 62·1; H, 4·9; Cl, 9·2; N, 7·2; S, 8·3%); $\lambda_{max.}$ 202, 233, 288, and 453 nm (ε 27,600, 27,400, 10,100, and 8500); $\nu_{max.}$ 1553 cm^{-1}; τ 2·07 (3H, m, Ar), 2·57 (2H, d, *J* 8 Hz, high-field half of Cbs signal), 2·88 (1H, d, *J* 7 Hz), 3·38 (1H, t, *J* 7 Hz), 6·32 (2H, t, *J* 7 Hz), 6·72 (2H, t, *J* 7 Hz), and 7·8—8·3 (8H, m); *m/e* 386 (*M*, 11%), 211 (100%); compound (X; R^1 = R^2 = H, R^3 = Cl) (1·6 g, total yield 48%); 7-p-*chlorophenylsulphonylimino*-4,5,7,8,9,10-*hexahydrocyclopenta*[c]*pyrrolo*-[3,2,1-ij]*quinoline* (XV; R = NCbs), needles (from acetonitrile), m.p. 268—271° (71 mg) (Found: C, 62·3; H, 4·7; N, 7·4. $C_{20}H_{17}ClN_2O_2S$ requires C, 62·4; H, 4·4; N, 7·3%); $\lambda_{max.}$ 219, 269, 310, 338sh, and 350 nm (ε 34,800, 35,800, 5600, 9800, and 12,100); $\nu_{max.}$ 1520 cm^{-1}; τ 2·02 (2H, d, *J* 8 Hz), 2·5—2·9 (5H, m), 5·50 (2H, t, *J* 8 Hz), 6·4—6·7 (4H, m), 6·86 (2H, t, *J* 8 Hz), and 7·75 (2H, quint, *J* 8 Hz); *m/e* 384 (6%) and 209 (100%): 10a-p-*chlorophenylsulphonylamino*-7-p-*chlorophenylsulphonylimino*-4,5,7,7a,-8,9,10,10a-*octahydrocyclopenta*[c]*pyrrolo*[3,2,1-ij]*quinoline* (XVI; Z = Cbs), prisms (91 mg) (from acetonitrile), m.p. 229—231° (Found: C, 54·4; H, 4·2; Cl, 12·2; N, 7·0; S, 10·9. $C_{26}H_{23}Cl_2N_3O_4S_2$ requires C, 54·2; H, 4·0; Cl, 12·3;

N, 7·3; S, 11·1%); $\lambda_{max.}$ 227, 278sh, 283, and 310 nm (ε 37,100, 17,100, 18,900, and 17,100); $\nu_{max.}$ 1548 and 3235 cm^{-1}; τ [$(CD_3)_2SO$] 1·40 (1H, NH), 2·09 (2H), 2·45 (2H), 2·6—3·6 (7H), 5·78 (1H), 5·9—6·2 (2H), 6·91 (2H), and 7·4—9·0 (6H); *m/e* 575 (*M*, 9%), and 209 (100%).

