The Reaction of 1,2,3,4-Tetrahydro-2,5-dimethyl-5*H*-pyrido[4,3-*b*]indole with Arenesulphonyl Azides

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The reaction of 1,2,3,4-tetrahydro-2,5-dimethyl-5*H*-pyrido[4,3-*b*]indole with toluene-*p*-sulphonyl azide yields 1,2,3,4,5,6-hexahydro-3,6-dimethyl-1-*p*-tolylsulphonyl[1,3]diazocino[5,4-*b*]indole. Toluene-*p*-sulphonyl azide dehydrogenates 1,4-dihydro-9-methylcarbazole yielding 9-methylcarbazole.

THE reactions of *N*-methyltetrahydrocarbazole and of *N*-methyltetrahydrocyclopent[*b*]indole with arenesulphonyl azides have been reported.[1] We have now examined the reactions of 1,2,3,4-tetrahydro-2,5-dimethyl-5*H*-pyrido[4,3-*b*]indole (I) with azides to determine the effect of introducing a heteroatom into the reduced ring of tetrahydrocarbazole.

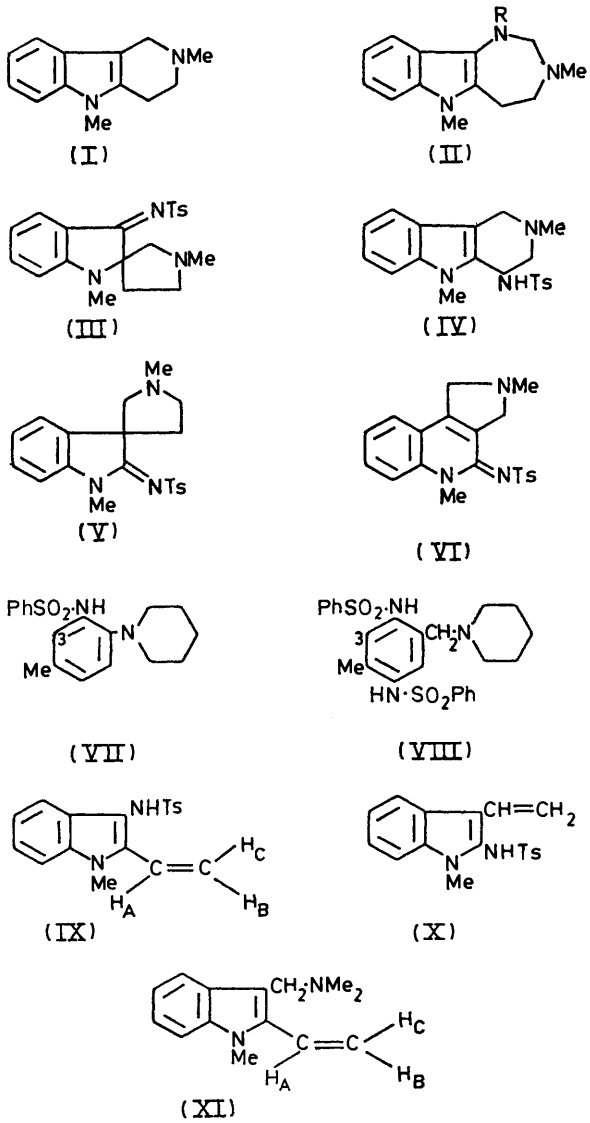
Compound (I) reacted smoothly with toluene-*p*-sulphonyl azide forming a colourless crystalline adduct (II; R = Ts) (50% yield); the i.r. spectrum of the compound contained no bands in the regions 1700—1600 (C=N) and 3600—3200 (NH) cm^{-1} and the u.v. spectrum was similar to that of 1,2-dimethyl-3-*p*-tolylsulphonylaminoindole.[2] These observations eliminate structures of types (III)—(VI) (*cf.* the products obtained from *N*-methyltetrahydrocarbazole [1]). The n.m.r. spectrum of the adduct (II; R = Ts) (in $CDCl_3$) contained signals at τ 7·45—7·85 (4H, m), 7·63 (s, tosyl Me), 7·55 (s, NMe), 6·45 (s, indole NMe), 5·62 (2H, s), 2·70—2·97 (5H, m, Ar), and 2·39—2·46 (3H, m, Ar). The signal of the isolated methylene group (5·62) is downfield of the signal from the protons at C-1 (τ 6·32) in compound (I). Compound (II; R = Ts) readily formed a methiodide; in the n.m.r. spectrum of this compound the signal of the methylene group appeared as a broad band (τ 4·2—5·2) suggesting that the rate of inversion of the seven-membered ring had been reduced; also the signals of some of the aromatic protons had moved upfield, the highest field signal appearing at τ 3·70. This shift may be caused by attraction between the positively charged nitrogen atom and the oxygen atoms of the sulphonyl group. Such an interaction orientates the toluene ring over part of the indole ring, producing mutual shielding. Upfield shifts of 0·5—1·0 p.p.m. for the C(3)H signal on protonation of compounds such as (VII) and (VIII) have been reported.[3] Boiling the methiodide with alkali gave the 2-vinylindole (IX), shown to contain an NH group ($\nu_{max.}$ 3240 cm^{-1}) and a vinyl group (n.m.r.). There was no n.m.r. signal

[1] A. S. Bailey, R. Scattergood, and W. A. Warr, *J. Chem. Soc.* (*C*), 1971, (*a*) p. 2479, (*b*) p. 3769.

