Reactions of 2-Acyl-1,3-dimethylindole Oximes and of 2-Acylamino-1,3-dimethylindole with Arenesulphonyl Azides

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2-Acyl-1,3-dimethylindole oximes react with arenesulphonyl azides to form derivatives of dihydroisoxazolo[4.5-*b*]-indole. The hydrolysis and methylation of these compounds have been examined. Beckmann rearrangement of the oximes yielded 2-acylamino-1,3-dimethylindoles and these compounds reacted with arenesulphonyl azides affording 2-acylimino-3-arylsulphonylamino-1,3-dimethylindolines.

We have investigated the reactions of a wide variety of indoles with arenesulphonyl azides [1-4] and noted that 9-methyl-1-oxotetrahydrocarbazole [4] did not react with these azides. 2-Acetyl-1,3-dimethylindole [5] was prepared and found to be unaffected by *p*-nitrobenzenesulphonyl azide; however the oxime (I; R = Me) reacted smoothly with *p*-chlorobenzenesulphonyl azide ($CbsN_3$) giving two products. The first of these was a 1 : 1 adduct (having lost nitrogen) to which we assign structure (II; R^1 = Me, R^2 = Cl); its u.v. spectrum showed that the indole chromophore had disappeared. In its n.m.r. spectrum (see Figure) the NMe signal (τ 7·72) was 0·57 p.p.m. upfield of the value reported [6] for $PhN(CH_3)_2$, showing marked shielding of the NMe group, and the signals of the four protons of the $ArSO_2$ group appeared as a single spike; similar behaviour is seen in the aromatic region of the spectrum of compound (VIII).[4] The mass spectrum of (II; R^1 = Me, R^2 = Cl) contained a very weak molecular ion, the highest important peak being due to M − MeCN. In order to demonstrate which methyl group was being lost, the reaction of the oxime (I; R = Et) with $CbsN_3$ was examined. The mass spectrum of the product (II; R^1 = Et, R^2 = Cl) contained a weak molecular ion and a strong peak at *m/e* 350 (M − EtCN). We thought that the loss of RCN might be occurring in the spectrometer inlet and so compounds (II; R^1 = Me, R^2 = Cl) and (II; R^1 = Et, R^2 = Cl) were sublimed and found to afford the same material (III). This material was identical with the second product isolated from the reaction between (I; R = Me) and $CbsN_3$. Vigorous

[1] A. S. Bailey, P. A. Hill, and J. F. Seager, *J.C.S. Perkin I*, 1974, 967.
[2] A. S. Bailey, A. J. Buckley, and J. F. Seager, *J.C.S. Perkin I*, 1973, 1809.
[3] A. S. Bailey, A. G. Holton, and J. F. Seager, *J.C.S. Perkin I*, 1972, 1003.
[4] A. S. Bailey, R. Scattergood, and W. A. Warr, *J. Chem. Soc.* (*C*), 1971, 2479.
[5] B. Douglas, J. L. Kirkpatrick, B. P. Moore, and J. A. Weisbach, *Austral. J. Chem.*, 1964, **17**, 246; K. Ishizumi, T. Shioiri, and S. Yamada, *Chem. and Pharm. Bull.* (*Japan*), 1967, **15**, 863.
[6] J. C. N. Ma and E. W. Warnhoff, *Canad. J. Chem.*, 1964, **43**, 1849.

alkaline hydrolysis of compounds (II; R^1 = Me, R^2 = Cl) and (III) gave the known [7] 3-hydroxy-1,3-dimethylindolin-2-one (IV). The reaction of *p*-nitrobenzenesulphonyl azide with the oxime (I; R = Me) gave compound (II; R^1 = Me, R^2 = NO_2), which was hydrolysed to (IV); thus these reactions are of general preparative value. The compounds appear to be in the ring-closed form rather than in the imino-form (V); the i.r. spectrum of (II; R^1 = Me, R^2 = Cl) in tetrahydrofuran contains a band at 1585 cm^{-1} in agreement with the reported [8] value for isoxazolines, and the signals in the aromatic region of the n.m.r. spectrum do not agree with an $ArSO_2N{=}C$ structure, and a compound of type (V) ought to be yellow since it contains the group ON=C–C=N– [*cf.* sugar osazones]. Further, the u.v. spectrum of the methylated product (VI; R = Cl) is similar to that of compound (II; R^1 = Me, R^2 = Cl).

