Some Reactions of 3-Diazo-1-methyl-2-*p*-tolylsulphonyliminoindoline and of 2-Arylsulphonylimino-1-methylindolines

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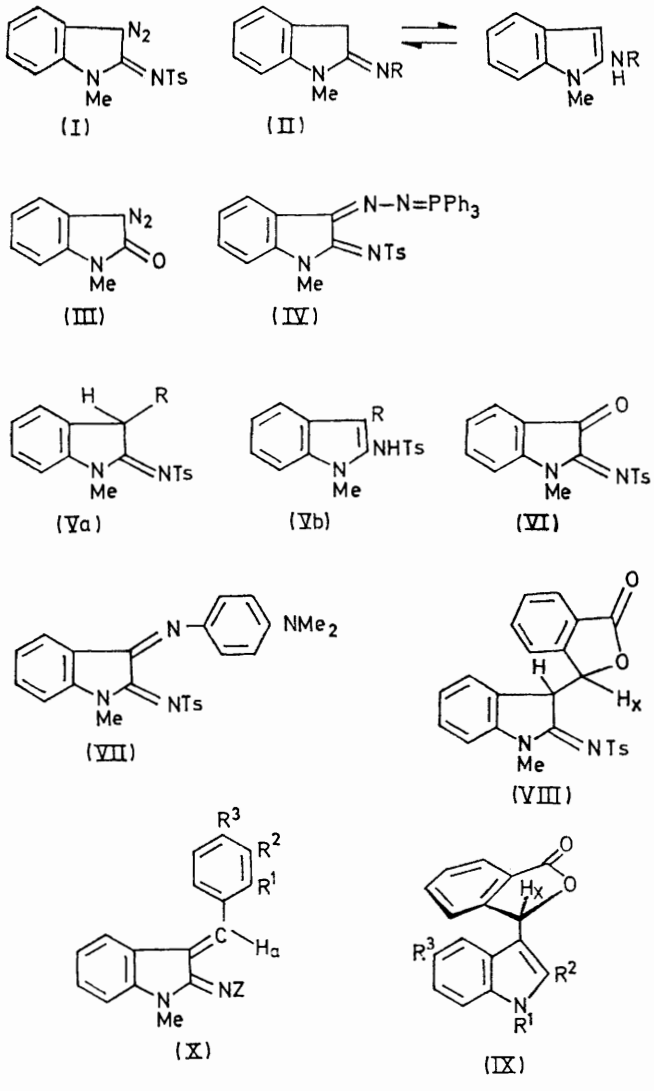
The reactions of 3-diazo-1-methyl-2-*p*-tolylsulphonyliminoindoline with triphenylphosphine and with a variety of acids have been examined; the compound is less reactive than 3-diazo-1-methyloxindole. The methylene group of a 2-arylsulphonylimino-1-methylindoline is reactive; condensation products are formed with *p*-nitrosodimethylaniline and with a variety of aromatic aldehydes.

THE preparations of 2-arylsulphonylimino-3-diazoindolines (I) and 2-arylsulphonyliminoindolines (II) have recently [1] been described; we now report some reactions of these compounds.

The diazo-compound (I) reacts with triphenylphosphine forming the phosphorane imine (IV); the reaction only occurs rapidly at 130°, in contrast to the behaviour of the oxindole (III) which reacts [2] rapidly with triphenylphosphine at room temperature. The diazo-compound did not couple with β-naphthol,[3] and yielded coloured amorphous material with phloroglucinol.[4] On treatment with hydrochloric, with hydrobromic, and with dichloroacetic acids the diazo-compound lost nitrogen [5,6] affording compounds (V; R = Cl, Br, or O·CO·$CHCl_2$, respectively). The n.m.r. spectrum ($CDCl_3$) of (V; R = Cl) showed that the compound was a mixture of two tautomers containing 45% of form (Va); in the same solvent (V; R = O·CO·$CHCl_2$) was entirely in form (Va). Compound (V; R = Br) was insoluble in deuteriochloroform but in dimethyl sulphoxide solution 15% of (Va) was present. The dimethyl sulphoxide solution of (V; R = Br) slowly deposited bright red crystals of 1-methyl-2-*p*-tolylsulphonyliminoindoxyl