1,2,5b,6,7,8,9,9a-*Octahydro*-9a-*methoxy*-5b-p-*nitrophenylsulphonylaminopyrrolo*[3,2,1-jk]*carbazole* (XVII).—A solution of the indole (IX) (1 g) and *p*-nitrobenzenesulphonyl azide (1·75 g) in methanol (15 ml) was boiled for 15 min, then cooled, and the solid was collected (1·64 g): chromatography afforded a further quantity (280 mg, total yield 89%). Recrystallisation (chloroform–methanol) afforded pale coloured *prisms*, m.p. 106—110° (decomp.) (Found: C, 58·2; H, 5·7; N, 9·8; S, 7·6. $C_{21}H_{23}N_3O_5S$ requires C, 58·7; H, 5·4; N, 9·8; S, 7·5%); $\lambda_{max.}$ 210, 252, and 265sh nm (ε 23,200, 11,700, and 10,300); $\nu_{max.}$ 3240 and 3035 cm^{-1}; τ 2·06 (2H, d, *J* 8 Hz), 2·46 (2H, d, *J* 8 Hz), 2·98 (1H, d, *J* 8 Hz), 3·3—3·7 (2H, m, Ar), 3·45 (1H, s, NH, exchanged D_2O), 6·52 (3H, s, OMe), 6·5—7·0 (2H, m), 7·1—7·3 (2H, m), and 7·8—9·3 (8H, m); *m/e* (*M* not detected) 397 (*M* − MeOH, 39%), 356 (3%), 211 (100%), and 194 (81%). When a sample of this material was heated at 110° (15 min), cooled, and triturated with methanol, 1,2,6,7,8,9-*hexahydro*-9-p-*nitrophenylsulphonylaminopyrrolo*[3,2,1-jk]*carbazole* (XIV; R = NO_2) was formed (60% yield), pale yellow prisms (from acetonitrile), m.p. 198—200° (Found: C, 60·7; H, 4·9; N, 10·4. $C_{20}H_{19}N_3O_4S$ requires C, 60·5; H, 4·8; N, 10·6%); $\lambda_{max.}$ 205, 232, and 280 nm (ε 29,200, 36,800, and 17,100); $\nu_{max.}$ 3240 cm^{-1}; τ [$(CD_3)_2SO$] 1·57 (2H, d, *J* 8 Hz), 1·8 (2H, d, *J* 8 Hz), 2·90 (1H, t, *J* 5 Hz), 3·1—3·2 (2H, m, Ar), 5·29 [1H, m, C(9)H], 5·79 (2H, t, *J* 7 Hz), 6·38 (2H, t, *J* 7 Hz), 7·42 (2H, m), and 8·0—8·5 (4H, m); *m/e* 397 (*M*, 47%), 211 (*M* − SO_2Ar, 22%, *m** 112·1), 210 (27%), 196 (*M* − $ArSO_2NH$, 90%, *m** 96·8), 195 (80%), and 194 (100%) [*cf.* mass spectrum [1] of (III; Y = CH_2)].

1,2,4,5-*Tetrahydro*-5-p-*nitrophenylsulphonyliminopyrrolo*-[3,2,1-hi]*indole*-4-*spirocyclopentane* (XIII; R = NO_2).—(*a*) The crude sample of (XVII) was boiled in (see above) n-propanol (10 ml) for 3 h, the solvent was removed *in vacuo*, and the residue was recrystallised from acetonitrile (yield 13%).

(*b*) The mother-liquors from the preparation of (XVII) yielded 3% on chromatography.

(*c*) The mother-liquors from preparation of (XIV; R = NO_2) contained 15%. The *imine* (XIII; R = NO_2) formed bright red prisms (from acetonitrile), m.p. 193—194° (Found: C, 60·7; H, 4·9; N, 10·4; S, 8·1. $C_{20}H_{19}N_3O_4S$ requires C, 60·5; H, 4·8; N, 10·6; S, 8·1%); $\lambda_{max.}$ 236, 289, and 456 nm (ε 26,500, 14,200, and 9200); $\nu_{max.}$ 1545 cm^{-1}; τ 1·67 (2H, d, *J* 8 Hz), 1·82 (2H, d, *J* 8 Hz), 2·10 [1H, d, *J* 8 Hz, C(6)H], 2·85 [1H, d, *J* 8 Hz, C(8)H], 3·35 [1H, t, *J* 8 Hz, C(7)H], 6·29 (2H, t, *J* 7 Hz), 6·70 (2H, t, *J* 7 Hz), and 7·9—8·3 (8H, m); *m/e* 397 (*M*, 20%) and 211 (100%). The residues from the boiling of (XVII) in propanol were chromatographed: 2-(*indolin*-7-*yl*)-2-p-*nitrophenylsulphonylaminocyclohexanone* (X; R^1 = R^2 = H, R^3 = NO_2) formed orange needles, m.p. 187—189° (from ethanol; 12% yield) (Found: C, 57·7; H, 5·2; N, 9·9; S, 7·5. $C_{20}H_{21}N_3O_5S$ requires C, 57·8; H, 5·1; N, 10·1; S, 7·7%); $\lambda_{max.}$ 203 and 256 nm (ε 25,600 and 12,300); $\nu_{max.}$ 1710, 3170, 3315, and 3365 cm^{-1}; τ [$(CD_3)_2SO$] 2·0—2·1 (3H, NH and low-field half of $ArSO_2$ signal), 2·45 (2H, d, *J* 8 Hz), 2·86 (1H, d, *J* 8 Hz), 3·2—3·6 (2H, m, Ar), 5·6—5·8 (1H, m, indole NH, exchanged D_2O), 6·3—7·0 (2H, m), and 7·0—8·6 (10H, m); *m/e* 415 (*M*, 67%), 397 (7%), 229 (70%), and 185 (100%).

