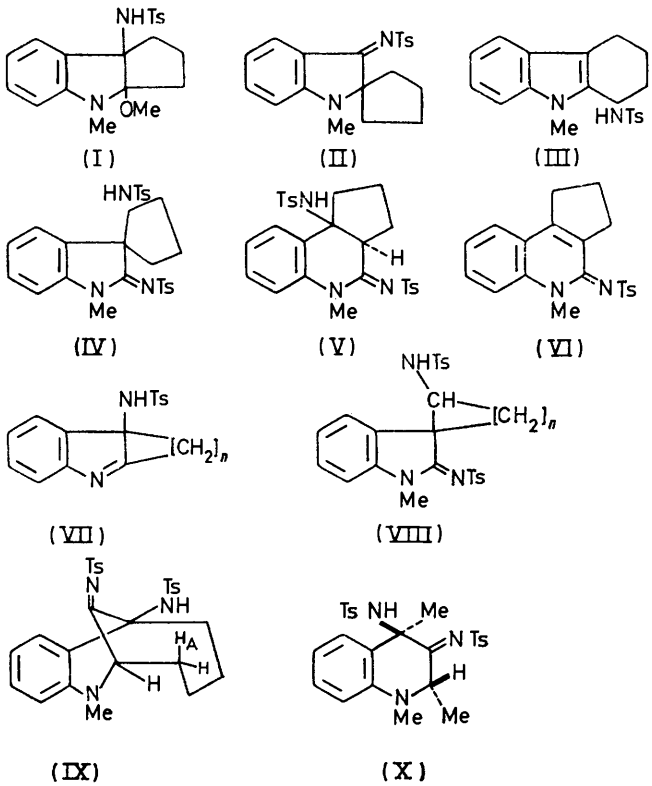
Reactions of Toluene-*p*-sulphonyl Azide with Derivatives of Cyclohept- and Cyclo-oct-indole

By **A. Sydney Bailey** * and **John F. Seager**, Dyson Perrins Laboratory, South Parks Road, Oxford OX1 3QY

5,6,7,8,9,10-Hexahydrocyclohept[*b*]indole reacts with tosyl azide to form 6,7,8,9,10,10a-hexahydro-10a-*p*-tolylsulphonylaminocyclohept[*b*]indole (VII; $n = 5$) in poor yield and its *N*-methyl derivative yields 1-methyl-2'-*p*-tolylsulphonylamino-2-*p*-tolylsulphonyliminoindole-3-spirocyclohexane (VIII; $n = 4$). 2,3,4,5,6,7-hexahydro-1-methyl-7-*p*-tolylsulphonylamino-12-*p*-tolylsulphonylimino-2,7-methano-1*H*-1-benzazepine (XI), 5-methyl-5,6,6a,7,8,9,10,10a-octahydro-10a-*p*-tolylsulphonylamino-6-*p*-tolylsulphonyliminophenanthridine (XI), and 5,6,7,8,9,10-hexahydro-5-methyl-10-*p*-tolylsulphonyliminocyclohept[*b*]indole (XXI). No 1:1 reaction products were isolated.

6,7,8,9,10,11-Hexahydro-5*H*-cyclo-oct[*b*]indole and its *N*-methyl derivative react in a similar manner to their lower homologues, although the NH derivative reacts smoothly in high yield, in contrast to its lower homologue.

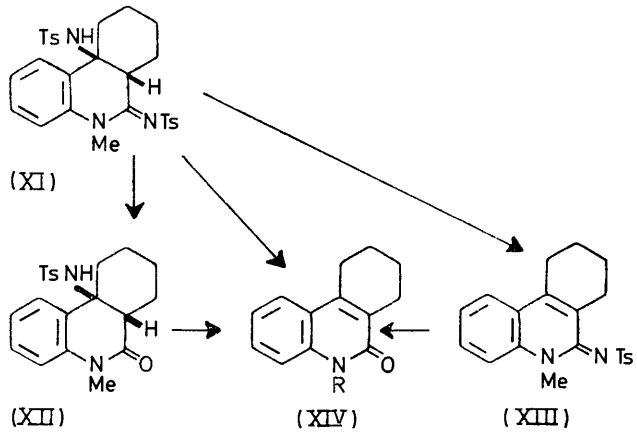
N-METHYLTETRAHYDROCYCLOPENT[*b*]INDOLE reacts rapidly with tosyl azide in methanol forming compound (I) in high yield [1] and *N*-methyltetrahydrocarbazole reacts with this azide to form five products (II)—(VI).[2,3] It was of interest to extend these observations by examining the reactions of derivatives of cyclohept- and cyclo-oct-indoles since it is known [4] that cycloheptene and cyclo-octene react faster with picryl azide than does cyclohexene.



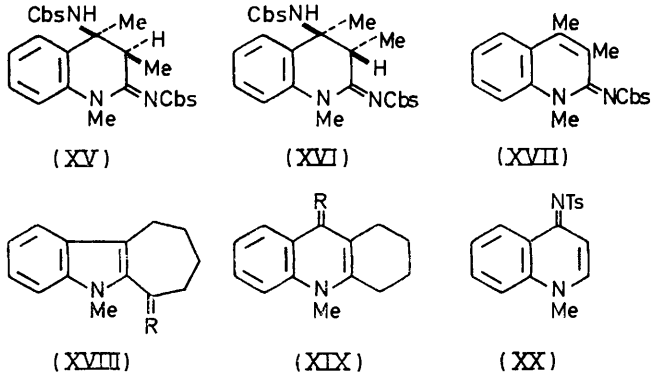
Hexahydrocyclohept[*b*]indole reacts rapidly with tosyl azide in a variety of solvents to give a tarry mixture of products from which no crystalline material could be obtained; however, by using excess of azide as solvent a small yield of the indolenine (VII; $n = 5$) was isolated; the spectral properties of this compound were similar to those of the compound (VII; $n = 4$) obtained from tetrahydrocarbazole and tosyl azide.[2] Hexahydro-*N*-methylcyclohept[*b*]indole reacted violently with the azide, the neat compounds exploding when mixed. The reaction was, therefore, run in a variety of solvents. In methanol the main product was compound (VIII; $n = 4$); the mass spectrum of the compound showing the characteristic fragmentation of the spiro-ring at C(3) with formation of fragments such as $TsNC_2H_4$. The spectrum was similar to that of compound (IV) although differences in intensities of the peaks suggest that the six-membered ring in (VIII; $n = 4$) is more stable than the five-membered ring in (IV) and that cleavage of the spiro-ring occurs after loss of one Ts group. The second compound isolated was assigned structure (IX); the compound was pale yellow, the u.v. spectrum contained a series of peaks and shoulders gradually falling in intensity, the highest peak in the mass spectrum appeared at *m/e* 171, and the i.r. spectrum contained bands at 3295 (NH) and 1600 cm^{-1} (non-conjugated C=N). The properties of this material are very similar to those of compound (X) which was obtained [1] in small quantity from the reaction between 2-ethyl-1,3-dimethylindole and tosyl azide. The structure of (X) has been confirmed by *X*-ray crystallography.[5] In the n.m.r. spectrum of (IX) the signal from the proton at C(2) is a doublet (τ 5·50, J 7 Hz) and not a quartet, showing that coupling with proton A is very small. The third product (XI) was obtained in small yield from the reaction in methanol but was the only product isolated from the reaction in pyridine–sodium hydroxide. The physical properties of (XI) are similar to those of (V) but the chemical properties are quite different; (V) is smoothly transformed into (VI) on boiling with 1,5-diazabicyclo[4.3.0]-non-5-ene (DBN) in ethanol for 6 h. In contrast (XI) was recovered after being boiled for 24 h with the same base in 2-methoxyethanol. Further, boiling (V) with alcoholic potassium hydroxide solution for 1·5 h resulted in elimination of toluene-*p*-sulphonamide and hydrolysis to form the corresponding quinolone; [2] however boiling

[1] A. S. Bailey, R. Scattergood, and W. A. Warr, *J. Chem. Soc.* (*C*), 1971, 3769.
[2] A. S. Bailey, R. Scattergood, and W. A. Warr, *J. Chem. Soc.* (*C*), 1971, 2479.
[3] A. S. Bailey, A. J. Buckley, and J. F. Seager, *J.C.S. Perkin I*, 1973, 1809.
[4] A. S. Bailey and J. E. White, *J. Chem. Soc.* (*B*), 1966, 819.
[5] T. S. Cameron, unpublished results.