[1] A. S. Bailey, A. J. Buckley, W. A. Warr, and J. J. Wedgwood, *J.C.S. Perkin I*, 1972, 2411.
[2] E. J. Moriconi and J. J. Murray, *J. Org. Chem.*, 1964, **29**, 3577.
[3] H. P. Patel and J. M. Tedder, *J. Chem. Soc.*, 1963, 4593.
[4] T. Severin, *Chem. Ber.*, 1959, **92**, 1517.
[5] J. M. Griffing and R. C. Elderfield, *J. Org. Chem.*, 1946, **11**, 123; B. R. Baker, M. V. Querry, A. F. Kadish, and J. H. Williams, *J. Org. Chem.*, 1952, **17**, 52.
[6] H. U. Daeniker and J. Druey, *Helv. Chim. Acta*, 1957, **40**, 2148.

(VI); the oxidation of benzylic halides by dimethyl sulphoxide is well known,[7] and (V; R = Cl) and (V; R = O·CO·$CHCl_2$) decomposed rapidly in dimethyl sulphoxide yielding (VI) (n.m.r. spectra could not be obtained in this solvent). The diazo-compound did not



react with boiling acetic acid in the presence of copper,[8] and with phosphoric, sulphuric, perchloric, formic, trichloroacetic, and trifluoroacetic acids dark brown tars were obtained.

The methylene group of compound (II; R = Ts) reacts readily with *p*-nitrosodimethylaniline affording the di-imine (VII), hydrolysis of which produces the indoxyl (VI) in good yield. In the mass spectrum of (VI) the $M - SO_2$ peak is almost as intense as that of the molecular ion, and the base peak (*m/e* 159) is the same as that of the diazo-compound (I).[1] Phthalaldehydic acid reacts[9] smoothly with indoles forming 3-phthalidylindoles; compound (II; R = Ts) reacts with this aldehyde yielding a product whose i.r. spectrum (Nujol) contained bands at 1592 (C=N) and 1752 cm^{-1} (C=O) but no band in the NH region, suggesting structure (VIII). However the n.m.r. spectrum [$(CD_3)_2SO$] of the material contained a signal at τ 1·79 (NH) and the peak at 3·55 (CH_x) was a singlet, showing the structure of the compound in solution to be (IX; R^1 = Me, R^2 = NHTs, R^3 = H). An unexpected feature of this spectrum was the appearance of signals at τ 3·85 (1H, d, *J* 8 Hz) and 3·20 (1H, t, *J* 8 Hz); these signals are at higher field than usual for protons attached to C(4—7) of an indole nucleus. Models of this compound indicate that the two aryl rings are arranged as shown in (IX), especially when there is a large substituent at C(2), and we suggest that these high-field signals are associated with the protons at C(4) and C(5). A sample of 1,2-dimethyl-3-phthalidylindole (IX; $R^1 = R^2$ = Me, R^3 = H) was prepared;[9] its n.m.r. spectrum showed signals at τ 3·70 (1H, d, *J* 8 Hz) and 3·25 (1H, t, *J* 8 Hz), but in the n.m.r. spectrum of 5-chloro-2-methyl-3-phthalidylindole (IX; R^1 = H, R^2 = Me, R^3 = Cl) these signals were absent, supporting this hypothesis.

Compound (II; R = Cbs) * reacted with benzaldehyde under acidic conditions forming two compounds, the di-indolylphenylmethane (XI; $R^1 = R^2$ = H, Z = Cbs) and *E*-3-benzylidene-2-*p*-chlorophenylsulphonylimino-1-methylindoline (X; $R^1 = R^2 = R^3$ = H, Z = Cbs). In the n.m.r. spectrum of the latter compound the signal for H_a appeared at very low field (τ 1·3) and the *E*-configuration was assigned by analogy with the spectral properties of the 3-benzylideneoxindoles [10] of known configuration.[11] Compound (II; R = Ts) reacted with *o*-nitrobenzaldehyde in pyridine solution forming the 1 : 1 reaction product *E*-1-methyl-3-(*o*-nitrobenzylidene)-2-*p*-tolylsulphonyliminoindoline (X; $R^1 = NO_2$, $R^2 = R^3$ = H, Z = Ts) (*cf.* the reaction of 1-methyloxindole with this aldehyde [11]). With four other aldehydes only the 2 : 1 reaction products (XI) were isolated. These di-indolylarylmethanes gave analytical data in good agreement with the proposed formulae; their u.v. spectra (ethanol) were consistent with an indole structure. The n.m.r. spectra [$(CD_3)_2SO$] showed the H_b signal as a sharp singlet in the range τ 4·0—4·3 and contained only one NMe signal (6·7) and a single CMe signal (7·7), showing the symmetry of the structure (see Figure 1). The NMe signal appears at unusually high field for an indole NMe, but models show that the molecule is very crowded, with the benzene rings of the $ArSO_2$ groups close to the NMe groups. The molecular ions could not be detected in the mass spectra of these compounds, the highest peaks corresponded to fragments (II) and (X). A sample of the 2 : 1 product (XI; R^1R^2 = O·CH_2·O, Z = Ts) de-