1,2,7,8,9,10-*Hexahydro*-6H-*cyclohepta*[b]*pyrrolo*[3,2,1-hi]-*indole* (XVIII).—The *indole* was obtained (60% yield) from cycloheptanone and 1-aminoindoline (5% sulphuric acid; 100°; 1 h); it formed needles (from ethanol), m.p. 129—131° (Found: C, 85·6; H, 7·9; N, 6·8. $C_{15}H_{17}N$ requires C, 85·3; H, 8·1; N, 6·6%); $\lambda_{max.}$ 212, 234, and 293 (ε 20,000, 30,400, and 7700); τ 2·85 (1H, d, *J* 8 Hz), 3·0—3·3 (2H, m, Ar), 5·67 (2H, t, *J* 7 Hz), 6·32 (2H, t, *J* 7 Hz), 7·1—7·3 (4H, m), and 8·0—8·5 (6H, m).

1,2,5,6-*Tetrahydro*-6-p-*tolylsulphonylamino*-5-p-*tolylsulphonylimino*-4,6-*butano*-4H-*pyrrolo*[3,2,1-ij]*quinoline* (XIX; Z = Ts).—(*a*) A solution of (XVIII) (2 g) and TsN_3 (3·8 g) in chloroform (20 ml; purified over alumina) was kept at room temp. for 48 h; the solvent was removed and the residue triturated with methanol. The solid was recrystallised from acetonitrile (3·06 g, 59% yield).

(*b*) The indole (1 g) and the azide (2 g) in pyridine afforded 500 mg and further material (425 mg) on chromatography. The *imine* (XIX; Z = Ts) formed yellow prisms, m.p. 186—187° (decomp.) (Found: C, 63·8; H, 5·6; N, 7·7; S, 11·7. $C_{29}H_{31}N_3O_4S_2$ requires C, 63·4; H, 5·7; N, 7·7; S, 11·7%); $\lambda_{max.}$ 212sh, 228sh, 251sh, and 310nm (ε 35,800, 24,000, 9700, and 2200); $\nu_{max.}$ 1640 and 3285 cm^{-1}; τ 2·09 (2H, d, *J* 8 Hz), 2·5—3·2 (7H, m), 3·32 (1H, d, *J* 8 Hz, Ar), 3·66 (1H, t, *J* 8 Hz, Ar), 4·44 (1H, s, NH, exchanged D_2O), 4·59 (1H, dd, *J* 8 and 3 Hz), 6·4—6·7 (2H, m), 6·8—7·1 (2H, m), 7·57 (3H, s, CMe), 7·66 (3H, s, CMe), and 7·6—9·3 (8H, m); *m/e* 549 (*M*, 7%), 394 (16%), 378 (5%), and 91 (100%).