The nitro-compound (II; R^1 = Me, R^2 = NO_2) was methylated with dimethyl sulphate–sodium hydroxide [to give (VI; R = NO_2)] but the corresponding chloro-compound afforded a mixture of methylation and hydrolysis products, and so the material was methylated with diazomethane to give (VI; R = Cl). The mass spectrum of this compound contained a molecular ion of medium intensity, a very small peak at *M* − MeCN, and a peak at *M* − MeCNO; the fragmentation is thus quite different from that of (II). The n.m.r. spectrum of (VI; R = Cl) at 35° is shown in the Figure; two of the Me signals and part of the aromatic region are broad whereas at 70° all the peaks have sharpened. The signal from the indoline NMe group is well downfield of the NMe signal of compound (II; R^1 = Me, R^2 = Cl). The n.m.r. spectrum of (VI; R = Cl) in pyridine solution was also examined; at 35° the spectrum contained a broad band at τ 6·9, a sharp band at 7·7, and a broad band at 8·1; at −30° the spectrum contained eight bands between τ 6·6 and 8·3. Other examples of the broadening of Me signals have been reported.[9]

Compound (II) is considered to be formed *via* the intermediate (VII); displacement of the N_2^+ by the hydroxy-group occurs rather than migration of the NCbs group to the 3-position (*cf.* the formation of an isoxazoline by treating a β-chloro-ketone with hydroxylamine [10]).

The oxime (I; R = Me) was found to undergo a

[7] P. L. Julian and J. Pikl, *J. Amer. Chem. Soc.*, 1935, **57**, 542; E. Giovannini and J. Rosales, *Helv. Chim. Acta*, 1963, **46**, 1332.

[8] 'Physical Methods in Heterocyclic Chemistry,' ed. A. R. Katritzky, Academic Press, New York, vol. II, 1963, p. 214.

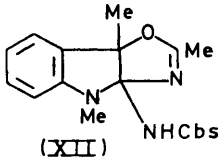
[9] K. D. Bartle, P. M. G. Bavin, D. W. Jones, and R. L'Amie, *Tetrahedron*, 1970, **26**, 911; H. Nakanishi, O. Yamamoto, M. Nakamura, and M. Oki, *Tetrahedron Letters*, 1973, 727.

[10] 'The Chemistry of Heterocyclic Compounds,' ed. A. Weissberger, 'Five- and Six-membered Compounds with Nitrogen and Oxygen,' Interscience, New York, 1962, p. 99.

Beckmann rearrangement under very mild conditions, affording the amide (IX; R = Me); Beckmann rearrangements involving *ortho*-disubstituted phenyl groups are often fast.[11] The n.m.r. spectrum of the compound supported structure (IX; R = Me) rather than the isomeric structure (X). Compound (IX; R = Me) reacted smoothly with *p*-chlorobenzenesulphonyl azide in propanol giving a 1 : 1 adduct (XI; R = Me) isomeric with (II; R^1 = Me, R^2 = Cl). The alternative structure (XII) seemed unlikely since this contains three nitrogen atoms attached to one carbon atom and would be expected to lose MeCN on sublimation, forming (III). The material in fact sublimed unchanged; in its mass spectrum the *M* — MeCN peak was very weak and the base peak, *m/e* 174, was shown (high resolution) to be *M* — Cbs — CH_2CO. The n.m.r. spectrum of the compound supported structure (XI) rather than (XIII); the proton signals of the Cbs group appeared as two close doublets at τ 2·55 and 2·75, those of the other aromatic protons appearing upfield as far as τ 3·8; similar spectral behaviour is shown by (XIV).[12] In contrast the signals from the protons of the Cbs group in compound (XV) [4] appeared as doublets, τ 2·05 and 2·52. Methylation of (XI; R = Me) afforded (XVI); and in the n.m.r. spectrum (35°) of this compound the signals of all four methyl groups appeared as sharp singlets. After the major product (XI) of the reaction had been separated a small quantity of (III) was isolated. This could have been formed either by loss of MeCN from a structure such as (XII) or *via* the diazonium cation (XVII). Compound (IX; R = Et) was also prepared from (I; R = Et) and afforded compound (XI; R = Et).