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

[3] I. Baxter and D. W. Cameron, *J. Chem. Soc.* (*B*), 1971, 696.

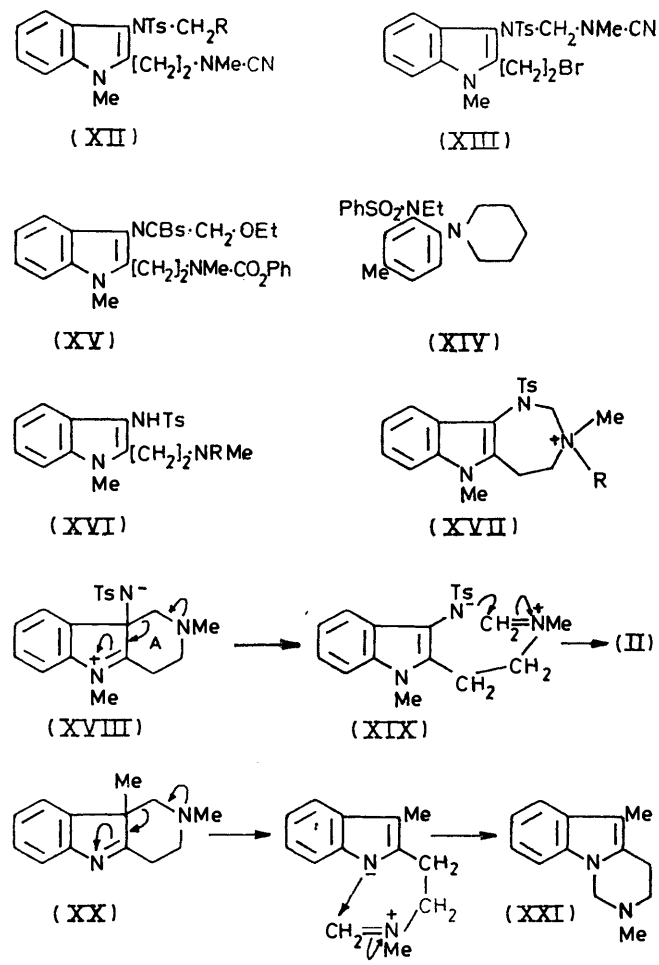
corresponding to the group $CH_2{\cdot}NMe_2$. The alternative 3-vinylindole structure (X) is unlikely to be easily derived from a pyrido[4,3-*b*]indole, and it is known that 3-vinylindoles are unstable in alkali.[4] The u.v. spectrum



Throughout, Ts = *p*-$MeC_6H_4{\cdot}SO_2$; CBs = *p*-$ClC_6H_4{\cdot}SO_2$

of compound (IX) was similar to that of compound (XI), prepared by heating the methiodide of (I) with alkali.

More evidence for structure (II) was obtained by treating the compound with cyanogen bromide in methylene chloride. The product could not be obtained crystalline but when boiled with methanol yielded a crystalline substance (XII; R = OMe), probably *via* the intermediate (XII; R = Br). The halogen atom in (XII; R = Br) would be reactive,[5] and it seems unlikely that the alternative product (XIII) of the Von Braun reaction would react with methanol under neutral conditions to form an ether. Further, attack would be expected at the isolated CH_2 group of (II).[6] The formation of ethers by the Von Braun reaction on yohimbine alkaloids has been reported.[7] The n.m.r.