* Cbs = *p*-ClC_6H_4·SO_2.

[7] N. Kornblum, W. J. Jones, and G. J. Anderson, *J. Amer. Chem. Soc.*, 1959, **81**, 4113; H. R. Nace and J. J. Monagle, *J. Org. Chem.*, 1959, **24**, 1792.

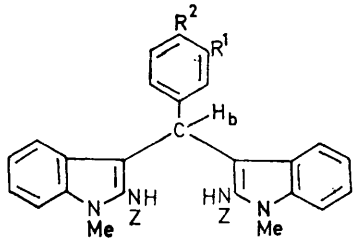
[8] P. Yates, *J. Amer. Chem. Soc.*, 1952, **74**, 5376.

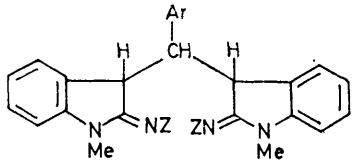
[9] W. E. Noland and J. E. Johnson, *J. Amer. Chem. Soc.*, 1960, **82**, 5143; C. W. Rees and C. R. Sabat, *J. Chem. Soc.*, 1965, 680.

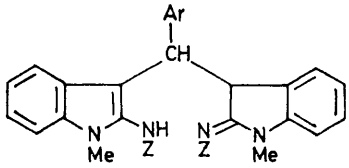
[10] R. J. Sundberg, 'The Chemistry of Indoles,' Academic Press, New York, 1970, pp. 39—56, 345—346.

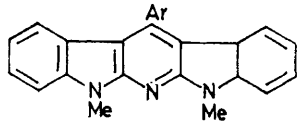
[11] R. W. Daisley and J. Walker, *J. Chem. Soc.* (*C*), 1971, 3357.

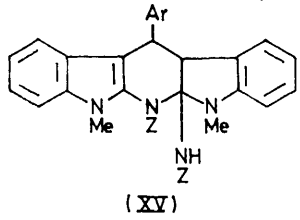
composed into its components (II; R = Ts) and (X; R^1 = H, R^2R^3 = O·CH_2·O, Z = Ts) either on boiling in chlorobenzene or on heating with hydrochloric acid in acetic acid solution. All the foregoing data are in good agreement with structure (XI). However the spectra of these compounds in $CDCl_3$ are completely different from those of solutions in $(CD_3)_2SO$ (see Figure 2).

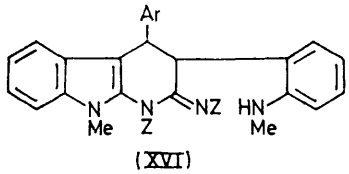

(XI)


(XII)


(XIII)


(XIV)


(XV)


(XVI)

Five spectra were obtained, including that of (XI; R^1 = R^2 = H, Z = Cbs), since we were so uncertain of the positions of the NMe signals. The solutions used for these n.m.r. determinations were colourless and the materials were recovered unchanged; small quantities of the orange-coloured compounds (X) would have been readily detected by t.l.c. The n.m.r. spectra of solutions in $CDCl_3$ cannot be explained simply on the basis that the solutions contained mixtures of (XI), (XII), and (XIII), by analogy with the behaviour of simple 1,3-dialkyl-2-arylsulphonylaminoindoles.[12] The τ value of the low-field NMe signal is low for a simple indole,[12] and the high-field NMe signal (7·4) corresponds to that of a methylaniline.[13] From the reactions of 2-amino-1-methylindole with aromatic aldehydes the pentacyclic compounds of structure (XIV) have been isolated.[14] Presumably these are formed *via* (XIII; Z = H) and (XV; Z = H) by loss of ammonia and oxidation, reactions similar to the formation of acridines from *m*-phenylenediamines and aldehydes.[15] This suggests that our materials may be forming structures of type (XV) and possibly opening the indole ring to give (XVI); such types of reaction are known.[16] All attempts to trap structures such as (XV) or (XVI) by alkylation or acylation of the materials in chloroform solution failed.