We hoped to extend the work by examining the reactions of other derivatives of 2-acetyl-1,3-dimethylindole, but with semicarbazide only a small quantity of the azine was obtained; and the ketone did not react with thiosemicarbazide and with *N*-methylhydrazine. The oxime of 2-acetyl-1-methylindole [13] reacted with $CbsN_3$ affording a poor yield of compound (XVIII); *cf.* the reaction of 1,2-dimethylindole with azides.[14]

Professor T. J. King (Nottingham) has confirmed the structures of compounds (VI; R = Cl) and (XI; R = Et) by *X*-ray crystallography. Details will be published separately.



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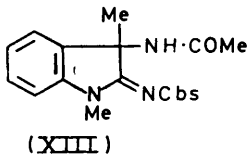

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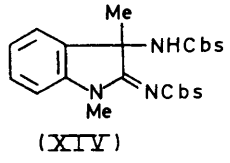

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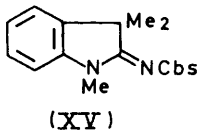

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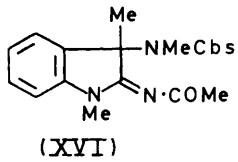
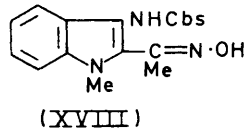
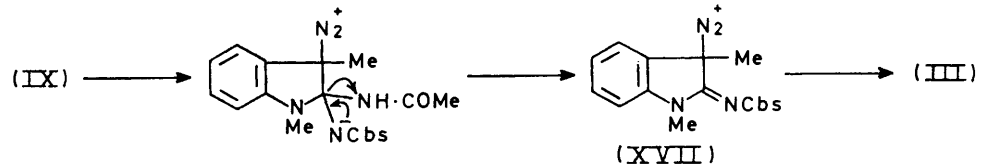


(XVI)



(XVIII)



(XVII)

EXPERIMENTAL

General details and instruments used have been reported.[1,4] 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, a dagger (†) indicates that a high resolution measurement has been made.

3a-p-*Chlorophenylsulphonylamino*-3a,8b-*dihydro*-3,4,8b-*trimethylisoxazolo*[4,5-b]*indole* (II; R^1 = Me, R^2 = Cl).—2-Acetyl-1,3-dimethylindole [5] was obtained (70% yield) by acetylating 1,3-dimethylindole with acetic anhydride–acetic acid, using boron trifluoride–ether as catalyst; $\lambda_{max.}$ 208, 239, and 309 nm (ε 8570, 7300, and 8600); τ 2·46—3·13 (m, Ar), 6·12 (NMe), 7·48 (CMe), and 7·52 (CMe). The *oxime* (I; R = Me), prepared (65% yield) in pyridine (45 min reflux), formed cream-coloured prisms, m.p. 161—162° (from benzene) (Found: C, 71·2; H, 7·0; N, 14·0. $C_{12}H_{14}N_2O$ requires C, 71·2; H, 7·0; N, 13·9%); $\lambda_{max.}$ (ether) 228 and 298 nm (ε 33,800 and 14,200); $\nu_{max.}$ 1405w and 3200br cm^{-1}; τ 0·81 (1H, s, OH), 2·42—3·05 (4H, m, Ar), 6·34 (3H, s, NMe), 7·68 (3H, s, CMe), and 7·74 (3H, s, CMe). A solution of the oxime (0·59 g) in pyridine (5 ml) containing $CbsN_3$ (0·62 g) was heated (100°) for 30 h. The solvent was removed and methanol (2 ml) added. The *isoxazoline* (II; R^1 = Me, R^2 = Cl) (0·41 g) formed prisms, m.p. 188—190° (from propan-1-ol) (Found: C, 55·2; H, 4·7; Cl, 9·0; N, 10·4; S, 7·7. $C_{18}H_{18}ClN_3O_3S$ requires C, 55·2; H, 4·6; Cl, 9·1; N, 10·7; S, 8·2%); $\lambda_{max.}$ 204, 231, and 300sh nm (ε 36,500, 18,700, and 2500); $\nu_{max.}$ 1587, 1610s, 1625, and 3250 cm^{-1}; $\nu_{max.}$ (tetrahydrofuran) 1497s,