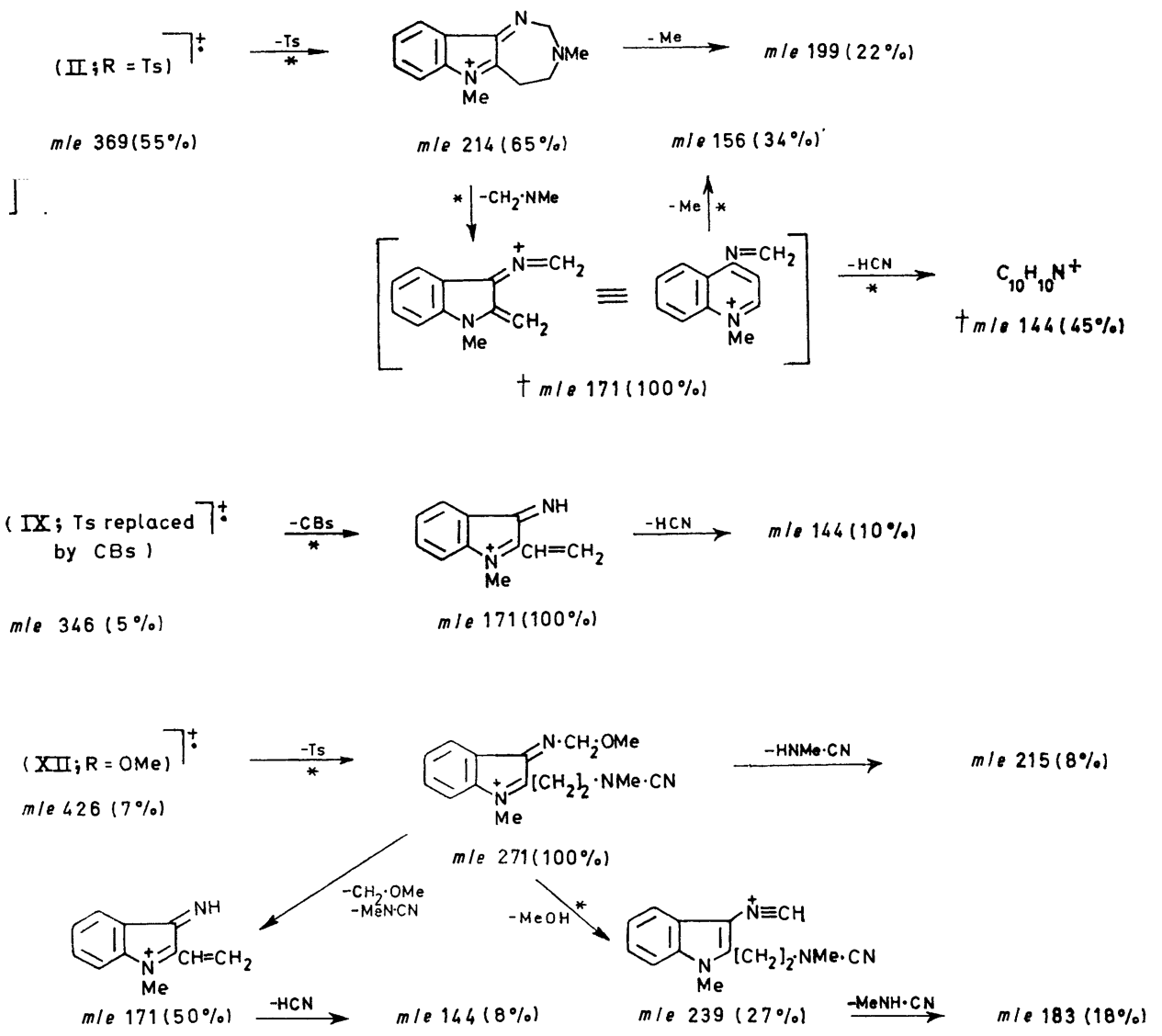
spectrum of compound (XII; R = OMe) (in CCl_4) contained signals at τ 7·60 (s, tosyl Me), 7·08 (s, cyanamide Me),[7] 6·6—6·9 (4H, m, $CH_2{\cdot}CH_2$), 6·56 (s, OMe), 6·21 (s, indole NMe), 5·12 (2H, q, *J* 10 Hz), 3·82 (1H, d, *J* 8 Hz, Ar), 3·38 (1H, t, *J* 8 Hz, Ar), 2·8—3·2 (2H, m, Ar), 2·92 (2H, d, *J* 8 Hz, Ar), and 2·52 (2H, d, *J* 8 Hz, Ar), showing non-equivalence of the methylene protons and marked upfield shifts of the aromatic protons [*cf.* the upfield shifts in (XIV)[3]]. Warming compound (I) with *p*-chlorobenzenesulphonyl azide gave the adduct (II; R = *p*-$ClC_6H_4{\cdot}SO_2$); the properties of this compound and Hofmann degradation to the analogue of compound (IX) confirmed its structure.

As an alternative to the Von Braun reaction, tertiary amines may be cleaved by phenyl chloroformate.[8] The

[4] L. J. Dolby and G. W. Gribble, *Tetrahedron*, 1968, **24**, 6380.
[5] H. Böhme, K. Hartke, and A. Müller, *Chem. Ber.*, 1963, **96**, 595; H. Böhme and A. Müller, *Arch. Pharm.*, 1963, **296**, 54.
[6] H. A. Hagemar, *Org. Reactions*, 1953, **7**, 211.
[7] J. D. Albright and L. Goldman, *J. Amer. Chem. Soc.*, 1969, **91**, 4317.
[8] J. D. Hobson and J. G. McCluskey, *J. Chem. Soc.* (*C*), 1967, 2015.

product of the reaction between compound (II; R = p-$ClC_6H_4{\cdot}SO_2$) and phenyl chloroformate was a glass which could not be crystallised; however, dissolving the glass in ethanol gave a small quantity of a crystalline solid whose spectroscopic properties support structure

Compound (XVI; R = Ts) was also obtained (9% yield) by prolonged boiling of a solution of compound (II; R = Ts) in propanol with tosyl azide. This observation suggested that (XVI; R = Ts) was being formed from (II) *via* the ion (XVII; R = Ts) (*cf.* the