[12] A. S. Bailey, A. J. Buckley, and W. A. Warr, *J.C.S. Perkin I*, 1972, 1626.

[13] J. C. N. Ma and E. W. Warnhoff, *Canad. J. Chem.*, 1965, **43**, 1849.

[14] R. S. Sagitullin, A. N. Kost, E. D. Matveeva, and N. I. Nemudrova, *Khim. geterotsikl. Soedinenii*, 1970, **7**, 920 (*Chem. Abs.*, 1971, **74**, 3532).

[15] ' Heterocyclic Compounds,' vol. 4, ed. R. C. Elderfield, Wiley, New York, 1952, pp. 515—516.

[16] Ref. 10, pp. 331—339.

EXPERIMENTAL

Details of instruments used have already been published.[17]

1-*Methyl*-2-p-*tolylsulphonylimino*-3-*triphenylphosphoranediylhydrazonoindoline* (IV).—(*a*) The diazo-compound (I) (100 mg) and triphenylphosphine (250 mg) were mixed and

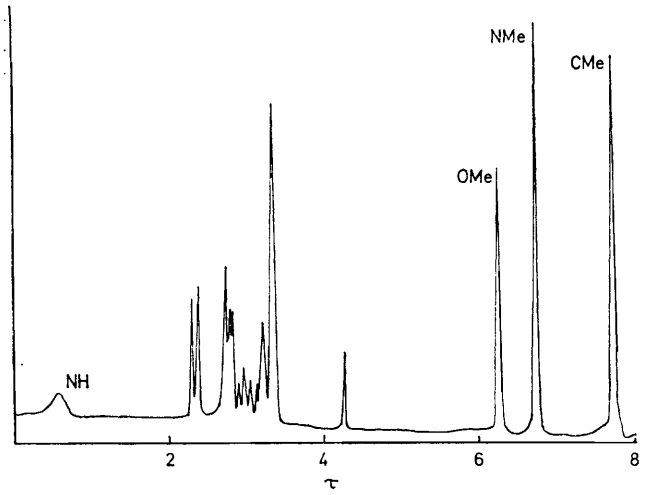


FIGURE 1 N.m.r. spectrum of compound (XI; R^1 = H, R^2 = OMe, Z = Ts) in $(CD_3)_2SO$; water and Me_2SO peaks omitted

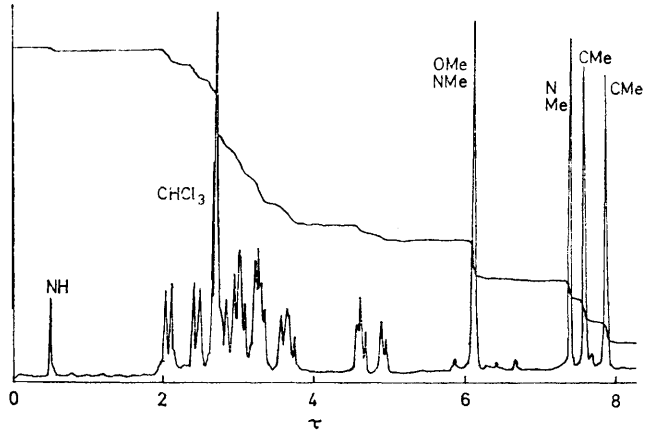


FIGURE 2 N.m.r. spectrum of compound (XI; R^1 = H, R^2 = OMe, Z = Ts) in $CDCl_3$

heated (130°; 10 min); the solid mass was ground up under ethyl acetate and recrystallised from 2-methoxyethanol (yield 75%).