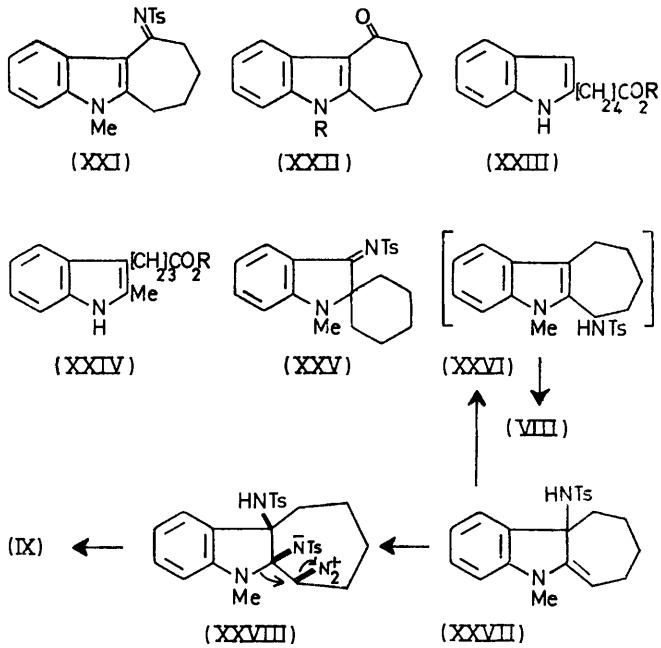
(XI) with alcoholic alkali for 24 h afforded the hydrolysis product (XII), no elimination occurring; and (XIV; R = Me) was only obtained directly from (XI) by boiling



it with potassium hydroxide in ethylene glycol. Elimination of $TsNH_2$ from (XI) to yield (XIII) was finally achieved either by sublimation of (XI) or by dissolving (XI) in trifluoroacetic acid at room temperature [this acid-catalysed reaction has also been carried out on (V) ⟶ (VI) and (XVI) ⟶ (XVII)]. Compound (XIII) showed a characteristic u.v. spectrum,[2] and hydrolysis of (XIII) provided another route to (XIV; R = Me), the latter being synthesised by the methylation of (XIV; R = H).[6] These observations suggest that the proton at C(6a) and the TsNH group at C(10a) in compound (XI) are in a *cis*-relationship. It has been shown[1] that (XV) readily eliminates *p*-chlorobenzenesulphonamide ($CbsNH_2$) on treatment with DBN whilst (XVI) affords a mixture of (XVI) and (XVII) after heating for 24 h with this base.



The final product was obtained in 4% yield from the reaction in acetic acid. The mass spectrum and analytical data suggested a formula $C_{21}H_{22}N_2O_2S$, *i.e.* the compound is isomeric with (XIII); the i.r. spectrum contained a band at 1512 cm^{-1} but no band due to NH. The n.m.r. spectrum showed τ 1·85 (1H, d, *J* 8 Hz), 2·02 (2H, d, *J* 8 Hz, low-field half of tosyl signal), 2·6—3·0 (5H, m, Ar), 6·31 (3H, s, NMe), 6·58 (2H, t, *J* 6 Hz), 7·03 (2H, t, *J* 6 Hz), 7·58 (3H, tosyl-Me), and 8·0—8·2 (4H, m). Structure (XVIII; R = NTs) was first considered since the formation of products of this type has been observed [*e.g.* compound (VIII) in ref. 1 and compound (V) in ref. 2]; such a structure failed to explain the signal at τ 1·85 in the n.m.r. spectrum of our material. The 4-quinolone-type structure (XIX; R = NTs) was next considered since it is known[7] that indoles may be converted into quinolones on oxidation, and such a



structure would explain the low-field signal in the n.m.r. spectrum. The preparation of compound (XX) has been described briefly.[8] A sample of (XX) was kindly supplied by Professor Renault and its u.v. spectrum was quite different from that of our material. We were then forced to consider structure (XXI) for which no model compounds were available. Hydrolysis of the sulphonylimine gave a carbonyl-containing compound whose n.m.r. spectrum still contained a signal at low field (τ 1·51); and the hydrolysis product was neither of the known compounds (XVIII; R = O)[9] or (XIX; R = O).[10] Compound (XXII; R = Me) is unknown although (XXII; R = H) has been prepared by the irradiation of acridine *N*-oxide followed by hydrogenation.[11] We attempted the synthesis from the phenylhydrazone of 5-acetylvaleric acid.[12] Using conditions

[6] B. K. Blount, W. H. Perkin, and S. G. P. Plant, *J. Chem. Soc.*, 1929, 1975.

[7] B. Witkop, J. B. Patrick, and M. Rosenblum, *J. Amer. Chem. Soc.*, 1951, **73**, 2641; B. Witkop and S. Goodwin, *ibid.*, 1953, **75**, 3371; E. Winterfeldt, *Annalen*, 1971, **745**, 23.

[8] J. Renault and J. C. Cartron, *Compt. rend.*, 1970, **270***C*, 1183; C. Feller and J. Renault, *Bull. Soc. chim. France*, 1972, 1112.

[9] K. Ishizumi, T. Shioiri, and S. Yamada, *Chem. and Pharm. Bull.* (*Japan*), 1967, **15**, 863.

[10] R. A. Reed, *J. Chem. Soc.*, 1944, 425.

[11] M. Ishikawa, C. Kaneko, and S. Yamada, *Tetrahedron Letters*, 1968, 4519; C. Kaneko, S. Yamada, I. Yokoe, and M. Ishikawa, *ibid.*, 1967, 1873.

[12] J. R. Schaeffer and A. O. Snoddy, *Org. Synth.*, 1951, **31**. 3.

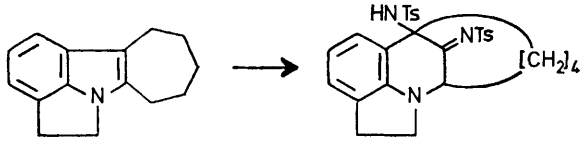
(ethanol–sulphuric acid)[13] for the Fischer indole synthesis which favoured the formation of (XXIII) the carboxy-group was esterified and the desired compound (XXIII; R = Et) was readily isolated as a crystalline solid whose structure was proved by its n.m.r. spectrum; the isomeric compound (XXIV; R = Et) was also obtained. Hydrolysis of the ester gave the desired acid (XXIII; R = H) which was cyclised to form (XXII; R = H), identical with the material prepared[11] from acridine *N*-oxide. Methylation of (XXII; R = H) yielded (XXII; R = Me) identical with the material obtained by hydrolysis of our reaction product, thus confirming structure (XXI).

No sign of any 1 : 1 products [*e.g.* (XXV) and (XXVI)] was obtained in these azide reactions [*cf.* the formation of (II) and (III) in good yields]; an attempt was made to isolate these by slowly adding azide to an excess of the indole, but only the four products described above were obtained. The yields of the various products are summarised in the Table. The formation of (VIII; $n = 4$)

Yields (%) of products from the reaction of *N*-methylhexahydrocyclohept[*b*]indole and tosyl azide

	Solvent			
Product	MeOH	C_5H_5N	C_5H_5N–NaOH	HOAc
(VIII; $n = 4$)	49	11		
(IX)	12	14		15
(XI)	10	15	64	35

via (XXVI) [obtained by a 1,3 shift from (XXVII)] is favoured in the least polar solvent while the addition of the second molecule of azide to (XXVII) occurs rapidly in pyridine and in acetic acid; the effect of solvent on these reactions[3] and on other dipolar addition reactions[14] has been reported. The different reactivities of (V) and (XI) suggests that addition of azide to (XXVII) occurs from the opposite side to that occurring with the corresponding compound in the tetrahydrocarbazole series. The formation of (IX) indicates that addition of the second

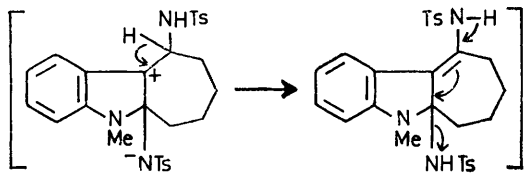


(XXIX) (XXX)

molecule of azide can occur *syn* to the TsNH group in (XXVII) affording the intermediate (XXVIII). This is the only configuration which allows the NMe and N_2^+ groups to be *trans* and coplanar and affords the correct geometry at C(2) in (IX); although the yield of (IX) is small (XXX) is obtained from (XXIX) in 59% yield.[15]

The action of heat on (VIII; $n = 4$) was examined in an attempt to form (XXI) by the route[16] indicated *via* (XXXI); tarry mixtures were obtained, and t.l.c. showed the absence of (XXI).