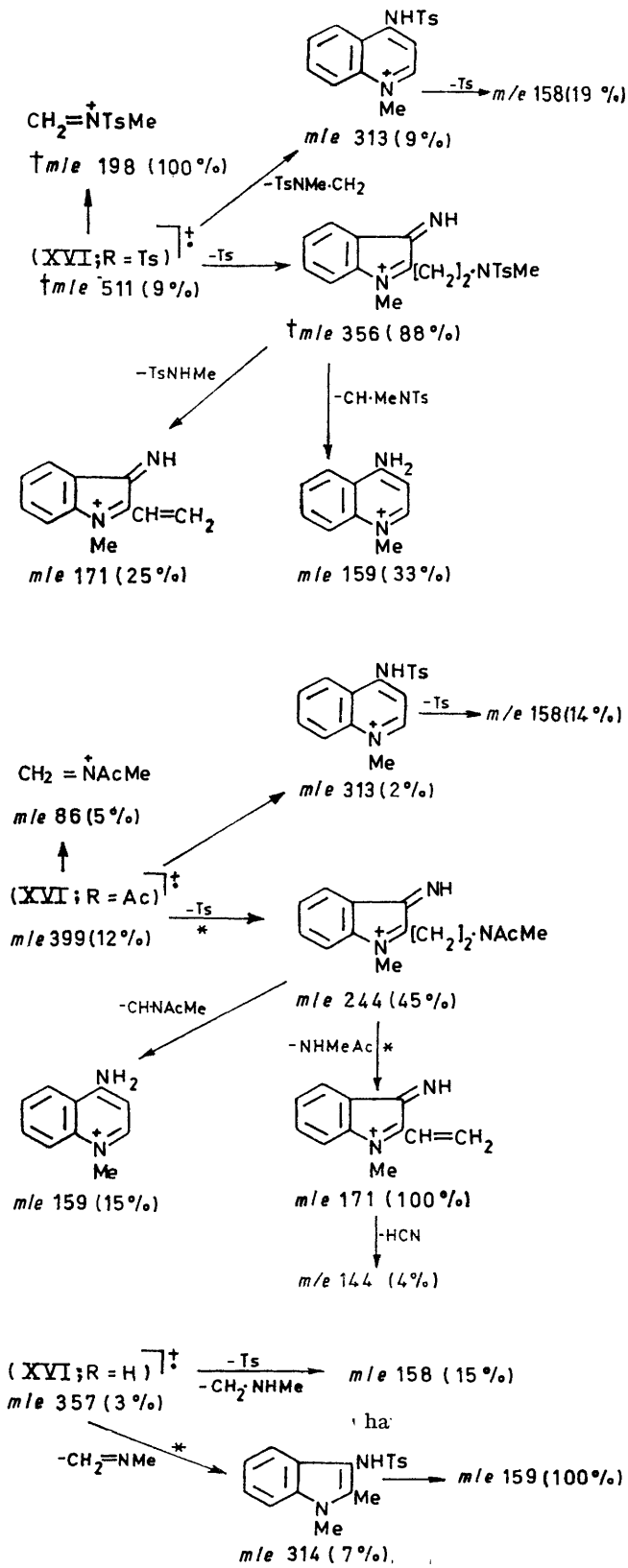


SCHEME 1

(XV). From the mother liquors of the preparation of (II; R = Ts) a small quantity of a second product (XVI; R = Ts) was isolated. The compound had the molecular formula $C_{26}H_{29}N_3S_2O_4$ (high resolution mass spectroscopy) and the stain produced by iodine on t.l.c. plates (bright red) was very similar to that produced by iodine on t.l.c. spots of 1,2-dimethyl-3-p-tolylsulphonylaminoindole. The base peak in the mass spectrum of (XVI; R = Ts) was m/e 198 ($CH_2{=}\overset{+}{N}MeTs$). The n.m.r. spectrum was in agreement with structure (XVI; R = Ts) and showed the upfield shift of the aromatic signals as described for compound (XII; R = OMe).

reaction of tosyl azide with aniline and with pyridine [9]); the seven-membered ring of the latter could then open with loss of formaldehyde. In support of this hypothesis we observed that compound (II; R = Ts) reacted smoothly at room temperature with acetic anhydride forming (XVI; R = Ac), presumably *via* (XVII; R = Ac). The spectral properties of the compound were in good agreement with this structure: in the n.m.r. spectrum ($CDCl_3$) some of the aromatic signals had shifted upfield and the $CO{\cdot}CH_3$ signal consisted of

[9] Houben-Weyl, 'Methoden der Organischen Chemie,' 1955, vol. 9, p. 654.



SCHEME 2

two singlets at τ 7·91 and 8·16 (ratio *ca.* 2 : 1). On adding a drop of trifluoroacetic acid the signals moved to τ 7·69 and 8·01 (ratio 2 : 1); in pyridine solution these signals appeared at τ 7·94 and 8·05 (ratio 1 : 2). The acetyl group in *N*-methylcyclohexylacetamide shows two signals in the n.m.r. spectrum.[10] Finally, compound (II; R = Ts) was hydrolysed by warming with dilute methanolic hydrochloric acid, forming the crystalline hydrochloride of (XVI; R = H). The free base (XVI; R = H) was a low-melting solid; we were unable to find a suitable solvent for recrystallisation but the compound was homogeneous on t.l.c. and its properties were in good agreement with the assigned structure. In a separate experiment compound (II; R = Ts) was heated with Brady's reagent, yielding formaldehyde 2,4-dinitrophenylhydrazone.

We consider that structure (II) is formed by the addition of the sulphonyl azide to the tetrahydropyridoindole followed by loss of nitrogen and rearrangement giving (XVIII) (*cf.* the reactions of *N*-methyltetrahydrocarbazole [1]). Ring A then opens forming species (XIX), and the seven-membered ring is formed by TsN^- attacking the $CH_2=\overset{+}{N}Me-$ group. A similar type of reaction sequence is observed in the formation of tetrahydropyrimido[3,4-*a*]indoles from 1,3-dialkyl-4-piperidones [(XX) ⟶ (XXI)].[11] The mass spectrum of compound (II; R = Ts) is given in Scheme 1; the molecular ion was intense (molecular compositions determined by high resolution spectrometry are indicated †). In the spectrum of compound (IX; Ts replaced by *p*-$ClC_6H_4\cdot SO_2$) (Scheme 1) the molecular ion is weak and the base peak, although it has the same composition as the base peak in the spectrum of (II), is probably of different structure since loss of HCN giving *m/e* 144 is important in the spectrum of (II) but not in the spectra of (IX) and (XII; R = OMe) (Scheme 1).