(*b*) The two components were boiled for 10 min in chlorobenzene solution and the solvent was evaporated off; yield 75% after recrystallisation. The *compound* formed canary-yellow crystals, m.p. 200° (decomp.) containing solvent (Found: C, 67·2; H, 5·8; N, 8·3; P, 4·6; S, 4·6. $C_{34}H_{29}N_4O_2PS,C_3H_8O_2$ requires C, 66·9; H, 5·6; N, 8·4; P, 4·7; S, 4·8%); $\nu_{max.}$ (N) 1508, 1578, and 3400br cm^{-1}; $\lambda_{max.}$ ($CHCl_3$) 242, 278, 302, 345, and 400sh nm (ε 11,800, 23,900, 4590, 7370, and 3160); *m/e* (no molecular ion) 326 [(I), 30%], 262 [$(Ph)_3P$, 100%], and 159 ($C_9H_7N_2O$, 48%). Since completion of this work the preparation of this compound has been recorded,[18] m.p. 206—207°.

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

3-*Chloro*-1-*methyl*-2-p-*tolylsulphonyliminoindoline* (V; R = Cl).—The diazo-compound (I) (0·5 g) was dissolved in benzene (20 ml) and conc. hydrochloric acid (2 ml) added. The mixture was shaken for 24 h and the benzene solution was washed with water and with sodium carbonate solution, dried ($MgSO_4$), and evaporated. After two recrystallisations from benzene the *compound* had m.p. 166—168° (0·28 g) (Found: C, 57·9; H, 4·4; Cl, 11·1; N, 8·0; S, 9·1. $C_{16}H_{15}ClN_2O_2S$ requires C, 57·4; H, 4·5; Cl, 10·6; N, 8·4; S, 9·6%); $\nu_{max.}$ (N) 1560, 1595, and 3230 cm^{-1}; $\lambda_{max.}$ 226 and 288 nm (ε 58,000 and 11,500); τ ($CDCl_3$) 7·59 (3H, s, tosyl Me), 6·72 (s, NMe indoline), 6·20 (s, NMe indole), 3·70 [s, C(3)H], 3·37 (s, NH, exchanged D_2O), 2·3—3·1 (6H, m, Ar), and 2·07 [d, *J* 8 Hz, low-field half of tosyl signal of (Va)] [ratio (Va) : (Vb) 45 : 55]; *m/e* 334 (M^+, 14%) and 179 (M − Ts, 100%).

When the reaction was repeated using conc. hydrobromic acid 3-*bromo*-1-*methyl*-2-p-*tolylsulphonyliminoindoline* (V; R = Br) was obtained, as pale yellow crystals from benzene (65% yield), m.p. 193—194° (decomp.) (Found: C, 51·0; H, 3·9; Br, 21·4; N, 7·4; S, 8·5. $C_{16}H_{15}BrN_2O_2S$ requires C, 50·7; H, 4·0; Br, 21·1; N, 7·4; S, 8·5%); $\nu_{max.}$ (N) 1590br, 1620, and 3240br cm^{-1}; $\lambda_{max.}$ 204, 225, 263, and 281 nm (ε 14,500, 28,800, 10,700, and 10,400); τ [$(CD_3)_2SO$] 7·59 (3H, s, tosyl Me), 6·74 (s, NMe indoline), 6·40 (s, NMe indole), 3·55 [s, C(3)H], 2·3—2·9 (6H, m, Ar), 2·13 [d, *J* 8 Hz, low-field half of tosyl signal of (Va)], and −0·45 (s, NH, exchanged D_2O) [ratio (Va) : (Vb) 15 : 85]; *m/e* 378 (M^+, 17%) and 222 (M − Ts − H) (100%).