(VIII)

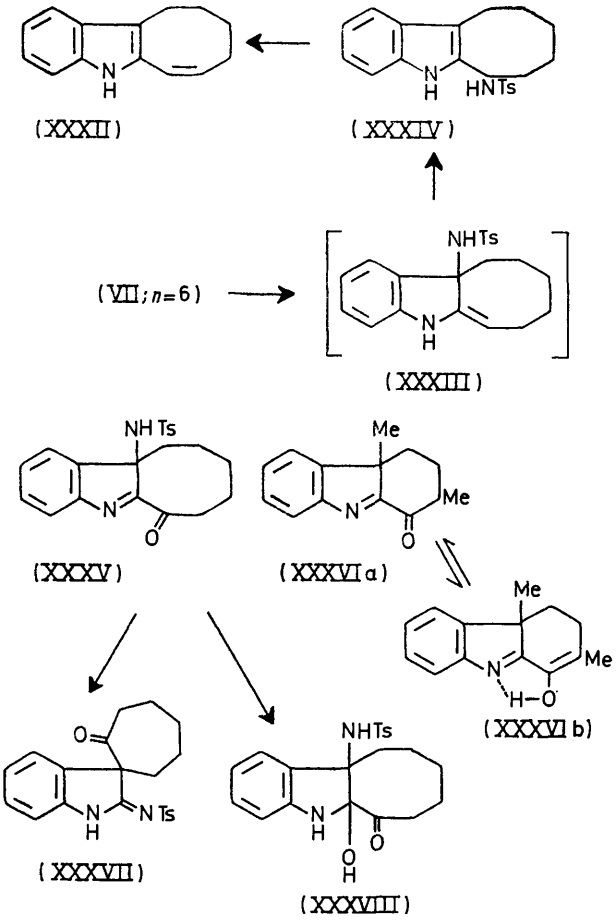


(XXXI)

In striking contrast to the behaviour of hexahydrocyclohept[*b*]indole with azides, hexahydro-5*H*-cyclo-oct-[*b*]indole reacted very smoothly with tosyl azide giving a good yield of compound (VII; $n = 6$), and compound (VII; $n = 6$, Cbs replacing Ts) was also obtained using *p*-chlorobenzenesulphonyl azide. The reaction of these azides with tetrahydrocarbazole in pyridine affords quinoline derivatives[3] but under these conditions hexahydrocyclo-octindole yielded only the indolenines (VII; $n = 6$) with both TsN_3 and $CbsN_3$. The action of heat on compound (VII; $n = 4$) results in the formation of (III; H replacing Me) and dihydrocarbazole dimer.[3] However, heating (VII; $n = 6$) afforded toluene-*p*-sulphonamide and compound (XXXII), presumably *via* (XXXIII) and (XXXIV). The u.v. spectrum of the compound was similar to that of a 2-vinylindole[17] and not a 3-vinylindole;[18] further, 3-vinylindoles are reported to be rather unstable. Boiling compound (VII; $n = 6$) in propanol gave toluene-*p*-sulphonamide, (XXXII), and (XXXIV). When tosyl azide was mixed with the hexahydrocyclo-octindole in acetic acid solution the oxidation product (XXXV) was obtained; the u.v. spectrum was similar to that reported[19] for (XXXVI) but the i.r. spectrum of our material showed no OH band, corresponding to a structure of type (XXXVIb) (*cf.* the spectral properties of cyclic 2-acylindoles as a function of ring size).[20] Compound (XXXV) is probably formed *via* (VII; $n = 6$) since a solution of the latter compound in acetic acid gradually formed (XXXV) in good yield; (XXXV) may also be obtained by shaking in air a solution of (VII; $n = 6$) in acetic acid in the presence of platinum black or, better, passing air through a solution of (VII; $n = 6$) in acetic acid containing a trace of copper(II) acetate. The formation of (XXXV) may arise by peroxidation of (VII; $n = 6$) *via* (XXXIII) (*cf.* the peroxidation of indoles to 2-acylindoles[21]) and it

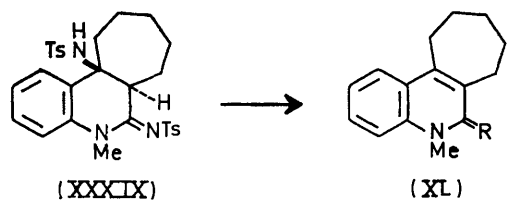
[13] M. H. Palmer and P. S. McIntyre, *J. Chem. Soc.* (*B*), 1969, 446.
[14] P. D. Kadaba, *Tetrahedron*, 1969, **25**, 3053; J. E. McMurry and A. P. Coppolino, *J. Org. Chem.*, 1973, **38**, 2821.
[15] J. F. Seager, D.Phil. Thesis, Oxford, 1973.
[16] (*a*) G. Jones and T. S. Stevens, *J. Chem. Soc.*, 1953, 2344; (*b*) R. J. Sundberg, ' The Chemistry of Indoles,' Academic Press, New York, 1970, pp. 316—319.
[17] A. S. Bailey, A. G. Holton, and J. F. Seager, *J.C.S. Perkin I*, 1972, 1003; F. E. Ziegler, E. B. Spitzner, and C. K. Wilkins, *J. Org. Chem.*, 1971, **36**, 1759.
[18] L. J. Dolby and G. W. Gribble, *Tetrahedron*, 1968, **24**, 6377.
[19] H. J. Teuber and D. Cornelius, *Chem. Ber.*, 1965, **98**, 2111.
[20] T. Shiori, K. Ishizumi and S. Yamada, *Chem. and Pharm. Bull.* (*Japan*), 1967, **15**, 1010.
[21] Ref. 16*b*, pp. 282—288.

is known [7] that the hexahydrocyclo-octindole is very readily oxidised to the 6-oxo-compound. Compound



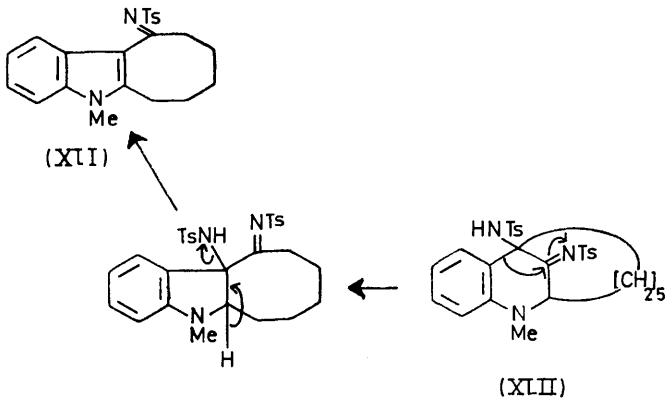
(XXXV) is rather insoluble, and on attempting to recrystallise it from 2-methoxyethanol an isomeric compound (XXXVII) was obtained [*cf.* the transformation of compound (X; Z = Cbs) to compound (XIX; R = H, Z = Cbs) described in ref. 3]. On warming with dilute alkali (XXXV) slowly added a molecule of water across the C=N bond, forming (XXXVIII), and similar products have been obtained from the reaction between tetrahydrocyclopentindole and tosyl azide.[1]

From the reaction between hexahydro-5-methyl-5*H*-cyclo-octindole four products have been isolated. The major product with ethanol, ether, or acetic acid as solvent was compound (XXXIX). The material showed



no molecular ion in the mass spectrum and on heating to its m.p. the compound lost toluene-*p*-sulphonamide forming (XL; R = NTs); this was also formed from (XXXIX) by boiling for 5 min in ethanol with DBN, in striking contrast to the behaviour of the lower homologue (XI). Treatment of (XXXIX) with aqueous alkali gave a mixture of (XL; R = NTs) and (XL; R = O). When pyridine was used as solvent the major product was (XL; R = NTs), no (XXXIX) being isolated. The second product was the spiro-compound (VIII; $n = 5$). In the mass spectrum the characteristic fragmentation of the spiro-ring was observed although the peaks were small. Compound (XLI) was isolated in small yield and its structure was assigned by comparison of its properties with those of (XXI); the final product isolated was the bridge derivative (XLII). Various samples of (XLII) had different m.p.s although they appeared to be pure by t.l.c. A small quantity of (XLII) was melted and compound (XLI) obtained in good yield, indicating how compounds of type (XLI) are formed in these reactions [*cf.* the formation [2] of tetrahydrocarbazole from (VII; $n = 4$) by borohydride reduction followed by loss of $TsNH_2$]. No 1 : 1 reaction products corresponding to (II) and (III) were isolated in these experiments. The yields of pure materials in this series were rather low since the separations were difficult and no attempt is made to discuss the proportions of products as a function of the solvents used.

The most striking feature of this study is the very ready elimination of $TsNH_2$ from compounds (V) and (XXXIX) in the presence of base, while (XI) is stable,



suggesting that the geometry of the ring-junction in (XI) is different from that of (V) and (XXXIX).