There were striking differences in the mass spectra of compounds (XVI; R = Ts) and (XVI; R = Ac) (Scheme 2); for the former the base peak was *m/e* 198 whereas for the latter the corresponding peak, *m/e* 86, was very small. The spectrum of (XVI; R = H) is included for comparison. Note that *m/e* 159 (*M* — Ts) is the base peak in the mass spectrum of 1,2-dimethyl-3-*p*-tolylsulphonylaminoindole.[2]

9-Methyl-1,4-dihydrocarbazole reacted smoothly with tosyl azide; the only product isolated was *N*-methylcarbazole (80% yield); presumably the initial adduct formed from the dihydrocarbazole and tosyl azide lost nitrogen and toluene-*p*-sulphonamide, forming the fully aromatic compound.

EXPERIMENTAL

General directions and instruments used have been reported.[1] 1,2,3,4-Tetrahydro-2-methyl-5*H*-pyrido[4,3-*b*]-

[10] R. Moriarty, *J. Org. Chem.*, 1963, **28**, 1296; W. A. Thomas, 'Annual Reports on N.M.R. Spectroscopy,' Academic Press, London, 1970, vol. 3, p. 109.

[11] C. J. Cattanach, A. Cohen, and B. Heath-Brown, *J. Chem. Soc.* (*C*), 1971, 359; A. Eböthner, P. Niklaus, and R. Süess, *Helv. Chim. Acta*, 1969, **52**, 629.

indole,[12] m.p. 170—171°, was methylated [13] to form the 2,5-dimethyl derivative (I), m.p. 68—69° (lit.,[14] 69—70°); $\lambda_{max.}$ 228, 284, and 293 nm (ε 30,600, 6340, and 5690); τ($CDCl_3$) 7·45 (3H, s, NMe), 7·18 [4H, s, C(3)H, C(4)H], 6·40 (3H, s, indole NMe), 6·32 [2H, s, C(1)H], and 2·6—3·0 (4H, m, Ar).

1,2,3,4,5,6-*Hexahydro*-3,6-*dimethyl*-1-p-*tolylsulphonyl*[1,3]-*diazocino*[5,4-b]*indole* (II; R = Ts).—(*a*) Compound (I) (0·25 g) and the toluene-*p*-sulphonyl azide (0·44 g) in propanol (2 ml) were heated (steam-bath) for 3 h. Next day the solid (0·20 g, 45%; m.p. 187—188°) was collected.

(*b*) The pyridoindole (1·9 g) and the azide (2·3 g) were heated together (45°; oil-bath) for 2 days; a little methanol was added and the solid was collected (2·0 g). The *product* formed prisms, m.p. 187—189° (from ethanol) (Found: C, 65·6; H, 6·6; N, 11·2; S, 8·8. $C_{20}H_{23}N_3O_2S$ requires C, 65·1; H, 6·2; N, 11·4; S, 8·7%); $\lambda_{max.}$ 225, 283, and 291 nm (ε 45,900, 10,080, and 9280). A solution of compound (II; R = Ts) (0·73 g) in methyl iodide (4 ml) was kept at room temp. for 24 h; the solid was collected (0·99 g) and crystallised from ethanol to give *needles* of the methiodide, m.p. 212—214° (Found: N, 8·0. $C_{21}H_{26}IN_3O_2S$ requires N, 8·2%); τ[$(CD_3)_2SO$] 7·55 (3H, s, tosyl Me), 6·78 (6H, s, NMe), 6·3—6·9 [4H, m, C(4)H, C(5)H], 6·25 (3H, s, indole NMe), 4·2—5·2 [2H, C(2)H], 3·70 (1H, d, *J* 8 Hz, Ar), 3·22 (1H, t, *J* 8 Hz, Ar), 2·91 (1H, t, *J* 8 Hz, Ar), 2·44—2·63 (3H, m, Ar), and 2·30 (2H, d, *J* 8 Hz, low-field half of Ts signal).

1-*Methyl*-3-p-*tolylsulphonylamino*-2-*vinylindole* (IX).—The foregoing methiodide (0·36 g) was dissolved in a mixture of ethanol (10 ml) and water (10 ml); the solution was boiled and potassium hydroxide (0·2 g) in ethanol (2 ml) and water (2 ml) was added. After heating for 50 min all the starting material had reacted (t.l.c.); the solvent was removed and the residue shaken with chloroform (100 ml) and water (150 ml). The chloroform extract was dried ($MgSO_4$) and evaporated and the residue was crystallised twice from methanol (0·1 g). The *olefin* formed prisms, m.p. 161—163° (Found: C, 65·9; H, 5·4; N, 8·5. $C_{18}H_{18}N_2O_2S$ requires C, 66·3; H, 5·5; N, 8·6%); $\lambda_{max.}$ 227 and 304 nm (ε 16,050 and 8280) (1-methyl-2-vinylindole [15] has $\lambda_{max.}$ 305 nm); $\nu_{max.}$ 3240 cm^{-1} (NH); τ($CDCl_3$) 7·62 (3H, s, tosyl Me), 6·29 (3H, s, indole NMe), 4·62 (1H, d, *J* 12 Hz, H_B), 4·33 (1H, d, *J* 18 Hz, H_C), 3·81br (1H, NH, exchanged in D_2O), 3·43 (1H, q, *J* 12 and 18 Hz, H_A), 3·0—3·16 (2H, m, Ar), 2·70—2·98 (4H, m, Ar), and 2·43 (2H, d, *J* 8 Hz, low-field half of tosyl signal).