4,5,7a,8,9,10,11,11a-*Octahydro*-11a-p-*tolylsulphonylamino*-7-p-*tolylsulphonylimino*-7H-*pyrrolo*[3,2,1-de]*phenanthridine* (XX; Z = Ts).—The methanol mother liquors (above) yielded 420 mg (8%) and the pyridine residues 15% on chromatography. The *phenanthridine* (XX; Z = Ts) formed needles (from ethanol), m.p. 245—248° (Found: C, 62·9; H, 5·7; N, 7·9; S, 11·9. $C_{29}H_{31}N_3O_4S_2$ requires C, 63·4; H, 5·7; N, 7·7; S, 11·7%); $\lambda_{max.}$ 225, 273, 283, and 313 nm (ε 31,900, 15,000, 16,700, and 18,200); $\nu_{max.}$ 1555 and 3335 cm^{-1}; τ 2·08 (2H, d, *J* 8 Hz), 2·6—2·8 (3H, m), 2·9—3·2 (6H, m), 5·52 (1H, s, NH, exchanged D_2O), 5·9—7·3 (5H, m), 7·57 (3H, s, CMe), 7·70 (3H, s, CMe), and 7·8—9·3 (8H, m); *m/e* 549 (*M*, 35%), 394 (8%), 379 (*M* − TsNH, 45%), 239 (394 − Ts, 12%), 224 (379 − Ts, 45%), and 223 (100%). When compound (XX; Z = Ts) (250 mg) was boiled for 2 h with NaOH (300 mg) in water (2 ml) and ethanol (5 ml) the dihydroquinolone (XXI; Z = Ts) was obtained (yield 77%). 4,5,7a,8,9,10,11,11a-*Octahydro*-11a-p-*tolylsulphonylaminopyrrolo*[3,2,1-de]*phenanthridin*-7-*one* formed prisms (from ethanol), m.p. 241—242° (Found: C, 66·3; H, 6·2; N, 6·9; S, 7·9. $C_{22}H_{24}N_2O_3S$ requires C, 66·7; H, 6·1; N, 7·1; S, 8·1%); $\lambda_{max.}$ 215, 233sh, 255, and 295 nm (ε 26,200, 12,600, 11,000, and 4200); $\nu_{max.}$ 1682 and 3100br cm^{-1}; τ 2·6—3·2 (7H, m), 4·38 (1H, NH, exchanged D_2O), 5·8—7·5 (5H, m), 7·68 (3H, s, CMe), and 8·0—9·2 (8H, m); *m/e* 396 (*M*, 25%), 241 (10%), and 226 (*M* − TsNH, 100%, *m** 129·0).

When the indole (2 g) was mixed with $CbsN_3$ (4·2 g) in purified chloroform, compound (XIX; Z = Cbs) (2·32 g) separated: 6-p-*chlorophenylsulphonylamino*-5-p-*chlorophenylsulphonylimino*-1,2,5,6-*tetrahydro*-4,6-*butano*-4H-*pyrrolo*[3,2,1-ij]*quinoline* formed yellow prisms (from acetonitrile), m.p. 183—185° (decomp.) (Found: C, 55·4; H, 4·5; Cl, 12·3; N, 7·3; S, 10·8. $C_{27}H_{25}Cl_2N_3O_4S_2$ requires