3-*Dichloroacetoxy*-1-*methyl*-2-p-*tolylsulphonyliminoindoline* (V; R = O·CO·$CHCl_2$).—The diazo-compound (I) (1 g) was stirred in benzene (80 ml) with dichloroacetic acid (2 ml). After 18 h the product was worked up in the usual way; it appeared (t.l.c.) to be a mixture and was chromatographed on silica (100 g) in benzene–ethyl acetate. Elution with benzene containing 2—10% ethyl acetate gave the *ester* (V; R = O·CO·$CHCl_2$) (0·28 g), m.p. 124—126° (from ethyl acetate) (Found: C, 50·1; H, 3·7; Cl, 16·4; N, 6·3; S, 7·5. $C_{18}H_{16}Cl_2N_2O_4S$ requires C, 50·6; H, 3·7; Cl, 16·6; N, 6·6; S, 7·5%); $\nu_{max.}$ (N) 1590 and 1783 cm^{-1}; $\lambda_{max.}$ 230, 276, 285, and 311 nm (ε 29,200, 11,500, 11,300, and 6750); τ ($CDCl_3$) 7·60 (3H, s, tosyl Me), 6·71, (3H, s, NMe), 3·90 (1H, s, O·CO·CCl_2H), 3·06 [1H, s, C(3)H], 2·3—2·9 (6H, m, Ar), and 2·17 (2H, d, *J* 8 Hz, low-field half of tosyl signal) [100% form (Va)]; *m/e* 426 (M^+, 28%), 271 (M − Ts, 37%), 187 (M − Ts − $CHCl_2$ − H, 96%), and 91 (100%). Fractions eluted with benzene–ethyl acetate (4 : 1) yielded 1-methyl-2-*p*-tolylsulphonyliminoindoxyl (VI) (0·25 g), m.p. 248—250°, identical (m.p., n.m.r., t.l.c.) with the sample described later. Solutions of (V; R = Cl) and (V; R = O·CO·$CHCl_2$) in dimethyl sulphoxide rapidly turned red and deposited crystals of (VI); a solution of (V; R = Br) deposited crystals more slowly, a 75% yield of (VI) being obtained in 4 days. A solution of the diazo-compound (I) in glacial acetic acid containing copper powder was boiled for 12 h; no reaction occurred.

Compound (I) was boiled in ethanol containing β-naphthol for 5 h. No change occurred. A few drops of alkali were then added and heating was continued for a further hour; t.l.c. then showed only starting materials. With phloroglucinol magenta-coloured amorphous materials were obtained.

1-*Methyl*-2-p-*tolylsulphonyliminoindoxyl* (VI).—Com-

[18] R. E. Harman, G. Wellman, and S. K. Gupta, *J. Org. Chem.*, 1973, **38**, 11.

pound (II; R = Ts) (1 g) and *p*-nitrosodimethylaniline (0·5 g) were dissolved in pyridine (20 ml). Next day the solvent was removed and methanol added. Recrystallisation of the resulting solid from benzene gave 3-p-*dimethylamino-phenylimino*-1-*methyl*-2-p-*tolylsulphonyliminoindoline* (VII), purple crystals, m.p. 210—211° (0·75 g) (Found: C, 66·6; H, 5·5; N, 13·0; S, 7·2. $C_{24}H_{24}N_4O_2S$ requires C, 66·7; H, 5·5; N, 13·0; S, 7·4%); $\nu_{max.}$ (N) 1573, 1600w, and 1632 cm^{-1}; $\lambda_{max.}$ (EtOH) 222nm, $\lambda_{max.}$ ($CHCl_3$) 261, 369, and 565 nm (ε 12,600, 35,700, 3500, and 14,200); τ ($CDCl_3$) 7·62 (3H, s, tosyl Me), 6·96 (6H, s, 2NMe), 6·61 (3H, s, NMe), 2·3—3·4 (10H, m, Ar), and 2·07 (2H, d, *J* 8 Hz, low-field half of tosyl signal); *m/e* 432 (M^+, 2%), 277 (*M* — Ts, 100%), and 135 ($C_8H_{11}N_2$, 16%). This reaction was repeated; after 48 h the pyridine was removed, hydrochloric acid (10%; 25 ml) was added to the residue, and the mixture was boiled for 30 min. The solid (1 g) was collected and recrystallised from chloroform–methanol; *compound* (VI) formed brilliant red crystals (0·7 g), m.p. 248—250° (Found: C, 60·9; H, 4·5; N, 8·7; S, 10·4. $C_{16}H_{14}N_2O_3S$ requires C, 61·2; H, 4·5; N, 8·9; S, 10·2%); $\nu_{max.}$ (N) 1603 and 1748 cm^{-1}; $\lambda_{max.}$ ($CHCl_3$) 259, 264, 300sh, and 454 nm (ε 34,000, 35,000, 3160, and 1690); τ [$(CD_3)_2SO$] 7·60 (3H, s, tosyl Me), 6·74 (3H, s, NMe), 2·2—2·9 (6H, m, Ar), and 2·15 (2H, d, *J* 8 Hz, low-field half of tosyl signal); *m/e* 314 (M^+, 58%), 250 (*M* — SO_2, 50%), and 159 (*M* — Ts, 100%).