EXPERIMENTAL

General directions 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 stated otherwise [D = $(CD_3)_2SO$]; i.r. spectra were measured 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. 5,6,7,8,9,10-Hexahydrocyclohept[*b*]indole, m.p. 144—145° (lit.,[22] 144°), and 6,7,8,9,10,11-hexahydro-5*H*-cyclo-oct[*b*]-

[22] W. H. Perkin and S. G. P. Plant, *J. Chem. Soc.*, 1928, 2583.

indole, m.p. 75—76° (lit.,[7] 72—74°), were methylated using sodamide–liquid ammonia–methyl iodide; 5,6,7,8,9,10-hexahydro-5-methylcyclohept[*b*]indole formed needles, m.p. 53—54° (lit.,[23] 50°), and 6,7,8,9,10,11-hexahydro-5-methyl-5*H*-cyclo-oct[*b*]indole formed an oil, b.p. 122—124° at 0·03 mmHg (lit.,[24] 212—213° at 17 mmHg).

6,7,8,9,10,10a-*Hexahydro*-10a-p-*tolylsulphonylaminocyclohept*[b]*indole* (VII; $n = 5$).—A mixture of 5,6,7,8,9,10-hexahydrocyclohept[*b*]indole (5 g) and tosyl azide (10·5 g) was kept at room temperature for 2 weeks. Benzene (5 ml) and cyclohexane (5 ml) were added and 10 days later the solid was collected and recrystallised from benzene (2·8 g, 33%), as pale yellow *needles*, m.p. 147—149° (Found: C, 67·7; H, 6·3; N, 8·1; S, 8·9. $C_{20}H_{22}N_2O_2S$ requires C, 67·8; H, 6·2; N, 7·9; S, 9·0%); $\lambda_{max.}$ 202, 224, and 263 nm (ε 28,000, 16,300, and 5250); $\nu_{max.}$ 3080br cm^{-1}; τ 2·6—3·2 (6H, m, Ar), 3·34 (1H, t, *J* 7 Hz), 3·53 (1H, d, *J* 7 Hz), 4·02 (1H, s, NH, exchanged D_2O), 6·7—7·2 (2H, m), 7·67 (3H, s, tosyl-Me), and 7·6—8·9 (8H, m); *m/e* 354 (M^+, 9%), 199 (M — Ts, 100), 182 (199 — NH_3, 21, *m** 166·5).

Reaction between N-*Methylhexahydrocyclohept*[b]*indole and Tosyl Azide.*—(a) The indole (2 g) was added to a solution of TsN_3 (4 g) in methanol (6 ml). After 24 h the solid which had separated was collected and recrystallised from acetonitrile affording colourless prisms. The acetonitrile mother-liquors were concentrated to give a mixture of colourless and of yellow prisms. These were separated manually (total yield of colourless material 2·65 g). 1-*Methyl*-2′-p-*tolylsulphonylamino*-2-p-*tolylsulphonyliminoindoline*-3-*spirocyclohexane* (VIII; $n = 4$) formed colourless prisms, m.p. 234—237°, from acetonitrile (Found: C, 62·9; H, 5·8; N, 7·9; S, 11·9. $C_{28}H_{31}N_3O_4S_2$ requires C, 62·6; H, 5·8; N, 7·8; S, 11·9%); $\lambda_{max.}$ 200, 224, 283, and 286sh nm (ε 43,400, 34,300, 16,300, and 12,200); $\nu_{max.}$ 1585 and 3250 cm^{-1}; τ (D) 2·04 (2H, d, *J* 8 Hz, low-field half of tosyl signal), 2·3—3·0 (10H, m, Ar), 3·25 (1H, d, *J* 9 Hz, NH, exchanged D_2O), 5·55 (1H, m), 6·63 (3H, s, NMe), 7·60 (3H, s, tosyl-Me), 7·66 (3H, s, tosyl-Me), and 8·1—9·0 (8H, m); *m/e* 537 (M^+, 13%), 339 (4), 327 (2), 313 (3), 301 (1), 382† (M — Ts, 89, *m** 271·7), 227 (382 — Ts, 12%), 211† (382 — $TsNH_2$, 19, *m** 116·6), 185† (382 — $TsNC_2H_4$, 100, *m** 89·6), 173 (382 — $TsNC_3H_4$, 17), and 159 (382 — $TsNC_4H_6$, 32).

The yellow prisms which had been separated by hand were recrystallised from acetonitrile yielding 2,3,4,5,6,7-*hexahydro*-1-*methyl*-7-p-*tolylsulphonylamino*-12-p-*tolylsulphonylimino*-2,7-*methano*-1H-1-*benzazonine* (IX) (650 mg, 12%), m.p. 163—165° (Found: C, 63·0; H, 5·7; N, 8·0; S, 12·2. $C_{28}H_{31}N_3O_4S_2$ requires C, 62·6; H, 5·8; N, 7·8; S, 11·9%), $\lambda_{max.}$ 202, 231, and 305 nm (ε 47,600, 31,300, and 1600); τ 2·13 (2H, d, *J* 8 Hz, low-field half of tosyl signal), 2·60 (2H, d, *J* 8 Hz, high-field half of tosyl signal), 2·7—3·1 (5H, m, Ar), 3·40 (1H, s, NH, exchanged D_2O), 3·44 (1H, d, *J* 7 Hz, Ar), 3·87 (1H, td, *J* 7 and 1 Hz, Ar), 4·19 (1H, dd, *J* 7 and 1 Hz, Ar), 5·50 (1H, d, *J* 7 Hz), 6·63 (1H, m), 7·20 (3H, s, NMe), 7·50 (3H, s, tosyl-Me), 7·63 (3H, s, tosyl-Me), and 7·7—8·6 (7H, m). Chromatography of the methanol mother-liquors from the isolation of (VIII; $n = 4$) on silica (eluting with benzene–ethyl acetate) gave 5,6,6a,7,8,9,10,-10a-*octahydro*-5-*methyl*-10a-p-*tolylsulphonylamino*-6-p-*tolylsulphonyliminophenanthridine* (XI), as prisms (from acetonitrile) m.p. 232—235° (Found: C, 62·6; H, 5·8; N, 7·9; S, 12·1. $C_{28}H_{31}N_3O_4S_2$ requires C, 62·6; H, 5·8; N, 7·8; S, 11·9%); $\lambda_{max.}$ 201, 223, 282, and 292sh nm (ε 36,200, 31,100, 19,600, and 18,100); $\nu_{max.}$ 3305 and 1534 cm^{-1}; τ (D) 2·18 (2H, d, *J* 8 Hz, low-field half of tosyl signal), 2·37 (1H, s, NH, exchanged D_2O), 2·5—3·2 (10H, m, Ar), 6·03 (1H, m), 7·03 (3H, s, NMe), 7·61 (3H, s, tosyl-Me), 7·70 (3H, s, tosyl-Me), and 7·9—9·4 (8H, m); *m/e* 537 (M^+, 3%), 367 (M — TsNH, 8), 211 (367 — H — Ts, 38), 91 (100).

(b) The indole (1 g) was mixed with tosyl azide (2 g) in pyridine (5 ml). After 4 days the solvent was removed and the residue triturated with methanol giving (VIII; $n = 4$) (300 mg, 11%); chromatography of the residue from the mother-liquors gave (IX) (390 mg, 14%) and (XI) (400 mg, 15%).

(c) The indole (1 g) was dissolved in pyridine (5 ml) containing 2M-sodium hydroxide (1 ml) and tosyl azide (2 g) was added. After 2 days compound (XI) (950 mg) was collected. Chromatography gave a further 780 mg of material: no other products were isolated.

(d) The indole (1 g) and azide (2 g) were dissolved in acetic acid (5 ml). After 10 days the solid (IX) (400 mg, 15%) was collected. The acetic acid was evaporated off and the residue recrystallised from acetonitrile giving (XI) (960 mg). Chromatography of the residues (silica, benzene–ethyl acetate) yielded 5,6,7,8,9,10-*hexahydro*-5-*methyl*-10-p-*tolylsulphonyliminocyclohept*[b]*indole* (XXI), as pale yellow needles, m.p. 177—179° (from ethanol) (80 mg, 4%) (Found: C, 68·5; H, 5·9; N, 7·6; S, 8·9. $C_{21}H_{22}N_2O_2S$ requires C, 68·9; H, 6·0; N, 7·7; S, 8·7%); $\lambda_{max.}$ 217, 263, 272sh, and 349 nm (ε 35,400, 10,200, 9200, and 21,700); $\nu_{max.}$ 1512 (C=N) cm^{-1}; *m/e* 366 (M^+, 36%), 302 (M — SO_2, 37, *m** 249·2), 301 (302 — H, 22, *m** 300·0), 211 (M — Ts, 100), and 169 (211 — C_3H_6, 90, *m** 135·4).