C, 54·9; H, 4·2; Cl, 12·0; N, 7·1; S, 10·9%); $\lambda_{max.}$ 213sh, 233, and 309 nm (ε 37,600, 33,500, and 3000); $\nu_{max.}$ 1637 and 3275 cm^{-1}; τ [$(CD_3)_2SO$] 1·46 (1H, NH, exchanged D_2O), 2·01 (2H, d, *J* 8 Hz), 2·29 (2H, d, *J* 8 Hz), 2·69 (2H, d, *J* 8 Hz), 2·84 (2H, d, *J* 8 Hz), 3·11 (1H, d, *J* 8 Hz), 3·5—3·9 (2H, m, Ar), 4·56 (1H, d, *J* 8 Hz), 6·4—6·7 (2H, m), 6·8—7·1 (2H, m), and 7·6—9·4 (8H, m). Chromatography gave more (XIX; Z = Cbs) (1·0 g, total yield 59%) followed by 7a,11a-*bis*-(p-*chlorophenylsulphonylamino*)-7-*ethoxy*-4,5,7a,8,9,10,11,11a-*octahydro*-7H-*pyrrolo*[3,2,1-de]-*phenanthridine* (XXIV; Z = Cbs). The compound formed prisms (from ethanol), m.p. 155—158° (yield 2%) (Found: C, 54·7; H, 5·0; Cl, 11·0; N, 6·6; S, 10·3. $C_{29}H_{31}Cl_2N_3O_5S_2$ requires C, 54·7; H, 4·9; Cl, 11·2; N, 6·6; S, 10·1%); $\lambda_{max.}$ 233 and 310 nm (ε 34,500 and 3800); $\nu_{max.}$ 3195 and 3275 cm^{-1}; τ 2·19 (2H, d, *J* 8 Hz, low-field half of Cbs signal), 2·3—2·8 (7H, m, Ar and NH), 3·13 (1H, d, *J* 8 Hz, Ar), 3·41 (1H, d, *J* 8 Hz, Ar), 3·65 (1H, t, *J* 8 Hz, Ar), 4·27 (1H, NH, exchanged D_2O), 5·00 [1H, s, C(7)H], 5·8—6·6 (4H, m), 7·05 (2H, t, *J* 8 Hz), 7·2—7·5 (1H, m), 7·6—9·8 (7H, m), and 8·61 (3H, t, *J* 8 Hz, $CH_2{\cdot}CH_3$); *m/e* 635 (*M*, 2%), 589 (*M* − EtOH, 6%), 414 (589 − Cbs, 100%), and 223 (414 − $CbsNH_2$, 50%). Finally 11a-p-*chlorophenylsulphonylamino*-7-p-*chlorophenylsulphonylimino*-4,5,7a,8,9-10,11,11a-*octahydro*-7H-*pyrrolo*[3,2,1-de]*phenanthridine* (XX; Z = Cbs) was eluted (195 mg), m.p. 203—205°, prisms (from ethanol) (Found: C, 54·7; H, 4·4; Cl, 12·1; N, 7·2; S, 10·9. $C_{27}H_{25}Cl_2N_3O_4S_2$ requires C, 54·9; H, 4·2; Cl, 12·0; N, 7·1; S, 10·9%); $\lambda_{max.}$ 227, 274, 284, and 313 nm (ε 37,100, 14,900, 16,200, and 19,100); $\nu_{max.}$ 1555 and 3200 cm^{-1}; τ [$(CD_3)_2SO$] 1·82 (1H, NH, exchanged D_2O), 2·03 (2H, d, *J* 8 Hz), 2·37 (2H, d, *J* 8 Hz), 2·64 (2H, d, *J* 8 Hz), 2·8—3·2 (5H, m), 5·9—7·5 (5H, m), and 7·9—9·4 (8H, m); *m/e* 589 (*M*, 24%), 414 (*M* − Cbs, 6%), 399 (*M* − CbsNH, 52%, *m** 270·3), 333 (11%), 239 (414 − Cbs, 13%), 224 (399 − Cbs, 60%, *m** 125·8), and 223 (100%).