1-*Methyl*-3-*phthalidyl*-2-p-*tolylsulphonylaminoindole* (IX; R^1 = Me, R^2 = NHTs, R^3 = H).—1-Methyl-2-*p*-tolylsulphonyliminoindole (1 g) and phthalaldehydic acid (2 g) were mixed and placed in an oil-bath at 125°. During 1 h the temperature of the bath was allowed to rise to 135°. The melt was cooled, powdered, and recrystallised from ethanol, yielding the *compound* as white needles, m.p. 199—200° (0·6 g) (Found: C, 66·5; H, 5·0; N, 6·2; S, 7·3. $C_{24}H_{20}N_2O_4S$ requires C, 66·7; H, 4·6; N, 6·5; S, 7·4%); $\nu_{max.}$ (N) 1490w, 1592br,s, 1662, and 1752s cm^{-1}; $\lambda_{max.}$ 222 and 282 nm (ε 54,800 and 12,400); τ [$(CD_3)_2SO$] 7·65 (3H, s, tosyl Me), 6·63 (3H, s, NMe), 3·85 [1H, d, *J* 8 Hz, C(4)H], 3·55 (1H, s, H_x), 3·20 [1H, t, *J* 8 Hz, C(5)H], 1·9—3·0 (10H, m, Ar), and 1·79 (1H, s, NH, exchanged D_2O); *m/e* 432 (M^+, 20%), 277 (*M* — Ts, 70%), and 133 ($C_8H_5O_2$, 100%). 1,2-Dimethyl-3-phthalidylindole (IX; R^1 = R^2 = Me, R^3 = H) had m.p. 202—204° (lit.,[9] 205°) (Found: C, 77·9; H, 5·4; N, 4·9. Calc. for $C_{18}H_{15}NO_2$: C, 78·0; H, 5·4; N, 5·0%); $\nu_{max.}$ (N) 1598, 1611, and 1743 cm^{-1}; $\lambda_{max.}$ 202, 223, 280, and 290 nm (ε 40,900, 54,400, 10,500, and 7640); τ [$(CD_3)_2SO$] 7·51 (3H, s, CMe), 6·30 (3H, s, NMe), 3·70 [1H, d, *J* 8 Hz, C(4)H], 3·25 [1H, t, *J* 8 Hz, C(5)H], 2·93 (1H, s, H_x), and 1·9—3·1 (6H, m, Ar); *m/e* 277 (M^+, 88%), 233 (*M* — CO_2, 84%), 232 (100%), 218 (233 — Me, 74%), and 217 (232 — Me, 64%). 5-Chloro-2-methylindole (1·65 g) and phthalaldehydic acid (1·55 g) were fused together (140°; 5 min) giving 5-*chloro*-2-*methyl*-3-*phthalidylindole* (IX; R^1 = H, R^2 = Me, R^3 = Cl), m.p. 193—194° (from ethanol) (64% yield) (Found: C, 68·9; H, 4·1; Cl, 11·9; N, 4·7. $C_{17}H_{12}ClNO_2$ requires C, 68·6; H, 4·0; Cl, 11·9; N, 4·7%); $\nu_{max.}$ (N) 1578w, 1600, 1610w, 1737br,s, and 2290 cm^{-1}; $\lambda_{max.}$ 201, 225, 280, and 297 nm (ε 31,100, 37,600, 5800, and 3700): τ [$(CD_3)_2SO$] 7·57 (3H, s, CMe), 3·67 (1H, s, H_x), 1·8—3·1 (7H, m, Ar) (NH not detected); *m/e* 297 (M^+, 98%), 252 (*M* — CO_2 — H, 98%), 238 (*M* — CO_2 — Me, 52%), 218 (*M* — CO_2 — Cl, 100%), and 217 (98%).

Reactions of 2-*Arylsulphonylimino*-1-*methylindolines with Simple Aromatic Aldehydes*.—It is important that the aldehydes used are of good quality; for example (II; R = Ts) with an old sample of anisaldehyde in pyridine gave (VI) in 60% yield.