1-*Methyl*-2-[2-(N-*methyl*-N-*cyano*)*amino*]*ethyl*-3-(N-*methoxymethyl*-N-p-*tolylsulphonyl*)*aminoindole* (XII; R = OMe).—Cyanogen bromide (1·47 mmol) in dry dichloromethane (15 ml) was added to compound (II) (0·512 g, 1·39 mmol) in dichloromethane (10 ml). Next day more cyanogen bromide (50 mg) was added, the solution was boiled for 3 h, and the solvent was removed *in vacuo*. Methanol (20 ml) was added; the solution was boiled for 1 h and most of the solvent was removed. Next day the solid was collected (0·18 g; m.p. 131—134°). Recrystallisation from methanol gave *prisms*, m.p. 133—135° (Found: C, 61·7; H, 6·2; N, 12·9%; *M*, 426. $C_{22}H_{26}N_4O_3S$ requires C, 62·0; H, 6·1; N, 13·1%; *M*, 426), $\lambda_{max.}$ 222, 282, and 291 nm (ε 35,300, 7590, and 6450); $\nu_{max.}$ (Nujol) 2220 cm^{-1}.

[12] V. Boekelheide and C. Ainsworth, *J. Amer. Chem. Soc.*, 1950, **72**, 2132; A. H. Cook and K. J. Reed, *J. Chem. Soc.*, 1945, 399.

1-p-*Chlorophenylsulphonyl*-1,2,3,4,5,6-*hexahydro*-3,6-*dimethyl*[1,3]*diazocino*[5,4-b]*indole*.—Compound (I) (4·4 g) and *p*-chlorobenzenesulphonyl azide (6·1 g) were boiled in methanol (15 ml) for 5 h. Next day the solid (4·0 g) was collected and recrystallised from ethanol, forming *prisms*, m.p. 145—166° (Found: N, 10·8%; *M*, 389. $C_{19}H_{20}ClN_3O_2S$ requires N, 10·8%; *M*, 389); $\lambda_{max.}$ 225, 284, and 292 nm (ε 40,000, 7940, and 7180); no bands in i.r. spectrum corresponding to NH or C=N; τ($CDCl_3$) 7·45—7·85 (4H, m), 7·56 (3H, s, NMe), 6·4 (3H, s, indole NMe), 5·60br [2H, s, C(2)H], 2·6—2·9 (5H, m, Ar), and 2·28—2·32 (3H, m, Ar). The *methiodide* formed white needles, m.p. 212—214° (from ethanol) (Found: C, 45·2; H, 4·3; N, 7·9; S, 6·3. $C_{20}H_{23}ClIN_3O_2S$ requires C, 45·2; H, 4·3; N, 7·9; S, 6·0%); $\lambda_{max.}$ 224, 283, and 291 nm (ε 70,400, 13,700, and 12,200); τ[$(CD_3)_2SO$] 6·74 (6H, s, NMe_2), 6·4—6·9 (4H, m), 6·23 (3H, s, indole NMe), 4·1—5·1 (2H, s), 3·66 (1H, d, *J* 8 Hz, Ar), 3·16 (1H, t, *J* 8 Hz, Ar), 2·84 (1H, t, *J* 8 Hz, Ar), 2·50 (1H, d, *J* 8 Hz, Ar), 2·30 (2H, d, *J* 9 Hz, high-field half of $ArSO_2$ signal), and 2·14 (2H, d, *J* 9 Hz, low-field half of $ArSO_2$ signal).

3-p-*Chlorophenylsulphonylamino*-1-*methyl*-2-*vinylindole* (IX; Ts replaced by *p*-$ClC_6H_4{\cdot}SO_2$).—This *compound*, obtained (50% yield) by the action of alkali on the methiodide, formed pale yellow prisms, m.p. 146—147° (Found: C, 59·1; H, 4·4; N, 7·8; S, 9·2%; *M*, 346. $C_{17}H_{15}ClN_2O_2S$ requires C, 58·95; H, 4·4; N, 8·1; S, 9·3%; *M*, 346); $\lambda_{max.}$ 231 and 303 nm (ε 39,600 and 18,300); $\nu_{max.}$ (Nujol) 3250 cm^{-1} (NH); τ($CDCl_3$) 6·27 (3H, s, indole NMe), 4·56 (1H, q, *J* 1·5 and 12 Hz, H_B), 4·29 (1H, q, *J* 1·5 and 18 Hz, H_C), 3·65br (1H, s, NH, exchanged in D_2O), 3·41 (1H, q, *J* 12 and 18 Hz, H_A), 2·7—3·1 (4H, m, Ar), 2·65 (2H, d, *J* 9 Hz), and 2·34 (2H, *J* 9 Hz).