1,2,6a,7,8,9,10,10a-*Octahydro*-6a-*hydroxypyrrolo*[3,2,1-de]-*acridin*-6-*one* (XXVIII).—Compound (XIX; Z = Ts) (500 mg) was boiled for 4 h in ethanol (10 ml) containing aqueous sodium hydroxide (2M; 10 ml). The mixture was diluted with water and extracted (chloroform). The residue formed pale yellow fluorescent prisms (from ethanol), m.p. 180—181° (175 mg) (Found: C, 74·1; H, 7·0; N, 5·8. $C_{15}H_{17}NO_2$ requires C, 74·1; H, 7·0; N, 5·8%); $\lambda_{max.}$ 238, 257sh, and 385 nm (ε 23,100, 8100, and 4900); $\nu_{max.}$ 1656 and 3490 cm^{-1}; τ 2·47 [1H, d, *J* 8 Hz, C(5)H], 2·78 [1H, d, *J* 8 Hz, C(3)H], 3·35 [1H, t, *J* 8 Hz, C(4)H], 6·0—6·3 (1H, m), 6·30 (1H, s, OH, exchanged D_2O), 6·7—7·0 (4H, m), and 8·0—8·9 (8H, m); *m/e* 243 (*M*, 100%), 226 (*M* − OH, 7%), 215 (*M* − 28, 15%), 201 (*M* − C_3H_6, 12%), 187 (21%), 172 (29%), and 119 (67%). Compound (XXVIII) (150 mg) was heated with polyphosphoric acid (2·5 g; 120°; 15 min). The mixture was cooled, diluted with water, basified (NaOH), and extracted ($CHCl_3$). The residue was recrystallised from benzene: 1,2,7,8,9,10-*hexahydropyrrolo*[3,2,1-de]*acridin*-6-*one* (XXIX) formed needles (79 mg), m.p. 230—232° (Found: C, 79·9; H, 6·7; N, 6·2. $C_{15}H_{15}NO$ requires C, 80·0; H, 6·7; N, 6·2%); $\lambda_{max.}$ 220, 243, 249, 278sh, 293sh, 305sh, 322sh, 333, and 349 nm (ε 22,100, 33,700, 33,400, 1300, 2300, 4100, 8800, 14,100, and 14,000); $\nu_{max.}$ 1630 cm^{-1}; τ 2·09 (1H, d, *J* 7 Hz), 2·7—3·0 (2H, m, Ar), 5·78 [2H, t, *J* 8 Hz, $C(1)H_2$], 6·65 [2H, t, *J* 7 Hz, $C(2)H_2$], 7·2—7·6 (4H, m), and 8·0—8·4 (4H, m); *m/e* 225 (*M*, 71%), 224 (100%), and 210 (65%).

6-p-*Chlorophenylsulphonylamino*-1,2-*dihydro*-4,6-*butano*-4H-*pyrrolo*[3,2,1-ij]*quinolin*-5(6H)-*one* (XXVI; Z = Cbs). —Sodium hydroxide (500 mg) in water (2 ml) was added dropwise to a stirred suspension of (XIX; Z = Cbs) (500 mg) in acetone (10 ml). The mixture was stirred for 15 min after the addition, poured into water, and neutralised (HCl). The solid was collected and recrystallised from ethanol. The *ketone* (XXVI; Z = Cbs) formed prisms (293 mg), m.p. 192—200° (decomp.) (Found: C, 60·5; H, 5·1; Cl, 8·3; N, 6·7; S, 7·5. $C_{21}H_{21}ClN_2O_3S$ requires C, 60·5; H, 5·0; Cl, 8·5; N, 6·7; S, 7·7%); $\lambda_{max.}$ 202, 228sh, 254sh, and 308 nm (ε 48,600, 21,000, 8700, and 2400); $\nu_{max.}$ 1723 and 3250 cm^{-1}; τ 2·47 (2H, d, *J* 8 Hz), 2·71 (2H, d, *J* 8 Hz), 2·9—3·1 (2H, m, Ar), 3·47 (1H, t, *J* 7 Hz, Ar), 4·16 (1H, NH, exchanged D_2O), 6·1—7·0 (5H, m), 7·7—9·0 (8H, m); *m/e* 416 (*M*, 18%), 241 (*M* − Cbs, 100%), and 224 (27%). This compound (200 mg) was heated (180°; 0·1 mmHg; 1·5 h). The residue was separated by p.l.c. giving starting material (50 mg) and a faster running material (89 mg). 6-p-*Chlorophenylsulphonylimino*-1,2,6a,7,8,9,10,10a-*octahydro*-6a-*hydroxy*-6H-*pyrrolo*[3,2,1-de]*acridine* (XXVII; Z = Cbs) formed bright orange prisms (from ethanol), m.p. 145—146° (Found: C, 60·5; H, 5·2; N, 6·7. $C_{21}H_{21}ClN_2O_3S$ requires C, 60·5; H, 5·0; N, 6·7%); $\lambda_{max.}$ 231, 293, and 438 nm (ε 24,800, 12,300, and 7800); $\nu_{max.}$ 1573 and 3410 cm^{-1}; τ 1·9—2·1 (3H, m, Ar), 2·56 (2H, d, *J* 8 Hz, high-field half of Cbs signal), 2·85 (1H, d, *J* 7 Hz, Ar), 3·37 (1H, t, *J* 7 Hz, Ar), 3·84 (1H, s, OH, exchanged D_2O), 6·0—7·0 (5H, m), and 7·8—8·6 (8H, m); *m/e* 416 (*M*, 15%), 241 (100%), and 224 (38%).