Reactions of Compound (XI).—The compound was recovered after being boiled for 24 h with 1,5-diazabicyclo-[4.3.0]non-5-ene (DBN) in 2-methoxyethanol. Compound (XI) (300 mg) was boiled for 24 h with potassium hydroxide (1 g) in ethanol (20 ml) and water (5 ml). The solution was poured into water and neutralised with acetic acid; the solid which separated was recrystallised from ethanol to give 6a,7,8,9,10,10a-*hexahydro*-5-*methyl*-10a-p-*tolylsulphonylaminophenanthridone* (XII) (160 mg), m.p. 250—253° (Found: C, 65·3; 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%); $\lambda_{max.}$ 205, 234, 253, and 282sh nm (ε 49,200, 12,300, 9800, and 2100); $\nu_{max.}$ 1650 (C=O) and 3065 (NH) cm^{-1}; τ 2·43 (1H, m, Ar), 2·7—3·2 (6H, m, Ar), 3·54 (1H, m, Ar), 4·70 (1H, s, NH, exchanged D_2O), 6·72 (1H, m), 7·09 (3H, s, NMe), 7·39 (1H, m), 7·70 (3H, s, tosyl-Me), and 8·0—9·1 (7H, m); *m/e* 384 (M^+, 23%), 229 (M — Ts, 15), 214 (M — TsNH, 100, *m** 119·3), 213 (22), and 187 (22). Compound (XI) (100 mg) was dissolved in trifluoroacetic acid (0·5 ml) and kept at room temperature for 2 days. The solution was poured into water, neutralised (sodium carbonate), and extracted with chloroform. The chloroform extract yielded 5,6,7,8,9-10-*hexahydro*-5-*methyl*-6-p-*tolylsulphonyliminophenanthridine* (XIII), m.p. 182—183°, as needles (45 mg) from ethanol (Found: C, 68·7; H, 6·0; N, 7·5; S, 8·9. $C_{21}H_{22}N_2O_2S$ requires C, 68·9; H, 6·0; N, 7·7; S, 8·7%); $\lambda_{max.}$ 217, 259, 342, and 350sh nm (ε 47,800, 25,200, 13,900, and 13,000); $\nu_{max.}$ 1490 cm^{-1}; τ 2·13 (2H, d, *J* 8 Hz, low-field half of tosyl signal), 2·2—2·8 (6H, m, Ar), 5·89 (3H, s, NMe), 6·9—7·3 (4H, m), 7·60 (3H, s, tosyl-Me), and 8·0—8·4 (4H, m);

[23] G. Plancher, B. Cecchetti, and E. Ghigi, *Gazzetta*, 1929, **59**, 334.

[24] P. Jacquignon and N. P. Buu-Hoï, *J. Org. Chem.*, 1957, **22**, 72.

m/e 366 (M^+, 7%), 302 (M − SO_2, 17), and 211 (M − Ts, 100). Sublimation of (XI) (130 mg) at 230° and 0·01 mmHg for 10 h gave a mixture of starting material and (XIII) (20 mg) separated by p.l.c. (silica, benzene–ethyl acetate 9 : 1, 3 runs). A solution of (XI) (1 g) in ethylene glycol (50 ml) containing water (10 ml) and potassium hydroxide (2 g) was heated (oil-bath, 150°) for 6 h. The solution was cooled, poured into water, and the solid collected. Recrystallisation from petrol (b.p. 60—80°) gave (XIV; R = Me) (240 mg), as needles, m.p. 100—101° (Found: C, 78·8; H, 7·2; N, 6·7. $C_{14}H_{15}NO$ requires C, 78·9; H, 7·0; N, 6·6%); $\lambda_{max.}$ 209sh, 227, 245sh, 264sh, 272, 281, 315sh, 324, and 366sh nm (ε 14,900, 30,000, 8790, 4140, 5650, 5050, 5000, 6300, and 4300); $\nu_{max.}$ 1640 cm^{-1}; τ 2·3—2·9 (4H, m, Ar), 6·28 (3H, s, NMe), 7·0—7·5 (4H, m), and 8·0—8·3 (4H, m); *m/e* 213 (M^+, 100%), 212 (M − H, 73, *m** 211·0) and 198 (M − Me, 87, *m** 184·1). Compound (XII) (200 mg) was sublimed and the sublimate recrystallised from ethanol yielding starting material (94 mg). The ethanol mother-liquors were evaporated and the residue extracted with petroleum. The extracts were concentrated yielding (XIV; R = Me) (30 mg). Alkaline hydrolysis of (XIII) for 2 h gave (XIV; R = Me) (64% yield). Tetrahydrophenanthridone (XIV; R = H) [6] (850 mg; m.p. 268—270°) was dissolved in ethanol (20 ml) containing potassium hydroxide (400 mg). The solvent was removed *in vacuo* and dimethyl sulphate (10 ml) added. The mixture was heated at 100° for 0·5 h, cooled, and potassium hydroxide solution (40%) added slowly. The mixture was extracted with ether, the ether was evaporated off, and the residue extracted with petroleum. *5-Methyl-7,8,9,10-tetrahydro-6-phenanthridone* formed needles, m.p. 99—100° (585 mg), identical with the material described above.

6,7,8,9-Tetrahydro-5-methylcyclohept[b]*indol*-10(5H)-*one* (XXII; R = Me).—Compound (XXI) (32 mg) and potassium hydroxide (300 mg) in ethanol (1 ml) and water (1 ml) were heated under reflux for 17 h. The solution was cooled, poured into water, and extracted with chloroform. Evaporation of the solvent gave a pale brown solid (14 mg), m.p. 130—135°; $\lambda_{max.}$ 212, 248, 263sh, and 304 nm (ε 18,500, 10,700, 6200, and 9400); $\nu_{max.}$ 1628 cm^{-1}; τ 1·51 (1H, m, Ar), 2·6—2·8 (3H, m, Ar), 6·37 (3H, s, NMe), 6·99 (2H, t, *J* 6 Hz), 7·22 (2H, t, *J* 6 Hz), and 7·9—8·3 (4H, m). This material was different from (XVIII; R = O), m.p. 61—63° (lit.,[9] 64·5—65·5°), and from (XIX; R = O), m.p. 170—173° (lit.,[10] 170—172°). 5-Acetylvaleric acid [12] (15 g) was mixed with phenylhydrazine (11·3 g). After 15 min the mixture was heated to 100° for 15 min. To ethanol (280 ml) containing water (40 ml) was added conc. sulphuric acid (304 ml) and 500 ml of this solution was poured onto the phenylhydrazone. The mixture was heated under reflux for 30 min (steam-bath) and then poured onto ice–water. The suspension was extracted with ether, the extracts washed (sodium carbonate), dried, and evaporated. The crystalline residue was boiled with ethanol (15 ml) and the solid collected next day. *Ethyl 5-(indol-2-yl)valerate* (XXIII; R = Et) formed plates, m.p. 93—95° (4·1 g) (Found: C, 73·3; H, 7·8; N, 5·6. $C_{15}H_{19}NO_2$ requires C, 73·5; H, 7·8; N, 5·7%); $\lambda_{max.}$ 210, 273, 278, 282, and 289 nm (ε 30,100, 7200, 7200, 7100, and 5800); $\nu_{max.}$ 1728 and 3360 cm^{-1}; τ 2·02br (1H, s, NH, exchanged D_2O), 2·47 (1H, m, Ar), 2·6—3·0 (3H, m, Ar), 3·76 [1H, s, C(3)H], 5·87 (2H, q, *J* 7 Hz, CH_3CH_2), 7·25 (2H, t, *J* 7 Hz), 7·66 (2H, t, *J* 7 Hz), 8·1—8·5 (4H, m), and 8·76 (3H, t, *J* 7 Hz, CH_3CH_2); *m/e* 245 (M^+, 37%), 200 (M − OEt, 19), 144 (M − $CH_2CH_2CO_2Et$, 63, *m** 84·6), 131 (M − $C_3H_5CO_2Et$, 55, *m** 70·0), and 130 (131 − H, 100, *m** 129·0). Evaporation of the ethanol gave a semi-solid mass which was dried on a porous tile. The solid was recrystallised from cyclohexane yielding *ethyl 4-(2-methylindol-3-yl)butyrate* (XXIV; R = Et) as needles (1·7 g), m.p. 65—68° (Found: C, 73·5; H, 7·7; N, 5·8. $C_{15}H_{19}NO_2$ requires C, 73·5; H, 7·8; N, 5·7%); $\lambda_{max.}$ 227, 283, and 291 nm (ε 41,200, 8800, and 7800); $\nu_{max.}$ 1726 and 3370 cm^{-1}; τ 2·27 (1H, s, NH, exchanged D_2O), 2·52 (1H, m, Ar), 2·7—3·0 (3H, m, Ar), 5·89 (2H, q, *J* 7 Hz, CH_3CH_2), 7·25 (2H, t, *J* 7 Hz), 7·65 [3H, s, C(2)Me], 7·66 (2H, t, *J* 7 Hz), 8·03 (2H, quint, *J* 7 Hz), and 8·77 (3H, t, *J* 7 Hz, CH_3CH_2); *m/e* 245 (M^+, 21%), 144 (M − $C_2H_4CO_2Et$, 100, *m** 84·6) and 143 (144 − H, 10, *m** 142·0). The sodium carbonate washings from the Fischer indole preparation were acidified, and the solid was collected, dried, and recrystallised from benzene (1·7 g). The material was identical with that obtained by alkaline hydrolysis of (XXIII; R = Et). *5-(Indol-2-yl)valeric acid* (XXIII; R = H) formed plates, m.p. 147—148°, from benzene (Found: C, 72·1; H, 7·0; N, 6·4. $C_{13}H_{15}NO_2$ requires C, 71·9; H, 6·9; N, 6·5%); $\lambda_{max.}$ 220, 273, 278, 282, and 289 nm (ε 29,800, 7400, 7500, 7400, and 6100); $\nu_{max.}$ 1714 and 3390 cm^{-1}; *m/e* 217 (M^+, 29%), 144 (19), 131 (45), and 130 (100). The acid (200 mg) and phosphoryl chloride (5 ml) were heated at 100° for 5 min, cooled, and poured into water. Extraction into chloroform and washing with sodium carbonate yielded a neutral fraction. *6,7,8,9-Tetrahydrocyclohept*[b]indol-10(5H)-one (XXII; R = H) formed prisms, m.p. 224—225° (sealed capillary), from ethanol (105 mg) (lit.,[11] 221°) (Found: C, 78·2; H, 6·6; N, 7·1. Calc. for $C_{13}H_{13}NO$: C, 78·4; H, 6·5; N, 7·0%). The i.r., n.m.r., and u.v. spectra of this material were identical with copies supplied by Professor Kaneko. Methylation of this material with dimethyl sulphate in acetone–sodium hydroxide solution gave *6,7,8,9-hexahydro-5-methylcyclohept*[b]*indol*-10(5H)-*one* (XXII; R = Me) (73% yield) as needles from ethanol, m.p. 135—137°, identical with the material obtained by hydrolysis of (XXI) (i.r., n.m.r., t.l.c.) (Found: C, 78·8; H, 7·2; N, 6·6. $C_{14}H_{15}NO$ requires C, 78·9; H, 7·0; N, 6·6%); $\nu_{max.}$ 1628 cm^{-1}; *m/e* 213 (M^+, 100%), 185 (M − CO, 28, *m** 160·7), 184 (80), and 144 (88).