3-(N-*Ethoxymethyl*-p-*chlorophenylsulphonylamino*)-1-*methyl*-2-[2-(N-*methylphenoxycarbonylamino*)*ethyl*]*indole* (XV).—Compound (II; R = *p*-$ClC_6H_4{\cdot}SO_2$) (1·04 g) in dry dichloromethane (15 ml) was added to a solution of phenyl chloroformate (0·42 g) in dichloromethane (3 ml). Next day dichloromethane (80 ml) was added and the solution was washed with aqueous sodium carbonate (10%; 100 ml) and 2M-hydrochloric acid (100 ml) and dried ($MgSO_4$). Evaporation yielded a glass which could not be obtained crystalline. A solution in ethanol (4—5 ml) slowly deposited a white *solid* (25% yield), m.p. 135—138° (Found: C, 59·9; H, 5·3; N, 7·4%; *M*, 555. $C_{28}H_{30}ClN_3O_5S$ requires C, 60·5; H, 5·4; N, 7·6%; *M*, 555); $\nu_{max.}$ (Nujol) 1724 cm^{-1} (C=O); τ(CCl_4) 8·82 (3H, t, *J* 7 Hz, $CH_2{\cdot}CH_3$), 6·81 (3H, s, NMe), 6·25—7·1 (6H, m, 3 × CH_2), 6·21 (3H, s, indole NMe), 5·03 (2H, m, $N{\cdot}CH_2{\cdot}O$), 3·70 (1H, d, *J* 8 Hz, Ar), 2·6—3·4 (10H, m, Ar), and 2·43 (2H, d, *J* 8 Hz, low-field half of $ArSO_2$ signal); *m/e* 555 (*M*, 5%), 380 (*M* − $ClC_6H_4{\cdot}SO_2$, 50%; *m** 260·2), 229 (380 − $MeNH{\cdot}CO_2Ph$, 97%; *m** 138·0), 183 (229 − C_2H_6O, 100%; *m** 146·4), and 171 ($C_{11}H_{11}N_2$, 60%).

1-*Methyl*-2-[2-(N-*methyl*-p-*tolylsulphonylamino*)*ethyl*]-3-p-*tolylsulphonylaminoindole* (XVI; R = Ts).—(*a*) The methanolic mother liquors from the preparation of compound (II; R = Ts) [preparation (*b*)] were evaporated and the residue was chromatographed on silica. Elution with benzene–ethyl acetate (9 : 1) gave *compound* (XVI; R = Ts) (2% yield), plates, m.p. 161—164° (from methanol) (Found:

[13] K. T. Potts and J. E. Saxton, *Org. Synth.*, 1960, **40**, 68.
[14] U. Hörlein, *Chem. Ber.*, 1954, **87**, 463.
[15] F. E. Ziegler, E. B. Spitzner, and C. K. Wilkins, *J. Org. Chem.*, 1971, **36**, 1759.

M, 511·1599. $C_{26}H_{29}N_3S_2O_4$ requires *M*, 511·1587); $\lambda_{max.}$ 224 and 283 nm (ε 29,100 and 8510); $\nu_{max.}$ (Nujol) 3259 cm^{-1} (NH): τ($CDCl_3$) 7·66 and 7·63 (2 × tosyl Me), 7·23 (3H, s, NMe), 6·5—7·1 (4H, m, $CH_2{\cdot}CH_2$), 6·26 (3H, s, indole NMe), 3·75 (1H, s, NH, exchanged in D_2O), 3·52 (1H, d, *J* 8 Hz, Ar), 3·25 (1H, t, *J* 8 Hz, Ar), 2·6—3·1 (6H, m, Ar), and 2·3—2·5 (4H, m, low-field halves of 2 tosyl signals).

(*b*) From the preparation of compound (II; R = Ts) in propanol the indole (XVI; R = Ts) was isolated in 9% yield.

(*c*) Compound (II; R = Ts) (500 mg) and tosyl azide (300 mg) were boiled under reflux in propanol (25 ml) for 7 days. The solvent was removed and the residue was filtered through silica in benzene–ethyl acetate (9 : 1). The solvent was removed and the residue crystallised from benzene, yielding toluene-*p*-sulphonamide (150 mg). The residue from this recrystallisation was recrystallised from methanol, affording (XVI; R = Ts) (yield 13%), identical (i.r.; t.l.c.) with the sample isolated in (*a*).

1-*Methyl*-2-[2-(N-*methylacetamido*)*ethyl*]-3-p-*tolylsulphonylaminoindole* (XVI; R = Ac).—The indole (II; R = Ts) (200 mg) was dissolved in the minimum of chloroform, and acetic anhydride (1 ml) was added. Next day the solvent was removed *in vacuo*; methanol was then added, the mixture was left for 1 h, and the solvent was removed. This process was repeated until all the excess of acetic anhydride had been destroyed. The residue was triturated with light petroleum (b.p. 60—80°) and then recrystallised from methanol (yield 150 mg) to give *prisms*, m.p. 195—197° (Found: C, 62·5; H, 6·4; N, 10·3; S, 8·2%; *M*, 399. $C_{21}H_{25}N_3O_3S$ requires C, 63·1; H, 6·3; N, 10·5; S, 8·0%; *M*, 399); $\nu_{max.}$ (Nujol) 1615 cm^{-1} (CO); τ($CDCl_3$) 7·63 (tosyl Me), 6·92 (3H, s, NMe), 6·3—7·1 (4H, m, $CH_2{\cdot}CH_2$), 6·23 (3H, s, indole NMe), 3·48 (1H, d, *J* 8 Hz, Ar), 3·41 (1H, s, NH, exchanged in D_2O), 3·23 (1H, t, *J* 8 Hz, Ar), 2·7—3·1 (4H, m, Ar), 2·38 (2H, d, *J* 8 Hz, low-field half of tosyl signal) (the acetyl signals are reported in the main section); τ (pyridine) 7·84 (s, tosyl Me), 7·12 (NMe), and 6·31 (indole NMe).