Action of TFA on the Bridged Compound (XIX; Z = Cbs). —A solution of (XIX; Z = Cbs) (400 mg) in TFA was kept at room temp. for 7 days; the acid was then removed and methanol (5 ml) added. The solid was collected and recrystallised from ethanol yielding (XXIV; Z = Cbs) (304 mg, 70%), m.p. 159—162°, identical (t.l.c., i.r.) with the material described earlier.

Reaction between the Cycloheptapyrroloindole (XVIII) *and* p-*Nitrobenzenesulphonyl Azide*.—The indole (2 g) and azide (4·4 g) were mixed in chloroform (25 ml). After 24 h the solvent was removed and acetonitrile (10 ml) added. The solid was collected and recrystallised from acetonitrile. 4,5,7a,8,9,10,11,11a-*Octahydro*-11a-p-*nitrophenylsulphonylamino*-7-p-*nitrophenylsulphonylimino*-7H-*pyrrolo*[3,2,1-de]-*phenanthridine* (XX; Z = *p*-$O_2N{\cdot}C_6H_4{\cdot}SO_2$) formed prisms, m.p. 245° (resolidifies and melts *ca.* 300°), not sharp since (XXIII) is being formed (Found: C, 53·4; H, 4·1; N, 11·8. $C_{27}H_{25}N_5S_2O_8$ requires C, 53·0; H, 4·1; N, 11·5%); $\lambda_{max.}$ ($CHCl_3$) 272, 305, and 322 nm (ε 26,900, 18,100, and 14,200); $\nu_{max.}$ 1564 and 3280 cm^{-1}; *m/e* (*M* not detected) 409 (*M* − $ArSO_2NH_2$, 7%), 344 (14%), and 223 (100%). The acetonitrile liquors were concentrated to small volume and the solid which separated was recrystallised from acetonitrile.

1,2,5,6-*Tetrahydro*-6-p-*nitrophenylsulphonylamino*-5-p-*nitrophenylsulphonylimino*-4,6-*butano*-4H-*pyrrolo*[3,2,1-ij]-*quinoline* (XIX; Z = *p*-$O_2N{\cdot}C_6H_4{\cdot}SO_2$) formed orange prisms, m.p. 129—137° (decomp.) (1·45 g) (Found: C, 53·7; H, 4·8; N, 13·6; S, 10·3. $C_{27}H_{25}N_5O_8S_2$,MeCN requires C, 53·4; H, 4·3; N, 12·9; S, 9·8%); $\lambda_{max.}$ 256 nm (ε 27,600); $\nu_{max.}$ 1632 (C=N), 2250 (C≡N), and 3220 (NH) cm^{-1}; τ 1·59, 1·73, 1·97, and 2·62 (each 2H, d, *J* 8 Hz, $ArSO_2$ signals), 3·07 (1H, d, *J* 7 Hz), 3·6—4·0 (2H, m, Ar), 4·35 (1H, dd, *J* 9 and 3 Hz), 4·40 (1H, s, NH, exchanged D_2O), 6·2—7·0 (5H, m), 7·99 (3H, s, MeCN), and 7·5—9·3 (7H, m). Chromatography of the residues gave, in order