7,8,9,10,11,11a-Hexahydro-11a-p-tolylsulphonylamino-6H-*cyclo-oct*[b]*indole* (VII; *n* = 6).—Hexahydro-5*H*-cyclo-oct-[*b*]indole (3 g) and tosyl azide (6 g) were kept at room temperature for 5 days, and benzene (15 ml) was then added. The solid was collected and recrystallised from benzene. *Compound* (VII; *n* = 6) formed needles (4·9 g, 88%), m.p. 163—164° (Found: C, 69·0; H, 6·5; N, 7·6; S, 8·6. $C_{21}H_{24}N_2O_2S$ requires C, 68·5; H, 6·5; N, 7·6; S, 8·7%); $\lambda_{max.}$ 204, 223, and 262 nm (ε 27,300, 23,100, and 4000); $\nu_{max.}$ 3090 cm^{-1}; τ 2·5—3·1 (6H, m, Ar), 3·29 (1H, t, *J* 8 Hz), 3·46 (1H, d, *J* 8 Hz), 4·08 (1H, s, NH), 6·8—7·4 (2H, m), 7·68 (3H, s, tosyl-Me), and 7·6—9·4 (10H, m); *m/e* 368 (M^+, 3%), and 213 (M − Ts, 100). The same material was obtained using pyridine or pyridine–sodium hydroxide as solvent. Reaction of the indole with *p*-chlorobenzenesulphonyl azide in benzene solution gave *11a-p-chlorobenzenesulphonylamino-7,8,9,10,11,11a-hexahydro*-6H-*cyclo-oct*[b]*indole* (80% yield) as fine needles, m.p. 169—171° (Found: C, 61·9; H, 5·7; Cl, 9·0; N, 7·3; S, 8·0. $C_{20}H_{21}ClN_2O_2S$ requires C, 61·8; H, 5·4; Cl, 9·1; N, 7·2; S, 8·2%); $\lambda_{max.}$ 201, 223, 229sh, 238sh, and 263 nm (ε 36,600, 26,900, 21,000, 13,400, and 4500); $\nu_{max.}$ 3245 cm^{-1}; τ (D) 1·44 (1H,

s, NH), 2·6—3·0 (6H, m, Ar), 3·32 (1H, t, *J* 8 Hz), 3·48 (1H, d, *J* 8 Hz), 7·0—7·6 (2H, m), and 7·6—9·6 (10H, m); *m/e* 388 (M^+, 1%) and 213 (*M* — Cbs, 100).

Action of Heat on (VII; *n* = 6).—The compound (3 g) was heated at 170° for 5 min, the melt was cooled, and methanol (10 ml) was added. The solid was collected and recrystallised from benzene–hexane to give 8,9,10,11-*tetrahydro*-5H-*cyclo-oct*[b]*indole* (XXXII) as plates (175 mg), m.p. 122—124° (Found: C, 85·2; H, 7·8; N, 7·1. $C_{14}H_{15}N$ requires C, 85·3; H, 7·6; N, 7·1%); $\lambda_{max.}$ 207, 236, and 303 nm (ε 23,500, 30,800, and 18,200); $\nu_{max.}$ 3375 cm^{-1}; τ 2·4—2·6 (2H, m, ArH and NH), 2·7—3·0 (3H, m, Ar), 3·64 (1H, d, *J* 11 Hz), 4·15 (1H, dt, *J* 11 and 8 Hz), 6·9—7·2 (2H, m), 7·5—7·8 (2H, m), and 7·9—8·6 (4H, m); *m/e* 197 (M^+, 93%), 196 (31), and 168 (*M* — C_2H_5, 100, *m** 143·2). The methanol mother-liquors were evaporated and benzene (10 ml) was added, yielding toluene-*p*-sulphonamide. Chromatography (silica, hexane–benzene–ethyl acetate mixtures) gave more (XXXII) (total yield 545 mg) and toluene-*p*-sulphonamide (total yield 1·38 g, 98%). A solution of (VII; *n* = 6) (3 g) in propan-1-ol (20 ml) was boiled for 24 h, the solvent removed, and methanol (10 ml) added. The solid was collected and recrystallised from ethanol to give 6,7,8,9,10,11-*hexahydro*-6-p-*tolylsulphonylamino*-5H-*cyclo-oct*[b]*indole* (XXXIV) as plates (390 mg), m.p. 192—193° (Found: C, 68·4; H, 6·6; N, 7·6; S, 8·6. $C_{21}H_{24}N_2O_2S$ requires C, 68·5; H, 6·5; N, 7·6; S, 8·7%); $\lambda_{max.}$ 225, 277sh, 284, and 291sh nm (ε 40,100, 6300, 6600, and 5600); $\nu_{max.}$ 3250 and 3380 cm^{-1}; τ 1·62 (1H, s, NH, exchanged D_2O), 2·24 (2H, d, *J* 8 Hz, low-field half of tosyl signal), 2·52 (1H, m, Ar), 2·7—3·0 (5H, m, Ar), 4·52 (1H, d, *J* 8 Hz, NH, exchanged D_2O), 5·15 (1H, m), 6·9—7·6 (2H, m), 7·66 (3H, s, tosyl-Me), and 8·0—9·0 (8H, m); *m/e* 368 (M^+, 74%), 213 (*M* — Ts, 92), 197 (*M* — $TsNH_2$, 20), 186 (53), 170 (197-C_2H_3, 44), and 130 (C_9H_8N, 100%).