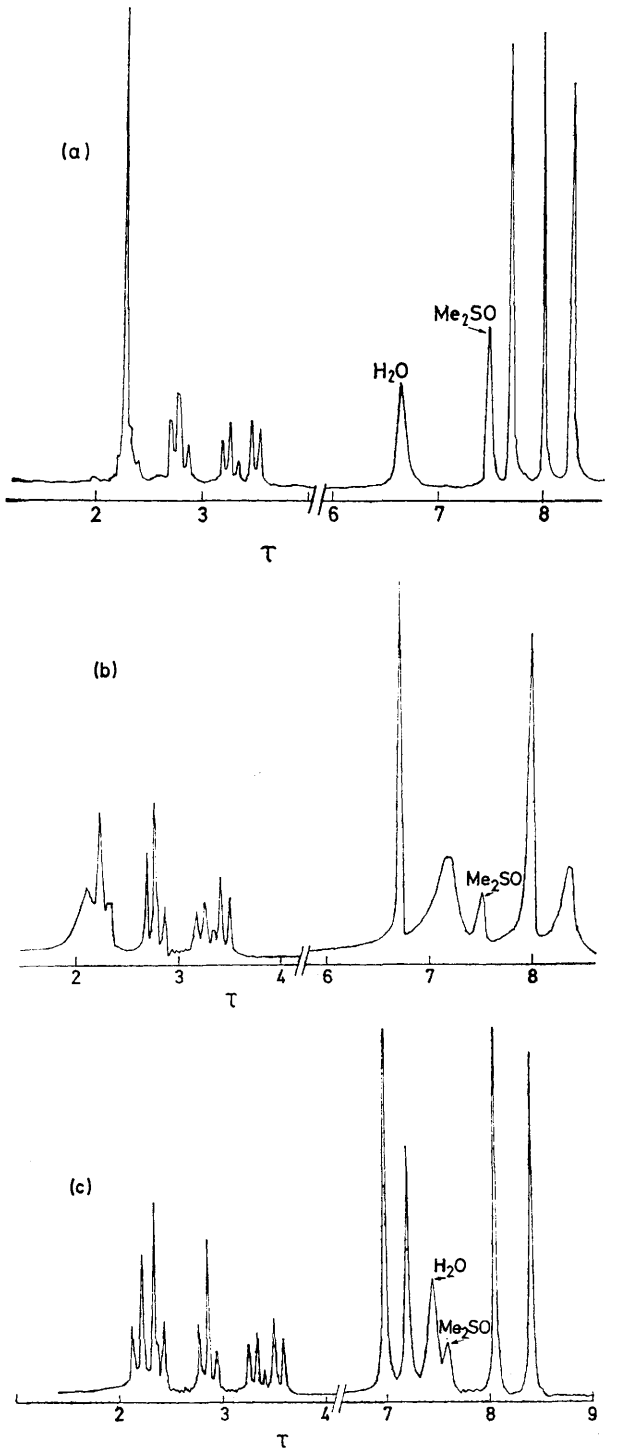
[11] L. G. Donaruma and W. Z. Heldt, *Org. Reactions*, 1960, **11**, 10, 22.

[12] A. S. Bailey, R. Scattergood, and W. A. Warr, *J. Chem. Soc.* (*C*), 1971, 3769.

[13] O. Diels and A. Köllish, *Ber.*, 1911, **44**, 263; F. Chastrette, *Bull. Soc. chim. France*, 1970, 1151.

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

1585, 1612s, and 3150br,s cm^{-1} (for n.m.r. see Figure); *m/e* 391 (M^+, 0·5%), 350 (M — MeCN, 37%), 335 (34%), 175 (350 — Cbs, 100%), 160 (40%), and 134 (175 — MeCN, 45%).



N.m.r. spectra [solvent$(CD_3)_2SO$] (a) of compound (II; R^1 = Me, R^2 = Cl) at 35°; and of compound (VI; R = Cl); (b) at 35° and (c) at 70°

2-p-*Chlorophenylsulphonylimino*-1,3-*dimethylindolin*-3-*ol* (III).—(*a*) The methanolic mother liquors from the isolation of (II; R^1 = Me, R^2 = Cl) were evaporated and the residue was triturated with ether.

(*b*) The oxime (I; R = Me) (1·2 g) was heated (100°) with $CbsN_3$ (1·3 g) in propanol (9 ml) for 50 h; the solid which separated (1·56 g) was recrystallised from propanol.