of elution, 1,2,7,8,9,10-*hexahydro*-6-p-*nitrophenylsulphonylimino*-6H-*cyclohepta*[b]*pyrrolo*[3,2,1-hi]*indole* (XXXV), yellow needles, m.p. 189—191° (from ethanol) (190 mg) (Found: C, 61·6; H, 5·0; N, 9·9; S, 7·8. $C_{21}H_{19}N_3O_4S$ requires C, 61·6; H, 4·7; N, 10·3; S, 7·8%); $\lambda_{max.}$ 210, 257, and 360 nm (ε 33,900, 24,000, and 31,000); $\nu_{max.}$ 1531 cm^{-1}; τ 1·66 and 1·84 (each 2H, d, *J* 8 Hz), 2·70 (1H, m), 2·9—3·1 (2H, m), 5·63 (2H, t, *J* 7 Hz), 6·3—6·6 (4H, m), 6·93 (2H, t, *J* 7 Hz), and 7·8—8·3 (4H, m); *m/e* 409 (*M*, 82%), 345 (*M* − SO_2, 100%), and 223 (*M* − $ArSO_2$, 94%): compound (XX; Z = *p*-$O_2N{\cdot}C_6H_4{\cdot}SO_2$) (120 mg, total yield 21%): compound (XIX; Z = *p*-$O_2N{\cdot}C_6H_4{\cdot}SO_2$) (30 mg): and finally 7-*ethoxy*-4,5,7a,8,9,10,11,11a-*octahydro*-7a,11a-*bis*-(p-*nitrophenylsulphonylamino*)-7H-*pyrrolo*[3,2,1-de]*phenanthridine* (XXIV; Z = *p*-$O_2N{\cdot}C_6H_4{\cdot}SO_2$), orange prisms (170 mg) (from ethanol), m.p. 158—160° (Found: C, 53·4; H, 4·8; N, 10·9; S, 9·9. $C_{29}H_{31}N_5O_9S_2$ requires C, 53·0; H, 4·7; N, 10·7; S, 9·7%); $\lambda_{max.}$ 258 nm (ε 25,200); $\nu_{max.}$ 3265br cm^{-1}; τ [$(CD_3)_2SO$] 1·31—1·6 (5H, m), 1·6—1·9 (3H, m), 2·0—2·5 (2H, m), 3·1—3·4 (2H, m), 3·74 (1H, t, *J* 8 Hz), 4·62 (1H, s), 5·9—6·6 (4H, m), 7·1 (2H, m), 8·74 (3H, t, *J* 7 Hz, $CH_2{\cdot}CH_3$), and 7·4—9·6 (8H, m).

A suspension of (XX; Z = *p*-$O_2N{\cdot}C_6H_4{\cdot}SO_2$) (250 mg) in ethanol (5 ml) and water (5 ml) containing sodium hydroxide (300 mg) was boiled for 30 min, then poured into water (25 ml), and the solid was collected. Recrystallisation from chloroform–methanol gave 4,5,8,9,10,11-*hexahydro*-7-p-*nitrophenylsulphonylimino*-7H-*pyrrolo*[3,2,1-de]*phenanthridine* (XXIII; R = NO_2) (156 mg, 93%), pale yellow needles, m.p. 312—314° (decomp.) (Found: C, 62·2; H, 4·8; N, 10·0; S, 7·9. $C_{21}H_{19}N_3O_4S$ requires C, 61·6; H, 4·7; N, 10·3; S, 7·8%); $\lambda_{max.}$ ($CHCl_3$) 268, 329sh, 342, and 357 nm (ε 40,300, 11,900, 17,600, and 15,600); $\nu_{max.}$ 1500 cm^{-1}; τ (TFA) 1·44 (2H, d, *J* 9 Hz), 1·74 (2H, d, *J* 9 Hz), 1·8—2·1 (3H, m, Ar), 4·52 (2H, t, *J* 7 Hz), 6·14 (2H, t, *J* 7 Hz), 6·56 (2H, t, *J* 7 Hz), 7·40 (2H, t, *J* 7 Hz), and 7·8—8·4 (4H, m); *m/e* 409 (*M*, 7%), 344 (5%), and 223 (100%).

A solution of (XIX; Z = *p*-$O_2N{\cdot}C_6H_4{\cdot}SO_2$) (200 mg) in propanol (10 ml) was boiled for 1 h; the solvent was then removed and the residue purified by chromatography. The major component was recrystallised from ethanol affording yellow prisms, m.p. 159—161° (137 mg) of (XXIV; Z = *p*-$O_2N{\cdot}C_6H_4{\cdot}SO_2$), identical (t.l.c., i.r.) with the material described earlier.

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