1-*Methyl*-2-(2-*methylaminoethyl*)-3-p-*tolylsulphonylaminoindole* (XVI; R = H) *Hydrochloride*.—Compound (II; R = Ts) (530 mg) was dissolved in methanol (4 ml) and 2M hydrochloric acid (4 ml). The solution was warmed (70°) for 35 min. Evaporation *in vacuo* yielded a white *solid* which formed needles (0·25 g), m.p. 247—249° (from ethyl acetate–methanol) (Found: C, 58·1; H, 6·0; N, 10·3. $C_{19}H_{24}ClN_3O_2S$ requires C, 57·9; H, 6·1; N, 10·6%); τ[$(CD_3)_2SO$] 7·64 (tosyl Me), 7·42 (3H, s, NMe), 6·96br (4H, s, $CH_2{\cdot}CH_2$), 6·27 (3H, s, indole NMe), 2·6—3·2 (6H, m, Ar), 2·40 (2H, d, *J* 8 Hz, low-field half of tosyl signal), 0·65br (2H, s, NH_2), and 0·50 (1H, s, NH); on adding D_2O the two signals at τ 0·50 and 0·65 disappeared. On adding sodium carbonate to a solution of the hydrochloride, the free base (XVI; R = H) separated; m.p. 63—71°. We did not find a suitable solvent for recrystallisation although the compound gave only one spot on t.l.c. and a molecular ion in the mass spectrum at *m/e* 357. The n.m.r. spectrum ($CDCl_3$) agreed with the structure: τ 7·63 (3H, s, tosyl Me), 7·60 (3H, s, NMe), 7·30 (4H, s, $CH_2{\cdot}CH_2$), 6·40 (3H, s, indole NMe), 5·63br (2H, s, NH, exchanged in D_2O), 2·6—3·2 (6H, m, Ar), and 2·39 (2H, d, *J* 8 Hz, low-field half of tosyl signal): see spectra reported for similar compounds.[11]

A sample of compound (II; R = Ts) (10 mg) was boiled for 2 min with aqueous 2,4-dinitrophenylhydrazine hydrochloride solution (Brady's reagent). A yellow solid separated; this was washed several times with boiling 2M-hydrochloric acid and recrystallised from a little methanol, yielding formaldehyde dinitrophenylhydrazone, identical with an authentic sample (t.l.c. and u.v. spectrum: $\lambda_{max.}$ 345 nm).[16]

3-*Dimethylaminomethyl*-1-*methyl*-2-*vinylindole* (XI).—Compound (I) (2 g) was dissolved in benzene (20 ml) and methyl iodide (5 ml) was added. Next day the solid (90% yield) was collected and recrystallised from aqueous methanol to give plates, m.p. 259—260° (decomp.). The methiodide (1·1 g) was boiled for 2 h in methanol (10 ml) and 4M-sodium hydroxide (50 ml). The solution was extracted with benzene, the extracts were dried ($MgSO_4$) and evaporated and the residue was crystallised from light petroleum (b.p. 60—80°) to give *prisms* (0·40 g), m.p. 57—59° (Found: C, 78·4; H, 8·5; N, 12·9. $C_{14}H_{18}N_2$ requires C, 78·5; H, 8·4; N, 13·1%); $\lambda_{max.}$ 228 and 303 nm (ε 17,000 and 8700); τ($CDCl_3$) 7·73 (6H, s, NMe_2), 6·43 (2H, s, $CH_2{\cdot}NMe_2$), 6·30 (3H, s, indole NMe), 4·55 (1H, q, *J* 2·0 and 11·5 Hz, H_B), 4·15 (1H, q, *J* 2·0 and 18·0 Hz, H_C), 3·15 (1H, q, *J* 11·5 and 18·0 Hz, H_A), 2·5—3·0 (4H, m, Ar), and 2·2—2·35 (1H, m, Ar), *m/e* 214 (*M*, 30%) and 170 (*M* − NMe_2, 100%) (no other peaks of intensity greater than 12%).

1,2-Dimethyl-3-*p*-tolylsulphonylaminoindole [2] had $\lambda_{max.}$ 225, 283, and 291 nm (ε 36,700, 7570, and 6670).

Reaction between 1,4-*Dihydro*-9-*methylcarbazole and Tosyl Azide*.—1,4-Dihydro-9-methylcarbazole (0·177 g) [17] and tosyl azide (0·280 g) were boiled for 5 h in ethanol (2 ml). The solution was cooled and the solid (0·141 g) which separated was identified as 9-methylcarbazole (m.p.; R_F value; i.r. spectrum). Evaporation of the ethanolic mother liquors yielded toluene-*p*-sulphonamide (R_F value and i.r. spectrum).

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