(*c*) Compound (II; R^1 = Me, R^2 = Cl) was sublimed (175°; 0·1 mmHg; 3 h). *Compound* (III) formed pale yellow needles, m.p. 144—146° (Found: C, 54·6; H, 4·3; Cl, 9·8; N, 7·9; S, 8·9. $C_{16}H_{15}ClN_2O_3S$ requires C, 54·8; H, 4·3; Cl, 10·1; N, 8·0; S, 9·1%); $\lambda_{max.}$ 210sh, 225, 277sh, 286, and 303 nm (ε 25,000, 36,000, 14,100, 15,500, and 14,000); $\nu_{max.}$ 1565s and 3365 cm^{-1}; τ 2·06 (2H, d, *J* 8 Hz, low-field half of Cbs signal), 2·5—3·2 (6H, m, Ar), 4·28 (1H, s, NH, exchanged with D_2O), 6·78 (3H, s, NMe), and 8·02 (3H, s, CMe); *m/e* 350 (M^+, 97%), 335 (87%), 175 (M — Cbs, 100%), and 160 (40%).

3-*Hydroxy*-1,3-*dimethylindolin*-2-*one* (IV).—(*a*) Compound (II; R^1 = Me, R^2 = Cl) (0·5 g) was boiled with potassium hydroxide (2·5 g) in ethanol–water (1 : 1; 20 ml) for 2·5 h; the mixture was then extracted with chloroform, yielding (IV) (130 mg).

(*b*) Compound (III) was hydrolysed under the same conditions. The indolinone formed prisms, m.p. 157—159° (from benzene) (lit.,[7] 152° and 148—149°) (Found: C, 67·4; H, 6·3; N, 7·8. Calc. for $C_{10}H_{11}NO_2$: C, 67·8; H, 6·2; N, 7·9%); $\lambda_{max.}$ 208, 257, and 287sh nm (ε 30,300, 6930, and 1400); $\nu_{max.}$ 1500w, 1618, 1705br,s, and 3310 cm^{-1}; τ 2·6—3·25 (4H, m, Ar), 6·49 (1H, s, OH, exchanged with D_2O), 6·81 (3H, s, NMe), and 8·39 (3H, s, CMe); *m/e* 177 (M^+, 74%), 162 (41%), 149 (M — CO, 35%), and 134 (100%).

3a-[p-*Chlorophenylsulphonyl*(*methyl*)*amino*]-3a,8b-*dihydro*-3,4,8b-*trimethylisoxazolo*[4,5-b]*indole* (VI; R = Cl).—Excess of ethereal diazomethane was added to an ice-cold solution of (II; R^1 = Me, R^2 = Cl) (0·5 g) in ethyl acetate (15 ml). After 5 h the solvents were removed and methanol was added. *Compound* (VI; R = Cl) formed prisms, m.p. 232—235° (from methyl cyanide) (250 mg) (Found: C, 56·3; H, 5·1; Cl, 8·5; N, 10·4; S, 7·9. $C_{19}H_{20}ClN_3O_3S$ requires C, 56·2; H, 4·9; Cl, 8·8; N, 10·3; S, 7·9%); $\lambda_{max.}$ ($CHCl_3$) 243, 268sh, and 303sh (ε 16,300, 8300, and 2800); $\nu_{max.}$ 1573, 1586, 1603s, and 1618 cm^{-1}; *m/e* 405 (M^+, 35%), 364 (2%), 348 (42%), 189 (364 — Cbs, 85%), 173 (348 — Cbs, 100%), and 160 (364 — CbsNMe, 61%).

3a,8b-*Dihydro*-3,4,8b-*trimethyl*-3a-p-*nitrophenylsulphonylaminoisoxazolo*[4,5-b]*indole* (II; R^1 = Me, R^2 = NO_2).—The oxime (I; R = Me) (0·5 g) and *p*-nitrobenzenesulphonyl azide (0·6 g) were heated (100°, 24 h) in propanol (5 ml). The material which separated was recrystallised from acetic acid to give yellow *prisms* (0·4 g), m.p. 166—168° (Found: C, 54·1; H, 4·6; N, 13·6; S, 7·5. $C_{18}H_{18}N_4O_5S$ requires C, 53·7; H, 4·5; N, 13·9; S, 8·0%); $\lambda_{max.}$ 203, 248, and 262 nm (ε 36,200, 12,300, and 12,400); $\nu_{max.}$ 1525s, 1613s, 1622, and 3285 cm^{-1}; τ [$(CD_3)_2SO$] 0·81 (1H, NH, exchanged with D_2O), 1·56 (2H, d, *J* 9 Hz, Ar), 2·05 (2H, d, *J* 9 Hz, Ar), 2·6—2·9 (2H, m, Ar), 3·27 (1H, t, *J* 8 Hz, Ar), 3·52 (1H, d, *J* 8 Hz, Ar), 7·77 (3H, s, NMe), 8·03 (3H, s, N=CMe), and 8·29 (3H, s, CMe); *m/e* (M^+ not observed) 361 (M — MeCN, 61%), 346 (361 — Me, 70%), 175 (100%), 160 (80%), and 134 (60%). Alkaline hydrolysis of (II; R^1 = Me, R^2 = NO_2) afforded (IV). Compound (II; R^1 = Me, R^2 = NO_2) (1·0 g) was dissolved in aqueous acetone containing potassium hydroxide and methylated with dimethyl sulphate. The N-*methyl compound* (VI; R = NO_2) formed yellow prisms (0·4 g), m.p. 230—232° (from methyl cyanide) (Found: C, 54·9; H, 4·9; N, 13·6; S, 7·6. $C_{19}H_{20}N_4O_5S$ requires C, 55·0; H,