The solvents were evaporated and benzene (10 ml) added. Toluene-*p*-sulphonamide (870 mg) separated. Chromatography yielded (XXXII) (505 mg), (XXXIV) (total yield 520 mg), and toluene-*p*-sulphonamide (130 mg).

7,8,9,10,11,11a-*Hexahydro*-11a-p-*tolylsulphonylamino*-*cyclo-oct*[b]*indol*-6-*one* (XXXV).—(a) The indole (500 mg) and azide (1 g) were dissolved in acetic acid (5 ml). After 3 weeks the solid was collected and recrystallised from acetonitrile, m.p. 204—206° (270 mg).

(b) Compound (VII; *n* = 6) (1 g) in acetic acid (20 ml) yielded (XXXV) (765 mg) after 4 weeks.

(c) A slow stream of air was passed through a solution of (VII; *n* = 6) (2 g) in acetic acid (40 ml) containing copper(II) acetate (100 mg). After 15 h the solvent was removed and a mixture of methanol (50 ml) and ammonia (100 ml; 2M) added. The solid was collected, boiled with acetonitrile (20 ml), and recrystallised from pyridine–methanol (yield 650 mg).

(d) A solution of (VII; *n* = 6) (1 g) in acetic acid (20 ml) containing platinum black (50 mg) was shaken in air for 2 weeks. The solvent was removed and the material extracted with boiling chloroform. The extract was washed with sodium carbonate solution, the chloroform removed, and the residue triturated with methanol (yield 820 mg). The *compound* formed needles, m.p. 205—207° (Found: C, 66·0; H, 5·9; N, 7·3; S, 8·2. $C_{21}H_{22}N_2O_3S$ requires C, 66·0; H, 5·8; N, 7·3; S, 8·4%); $\lambda_{max.}$ 201, 231, 287sh, and 305 nm (ε 32,500, 16,600, 5200, and 6200); $\nu_{max.}$ 1692 and 3225 cm^{-1}; τ (D) 1·2br (1H, s, NH, exchanged D_2O), 2·41 (1H, d, *J* 8 Hz, Ar), 2·76 (1H, t, *J* 8 Hz, Ar), 2·9—3·1 (4H, m, Ar), 3·18 (1H, t, *J* 8 Hz, Ar), 3·46 (1H, d, *J* 8 Hz, Ar), 6·0—6·5 (1H, m), 7·73 (3H, s, tosyl-Me), and 7·3—9·2 (9H, m) (an interesting feature of this spectrum is the upfield-shift of the 4 protons of the tosyl group); *m/e* 382 (M^+, 7%), 354† (*M* — CO, 7, *m** 328·1), 325 (*M* — C_2H_5CO, 8), 318 (*M* — SO_2, 15, *m** 264·7), 227 (*M* — Ts, 100), and 199† (*M* — Ts — CO, 96%). Experiment (d) was repeated and the crude material boiled in 2-methoxyethanol; nothing separated on cooling the solution and so the solvent was removed. Methanol was added to the residue, and the solid was collected and recrystallised from ethanol to give 2′-*oxo*-2-p-*tolylsulphonyliminoindoline*-3-*spirocycloheptane* (XXXVII) as cream coloured prisms (333 mg), m.p. 173—174° (Found: C, 66·0; H, 5·9; N, 7·3; S, 8·0. $C_{21}H_{22}N_2O_3S$ requires C, 66·0; H, 5·8; N, 7·3; S, 8·4%); $\lambda_{max.}$ 224, 279, 291sh, and 302sh nm (ε 24,800, 15,900, 11,400, and 8650); $\nu_{max.}$ 1610 (C=N), 1703 (C=O), and 3270 (NH) cm^{-1}; τ 0·1 (1H, s, NH, exchanged D_2O), 2·18 (2H, d, *J* 8 Hz, low-field half of tosyl group), 2·6—3·1 (6H, m, Ar), 6·8—7·1 (1H, m), 7·1—7·5 (1H, m), 7·60 (3H, s, tosyl-Me), and 7·6—8·4 (8H, m); *m/e* 382 (M^+, 22%), 354 (*M* — CO, 28, *m** 328·1), 325 (354 — C_2H_5, 28, *m** 298·4), 227 (*M* — Ts, 68), and 199 (354 — Ts, 100, *m** 111·9).

5a-*Hydroxy*-5,5a,7,8,9,10,11,11a-*octahydro*-11a-p-*tolylsulphonylaminocyclo-oct*[b]*indol*-6-*one* (XXXVIII).—A suspension of (XXXV) (500 mg) in sodium hydroxide solution (2M; 10 ml) was heated on a steam-bath. A deep orange solution was formed and after 30 min solid began to separate. After a further 1·5 h heating the solid was collected and recrystallised from ethanol to give *needles* (105 mg), m.p. 240—241° (Found: C, 62·5; H, 6·1; 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%); $\lambda_{max.}$ 233, 250, 257, and 283 nm (ε 13,200, 10,300, 8900, and 2500); $\nu_{max.}$ 1707 (C=O), 3275 (NH), and 3420 (OH) cm^{-1}; τ (D) 0·10 (1H, s, NH, exchanged D_2O), 2·71 (1H, dd, *J* 8 and 2 Hz, Ar), 2·8—3·2 (6H, m, Ar), 3·64 (1H, s, NH or OH, exchanged D_2O), 3·68 (1H, dd, *J* 8 and 2 Hz, Ar), 4·69 (1H, s, NH or OH, exchanged D_2O), 7·0—7·3 (1H, m), 7·71 (3H, s, tosyl-Me), and 7·8—9·2 (9H, m); *m/e* 400 (M^+, 10%), 372 (*M* — CO, 7, *m** 346·0); 245 (*M* — Ts, 100), 228 (245 — OH, 46, *m** 212·2), 227 (41), and 217 (372 — Ts, 56, *m** 126·6).

5,6,6a,8,9,10,11,11a-*Octahydro*-5-*methyl*-11a-p-*tolylsulphonylamino*-6-p-*tolylsulphonylimino*-7H-*cyclohepta*[c]*quinoline* (XXXIX).—*Method* (a). To a solution of 6,7,8,9,10,11-hexahydro-5-methyl-5*H*-cyclo-oct[*b*]indole (2 g) in ether (25 ml) was added tosyl azide (3·9 g). After 2 weeks the solid was collected and recrystallised from propan-1-ol (yield 2·39 g).

(b) The indole (1 g) was mixed with the azide (1·9 g) in acetic acid (10 ml). After 4 days the solid was collected (420 mg).

(c) The azide (3·9 g) and indole (2 g) in ethanol (20 ml) gave 2·3 g of solid after 2 days.

Compound (XXXIX) formed plates, m.p. 207—209°, from propan-1-ol (Found: C, 63·4; H, 6·2; N, 7·6; S, 11·9. $C_{29}H_{33}N_3O_4S_2$ requires C, 63·2; H, 6·0; N, 7·6; S, 11·6%); $\lambda_{max.}$ 224 and 287 nm (ε 26,100 and 15,200); $\nu_{max.}$ 1536 and 3230 cm^{-1}; τ 2·11 (2H, d, *J* 8 Hz, low-field half of tosyl signal), 2·44 (1H, m, Ar), 2·6—2·9 (4H, m, Ar), 3·0—3·4 (5H, m, Ar), 4·00 (1H, s, NH, exchanged D_2O), 6·5—6·9 (1H, m), 7·0—7·4 (2H, m), 7·23 (3H, s, NMe), 7·56 (3H, s, tosyl-Me), 7·76 (3H, s, tosyl-Me), and 6·7—9·2 (8H, m); *m/e* (M^+ 551 not detected) 380 (*M* — $TsNH_2$, 5%) and 225 (380 — Ts, 100, *m** 133·2).

5,6,8,9,10,11-*Hexahydro-5-methyl*-6-p-*tolylsulphonylimino*-7H-*cyclohepta*[c]*quinoline* (XL; R = NTs).—*Method* (d). Compound (XXXIX) (250 mg) and DBN (60 mg) were boiled for 5 min in ethanol (yield 143 mg, 83%).

(e) Compound (XXXIX) (200 mg) was heated slowly to its m.p. and then cooled, dissolved in chloroform, and the chloroform washed with sodium hydroxide solution. The neutral fraction was (XL) (96 mg).

(f) The indole (2 g) and azide (3·9 g) were kept 2 days in pyridine (10 ml). The solvent was removed and acetonitrile (10 ml) added (yield 440 mg).