4·8; N, 13·5; S, 7·7%); $\lambda_{max.}$ ($CHCl_3$) 270sh nm (ε 12,000); $\nu_{max.}$ 1537 and 1608 cm^{-1}; τ 1·66 (2H, d, *J* 8 Hz), 1·90br (2H, s), 2·6—2·9 (2H, m), 3·2 (1H, t, *J* 8 Hz), 3·57 (1H, d, *J* 8 Hz), 6·6—7·4br (6H, s), 7·88 (3H, s, CMe), and 8·2—8·8br (3H, s); *m/e* 416 (M^+, 20%), 359 (*M* — MeCNO, 24%), 189 (43%), 173 (100%), and 160 (34%).

3a-p-*Chlorophenylsulphonylamino*-3-*ethyl*-3a,8b-*dihydro*-4,8b-*dimethylisoxazolo*[4,5-b]*indole* (II; R^1 = Et, R^2 = Cl).—1,3-*Dimethyl*-2-*propionylindole*, prepared from 1,3-dimethylindole and propionic anhydride with boron trifluoride–ether as catalyst, formed white needles, m.p. 113—114° (from ethanol) (yield 50%) (Found: C, 77·7; H, 7·4; N, 6·9. $C_{13}H_{15}NO$ requires C, 77·6; H, 7·5; N, 7·0%); $\nu_{max.}$ 1517 and 1650br,s cm^{-1}; τ 2·3—3·0 (4H, m), 6·10 (NMe), 7·10 (2H, q, *J* 7 Hz), 7·43 (CMe), and 8·76 (3H, t, *J* 7 Hz). The *oxime* (I; R = Et) formed prisms, m.p. 161—162°: (from cyclohexane) (Found: C, 71·9; H, 7·4; N, 12·9. $C_{13}H_{16}N_2O$ requires C, 72·2; H, 7·4; N, 13·0%); $\nu_{max.}$ 3250 cm^{-1}. The oxime was treated with $CbsN_3$ as already described giving the *isoxazoline* (II; R^1 = Et, R^2 = Cl) (50% yield) as prisms, m.p. 166—168° (from ethanol) (Found: C, 55·9; H, 4·9; Cl, 8·5; N, 10·2; S, 7·7. $C_{19}H_{20}ClN_3O_3S$ requires C, 56·2; H, 4·9; Cl, 8·9; N, 10·3; S, 7·9%); $\lambda_{max.}$ 205, 232, and 300sh nm (ε 44,100, 23,700, and 2800); $\nu_{max.}$ 1579, 1613, and 3250 cm^{-1}; τ [$(CD_3)_2SO$] 1·10 (1H, NH), 2·30 (4H, s, Cbs), 2·6—2·9 (2H, m, Ar), 3·30 (1H, t, *J* 8 Hz), 3·52 (1H, d, *J* 8 Hz), 7·70 (3H, s, NMe), 7·71 (2H, q, *J* 7 Hz, CH_2·CH_3), 8·35 (3H, s, CMe), and 8·90 (3H, t, *J* 7 Hz); *m/e* 405 (M^+, 2%), 350 (42%), 335 (37%), 175 (100%), and 160 (50%). Sublimation of this compound afforded compound (III) (m.p., i.r. spectrum, t.l.c.).

2-*Acetylimino*-3-p-*chlorophenylsulphonylamino*-1,3-*dimethylindoline* (XI; R = Me).—The oxime (I; R = Me) (2·0 g) was dissolved in acetic acid (70 ml) and concentrated sulphuric acid (10 ml) was added. Two hours later the solution was poured into water (100 ml) and the solid was collected and recrystallised from propanol. 2-*Acetylamino*-1,3-*dimethylindole* formed needles (1·1 g), m.p. 227—230° (Found: C, 71·2; H, 6·9; N, 13·9. $C_{12}H_{14}N_2O$ requires C, 71·2; H, 7·0; N, 13·9%); $\lambda_{max.}$ 228, 287, and 293sh nm (ε 41,300, 9300, and 8000); $\nu_{max.}$ 1540, 1661, and 3210br cm^{-1}; τ [$(CD_3)_2SO$] 0·33 (1H, NH), 2·5—3·1 (4H, m, Ar), 6·53 (3H, s, NMe), and 7·91 (6H, s, CMe and COMe). The amide (IX; R = Me) (3·0 g) and $CbsN_3$ (3·0 g) were heated (100°; 24 h) in propan-1-ol (12 ml). The solid (4 g) which separated on cooling was collected and recrystallised from ethanol. The *indoline* (XI; R = Me) formed prisms, m.p. 165—167° (from ethanol) (Found: C, 54·9; H, 4·7; Cl, 9·1; N, 10·6; S, 8·0. $C_{18}H_{18}ClN_3O_3S$ requires C, 55·2; H, 4·6; Cl, 9·1; N, 10·7; S, 8·2%); $\lambda_{max.}$ 230sh, 271, and 305sh nm (ε 19,000, 9900, and 3800); $\nu_{max.}$ 1498w, 1609, 1647, 1673, 1696w, and 3174 cm^{-1}; $\nu_{max.}$ (tetrahydrofuran) 1615, 1675, 1695, and 3170 cm^{-1}; τ [$(CD_3)_2SO$] 2·5—2·9 (5H, m), 7·10 (1H, d, *J* 8 Hz), 7·55 (1H, t, *J* 8 Hz), 7·80 (1H, d, *J* 8 Hz), 6·88 (3H, s, NMe), 7·69 (3H, s, COMe), and 8·42 (3H, s, CMe) (NH not detected); *m/e* 391 (M^+, 16%), 376 (11%), 350 (*M* — MeCN, 2%), 333 (*M* — MeCONH, 7%), 216 (*M* — Cbs, 85%), and 174† (*M* — Cbs — CH_2CO, 100%). The compound was recovered unchanged on sublimation. The propanolic mother liquors from the preparation of (XI; R = Me) were evaporated, and methanol was added yielding compound (III) (1·0 g). Methylation (CH_2N_2; 12 h) of (XI; R = Me) afforded the N-*methyl derivative* (XVI), white prisms, m.p. 135—137° (from methanol) (Found: M^+, 405·0906. $C_{19}H_{20}ClN_3O_3S$ requires *M*, 405·0914); $\lambda_{max.}$ (MeOH) 220sh and 273 nm (ε 20,000 and 10,100); τ 2·6—3·6 (8H, m, Ar), 6·75 (NMe), 6·86 (NMe), 7·59 (COMe), and 8·18 (CMe); *m/e* 405 (7%), 230 (48%), 202 (92%), 201 (78%), 160 (73%), and 159 (*M* — CbsNMe — CH_2CO, 100%).

3-p-*Chlorophenylsulphonylamino*-1,3-*dimethyl*-2-*propionyliminoindoline* (XI; R = Et).—The oxime (I; R = Et) was rearranged to give the amide (IX; R = Et) with acetic and sulphuric acids. 1,3-*Dimethyl*-2-*propionylaminoindole* (IX; R = Et) formed white needles, m.p. 181—183° (from benzene) (Found: C, 72·2; H, 7·5; N, 12·8. $C_{13}H_{16}N_2O$ requires C, 72·2; H, 7·4; N, 13·0%); $\nu_{max.}$ 1595, 1625, 1670br, and 3260s cm^{-1}; τ [$(CD_3)_2SO$] 0·37br (1H, s, NH), 2·5—3·1 (4H, m, Ar), 6·52 (3H, s, NMe), 7·6 (2H, q, *J* 7 Hz, CH_2·CH_3), 7·91 (3H, s, CMe), and 8·85 (3H, t, *J* 7 Hz, CH_2·CH_3). The amide (1·5 g) was heated with $CbsN_3$ in propanol (100°; 29 h). The *iminoindoline* (XI; R = Et) (1·6 g) formed prisms, m.p. 129—131° (from ethanol) (Found: C, 56·3; H, 5·0; Cl, 8·9; N, 10·3; S, 7·7. $C_{19}H_{20}ClN_3O_3S$ requires C, 56·2; H, 4·9; Cl, 8·8; N, 10·3; S, 7·9%); $\nu_{max.}$ 1604, 1640, 1667, and 3185 cm^{-1}; τ 2·0 (1H, s, NH, exchanged with D_2O), 2·7—3·3 (8H, m, Ar), 6·97, (3H, s, NMe), 7·42 (2H, q, *J* 8 Hz), 8·40 (3H, s, Ce), and 8·82 (3H, t, *J* 8 Hz).