Chromatography of the residue from method (b) gave 230 mg and from method (c) 94 mg. The *compound* formed prisms, m.p. 146—147° (from methanol) (Found: C, 68·8; H, 6·2; N, 7·3; S, 8·6. $C_{22}H_{24}N_2O_2S$ requires C, 69·5; H, 6·3; N, 7·4; S, 8·4%); $\lambda_{max.}$ 218, 259, 307sh, 348, and 356sh nm (ε 43,300, 25,400, 6300, 13,200, and 11,700); $\nu_{max.}$ 1495 cm^{-1}; τ 1·9—3·1 (8H, m, Ar), 5·83 (3H, s, NMe), 6·7—7·0 (4H, m), 7·63 (3H, s, tosyl-Me), and 8·0—8·9 (6H, m); *m/e* 380 (M^+, 5%), 316 (M — SO_2, 3, *m** 262·8), 225 (M — Ts, 100, *m** 133·2), and 198 (225 — HCN, 26).

5,7,8,9,10,11-*Hexahydro-5-methylcyclohepta*[c]-*quinolin*-6-*one* (XL; R = O).—Compound (XXXIX) (500 mg) was boiled for 5 min with ethanol (2 ml) and sodium hydroxide (2N; 2 ml). The mixture was diluted with water and extracted with chloroform, and the residue from evaporation was recrystallised from methanol giving (XL; R = NTs) (96 mg). P.l.c. of the mother-liquors gave *compound* (XL; R = O) as prisms (70 mg), m.p. 100—102° (from aqueous methanol) (Found: C, 79·1; H, 7·5; N, 6·2. $C_{15}H_{17}NO$ requires C, 79·3; H, 7·5; N, 6·2%); $\lambda_{max.}$ 211sh, 232, 248sh, 271sh, 278, 288, 320sh, 331, and 345 nm (ε 20,600, 42,000, 8300, 6000, 8100, 7400, 6500, 8100, and 5500); $\nu_{max.}$ 1635 cm^{-1}; τ 2·0—3·0 (4H, m, Ar), 6·27 (3H, s, NMe), 6·8—7·1 (4H, m), and 7·8—8·8 (6H, m); *m/e* 227 (M^+, 100%), 226 (38), 212 (M — Me, 59, *m** 198·0), 199 (M — CO, 34), and 198 (88).

1-*Methyl*-2′-p-*tolylsulphonylamino*-2-p-*tolylsulphonyliminoindoline*-3-*spirocycloheptane* (VIII; *n* = 5).—Chromatography (silica, benzene–ethyl acetate) of the residue from method (a) gave this compound (64 mg), from method (c) (200 mg), and from method (f) (91 mg). The *indoline* (VIII; *n* = 5) formed needles, m.p. 170—172°, from ethanol (Found: C, 63·0; H, 5·9; N, 7·6; S, 11·5. $C_{29}H_{33}N_3O_4S_2$ requires C, 63·2; H, 6·0; N, 7·6; S, 11·6%); $\lambda_{max.}$ 205, 226, 281sh, 287, and 305 nm (ε 31,800, 37,400, 13,900, 15,200, and 11,500); $\nu_{max.}$ 1570 and 3190 cm^{-1}; τ 2·04 (2H, d, *J* 8 Hz), 2·54 (1H, NH, exchanged D_2O), 2·6—3·3 (10H, m, Ar), 4·1—4·6 (1H, m), 5·0—5·3 (2H, m), 6·92 (3H, s, NMe), 7·57 (3H, s, tosyl-Me), 7·67 (3H, s, tosyl-Me), and 7·1—9·6 (8H, m); *m/e* 551 (M^+, 9%), 468 (31), 396 (M — Ts, 9, *m** 284·6), 368 (M — $TsNCH_2$, 1), 314 (M — $TsNC_5H_8$, 33, *m** 178·9), and 91 (100).

6,7,8,9,10,11-*Hexahydro-5-methyl*-11-p-*tolylsulphonylimino*-5H-*cyclo-oct*[b]*indole* (XLI).—Isolated by chromatography: method (a) (yield 50 mg), (b) (yield 92 mg), and (f) (yield 184 mg). The *compound* formed cream coloured plates, m.p. 193—195° (from propanol) (Found: C, 69·7; H, 6·6; N, 7·2; S, 7·9. $C_{22}H_{24}N_2O_2S$ requires C, 69·5; H, 6·3; N, 7·4; S, 8·4%); $\lambda_{max.}$ 213, 256, 267, 274, and 342 nm (ε 38,500, 11,800, 10,400, 10,000, and 14,700); $\nu_{max.}$ 1514 cm^{-1}; τ 1·77 [1H, d, *J* 8 Hz, C(1)H], 2·05 (2H, d, *J* 8 Hz, low-field half of tosyl signal), 2·6—3·0 (5H, m, Ar), 6·32 (3H, s, NMe), 6·49 (2H, t, *J* 7 Hz), 6·81 (2H, t, *J* 7 Hz), 7·56 (3H, s, tosyl-Me), and 7·8—8·7 (6H, m); *m/e* 380 (M^+, 22%), 316 (11, *m** 262·6), 225 (M — Ts, 100), and 198 (225 — HCN, 19, *m** 174·2).

1,2,3,4-*Tetrahydro*-1-*methyl*-2,4-*pentano*-4-p-*tolylsulphonylamino*-3-p-*tolylsulphonyliminoquinoline* (XLII).—The compound was isolated by chromatography and the results are summarised below.

Method	Yield (mg)	M.p. (°)
(a)	240	167—172
(b)	252	168—173
(c)	205	173—175
(f)	15	165—169

The samples were pure by t.l.c. and all darkened and became opaque above 130°. The *compound* formed pale yellow prisms from methanol–chloroform (Found: C, 62·9; H, 6·2; N, 7·7; S, 11·5. $C_{29}H_{33}N_3O_4S_2$ requires C, 63·2; H, 6·0; N, 7·6; S, 11·6%); $\lambda_{max.}$ 230 and 290 nm (ε 25,900 and 2200); $\nu_{max.}$ 1608 and 3245 cm^{-1}; τ 2·06 (2H, d, *J* 8 Hz), 2·61 (d, *J* 8 Hz), 3·5—3·9 (3H, m, Ar), 4·22 (1H, NH, exchanged D_2O), 6·2—6·5 (2H, m), 6·8—7·2 (1H, m), 7·30 (3H, s, NMe), 7·49 (3H, s, tosyl-Me), 7·69 (3H, s, tosyl-Me), and 7·7—9·0 (8H, m); *m/e* 551 (M^+, 0·1%), 380 (M — $TsNH_2$, 34), 316 (380 — SO_2, 12, *m** 262·6), 225 (380 — Ts, 100), and 198 (225 — HCN, 22, *m** 174·2). Compound (XLII) (70 mg) was heated (oil-bath, 180°) for 5 min. Methanol (0·5 ml) was then added and the product recrystallised from propanol yielding (XLI) (identified by m.p., t.l.c., i.r.) (30 mg, 62% yield).

2-p-*Chlorobenzenesulphonylimino*-1,2-*dihydro*-1,3,4-*trimethylquinoline* (XVII).—Compound (XVI) [1] (200 mg) was dissolved in trifluoroacetic acid (1 ml) and kept for 2 days. The usual work-up [see preparation of (XIII)] gave the *quinoline* (XVII), as needles, m.p. 178—179° (from acetonitrile) (yield 107 mg) (Found: C, 59·9; H, 4·7; Cl, 9·7; N, 7·9; S, 9·3. $C_{18}H_{17}ClN_2O_2S$ requires C, 59·9; H, 4·7; Cl, 9·9; N, 7·8; S, 8·9%); $\lambda_{max.}$ 215, 259, and 343 nm (ε 40,700, 21,700, and 9500); $\nu_{max.}$ 1503 cm^{-1}; τ 2·03 (1H, d, *J* 8 Hz, Ar), 2·09 (2H, d, *J* 8 Hz, low-field half of Cbs signal), 2·2—2·8 (5H, m, Ar), 5·86 (3H, s, NMe), 7·40 (3H, s, CMe), and 7·60 (3H, s, CMe); *m/e* 360 (M^+, 3%), 296 (M — SO_2, 19, *m** 243·4), 185 (M — Cbs, 100), and 158 (185 — HCN, 9, *m** 134·9). Similarly, compound (V) gave (VI), yield 59%.

5,8,9,10-Tetrahydrocyclohept[*b*]indol-6(7*H*)-one was prepared by periodate oxidation [25] of hexahydrocyclohept[*b*]-indole, m.p. 147—149° (lit.,[9] 144·5—147°) (yield 14%). Methylation gave (XVIII; R = O), m.p. 61—63° (lit.,[9] 64·5—65·5°). 10-Methyl-1,2,3,4-tetrahydroacridone (XIX; R = O) [10] had m.p. 170—173° (lit.,[10] 170—172°).

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