2-*Acetyl*-3-p-*chlorophenylsulphonylamino*-1-*methylindole Oxime* (XVIII).—2-Acetyl-1-methylindole had m.p. 71—72° (lit.,[13] 72°); $\nu_{max.}$ 1670 cm^{-1}; $\lambda_{max.}$ 206, 235, and 305 nm (ε 19,000, 13,900, and 27,700); τ 2·3—3·0 (5H, m, Ar), 5·92 (3H, s, NMe), and 7·40 (3H, s, CMe). The *oxime* formed needles, m.p. 165—166° (from ethanol–water, 10 : 1) (Found: C, 70·3; H, 6·5; N, 14·9. $C_{11}H_{12}N_2O$ requires C, 70·4; H, 6·4; N, 14·8%); $\nu_{max.}$ 1610 and 3300br cm^{-1}; τ [$(CD_3)_2SO$] 2·4—3·3 (5H, m, Ar), 6·10 (3H, s, NMe), 6·70 (1H, s, OH, exchanged with D_2O), and 7·88 (3H, s, CMe). The oxime (0·45 g) and $CbsN_3$ (0·52 g) were heated in pyridine (5 ml) (100°; 15 h). The resulting oil was chromatographed on silica; benzene–ethyl acetate (10 : 1) yielded an oil which crystallised on trituration with methanol. The solid was recrystallised from methanol yielding the *sulphonamide* (XVIII), pale orange crystals (0·13 g), m.p. 187—188° (Found: C, 54·2; H, 4·3; N, 11·2. $C_{17}H_{16}ClN_3SO_3$ requires C, 54·2; H, 4·2; N, 11·1%); $\lambda_{max.}$ (Et_2O) 230 and 298 nm (ε 34,000, and 14,000); $\nu_{max.}$ 1470, 1590, and 3400br cm^{-1}; τ [$(CD_3)_2SO$] —1·5 and 0·35 (each 1H, s, exchanged with D_2O, OH and NH), 2·3—3·2 (8H, m, Ar), 6·25 (3H, s, NMe), and 7·88 (3H, s, CMe); *m/e* 377 (M^+, 7%), 202 (*M* — Cbs, 100%), 185 (202 — OH, 52%), and 172 (20%).

2-Acetyl-1,3-dimethylindole was boiled with semicarbazide hydrochloride for 6 h in pyridine. Starting material (90%) was recovered but the *azine* (9%) was isolated as pale yellow crystals, m.p. 188—189° (from ethanol) (Found: C, 77·7; H, 7·0; N, 15·3. $C_{24}H_{26}N_4$ requires C, 77·7; H, 7·0; N, 15·2%); $\lambda_{max.}$ (Et_2O) 212 and 342 nm (ε 28,300 and 17,500); $\nu_{max.}$ 1600 cm^{-1}; τ 2·4—3·0 (8H, m, Ar), 6·10 (6H, s, NMe), and 7·50 and 7·55 (12H, s, CMe), *m/e* 370 (*M*, 45%) and 185 (100%).

2-p-*Chlorophenylsulphonylimino*-1,3,3-*trimethylindoline* (XV).—Prepared[4] from 1,3,3-trimethyl-2-methyleneindoline and $CbsN_3$, *compound* (XV) formed prisms, m.p. 179—181° (from propanol) (Found: C, 58·4; H, 4·8; N, 7·9. $C_{17}H_{17}ClN_2O_2S$ requires C, 58·5; H, 4·9; N, 8·0%); τ 2·05 (2H, d, *J* 8 Hz), 2·52 (2H, d, *J* 8 Hz), 2·6—3·2 (4H, m, Ar), 6·63 (NMe), and 8·25 (CMe).

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