Benzaldehyde (0·4 g) and (II; R = Cbs) (1 g) were dissolved in glacial acetic acid (50 ml) and concentrated hydrochloric acid (1 ml) was added. The solution was heated at 100° for 1 h, the solvent was removed, and methanol (20 ml) was added. The solid obtained was shown (t.l.c.) to be a mixture of two components. It was dissolved in the minimum of hot acetic acid and an equal volume of methanol was added. The solid was collected from the hot solution. *Bis*-2-p-*chlorophenylsulphonylamino*-1-*methylindol*-3-*yl*-(*phenyl*)*methane* (XI; R^1 = R^2 = H, Z = Cbs) (150 mg) had m.p. 208—210° (Found: C, 60·5; H, 4·0. Cl, 9·7; N, 7·5; S, 8·7. $C_{37}H_{30}Cl_2N_4O_4S_2$ requires C, 60·9; H, 4·1; Cl, 9·7; N, 7·7; S, 8·8%); $\nu_{max.}$ (N) 1565br,s, 1604w, and 3120w cm^{-1}; $\lambda_{max.}$ 223 and 283 nm (ε 57,000 and 28,000). On cooling the acetic acid–methanol mother-liquors large orange crystals (200 mg) of (E)-3-*benzylidene*-2-p-*chlorophenylsulphonylimino*-1-*methylindoline* (X; R^1 = R^2 = R^3 = H, Z = Cbs) separated, m.p. 215—216° (Found: C, 64·6; H, 4·0; Cl, 8·7; N, 6·8; S, 8·1. $C_{22}H_{17}ClN_2O_2S$ requires C, 64·6; H, 4·2; Cl, 8·7; N, 6·8; S, 7·8%); $\nu_{max.}$ (N) 1525 and 1575 cm^{-1}; $\lambda_{max.}$ 210, 275, 320, and 360sh nm (ε 47,000, 30,000, 5700, and 3000); τ ($CDCl_3$) 6·50 (3H, s, NMe), 2·2—3·2 (11H, m, Ar), 1·95 (2H, d, *J* 8 Hz, low-field half of Cbs signal), and 1·3 (1H, s, H_a); *m/e* 408 (M^+, 1·2%), 233 (*M* — Cbs, 17%), 232 (100%), and 217 (232 — Me, 23%). *o*-Nitrobenzaldehyde (0·51 g) and (II; R = Ts) (1·0 g) were dissolved in pyridine (20 ml). After 5 days the pyridine was removed and methanol (10 ml) added. The solid was recrystallised from benzene forming yellow needles (1·0 g) of (E)-1-*methyl*-3-(o-*nitrobenzylidene*)-2-p-*tolylsulphonylimindoline* (X; R^1 = NO_2, R^2 = R^3 = H, Z = Ts), m.p. 223—225° (Found: C, 63·4; H, 4·4; N, 9·6; S, 7·2. $C_{23}H_{19}N_3O_4S$ requires C, 63·8; H, 4·4; N, 9·7; S, 7·4%); $\lambda_{max.}$ 206, 271, 321, and 380sh nm (ε 48,000, 31,900, 5400, and 2790); τ ($CDCl_3$) 7·57 (3H, s, tosyl Me), 6·48 (3H, s, NMe), 1·9—3·4 (12H, m, Ar), 1·62 (1H, dd, *J* 8 and 2 Hz, R^2 = H), and 0·95 (1H, s, H_a); τ [$(CD_3)_2SO$] 7·59, 6·52, 1·9—3·5, 1·61, and 1·10; τ ($CF_3{\cdot}CO_2H$) 7·50, 5·87, 1·8—2·9, 1·41, and 1·26; *m/e* 433 (M^+, 15%), 387 (*M* — NO_2, 7%), 278 (*M* — Ts, 83%), 232 (*M* — Ts — NO_2, 94%), 231 (92%), 155 ($C_{10}H_7N_2$, 90%), and 91 (100%).

Purified anisaldehyde (1·1 g) and (II; R = Ts) (4·8 g) were dissolved in pyridine (20 ml); after 4 days the usual work-up gave material (5·0 g, 87%) of m.p. 182—185°. A sample recrystallised from chloroform–methanol was found to contain chloroform (Found: Cl, 20%). The material was purified by dissolving it in hot ethyl methyl ketone and adding an equal volume of methanol. *Bis*-1-*methyl*-2-p-*tolylsulphonylaminoindol*-3-*yl*-(p-*methoxyphenyl*)*methane* (XI; R^1 = H, R^2 = OMe, Z = Ts) formed cubic crystals, m.p. 183—186° (Found: C, 67·0; H, 5·3; N, 7·7; S, 8·8. $C_{40}H_{38}N_4O_5S_2$ requires C, 66·8; H, 5·3; N, 7·8; S, 8·9%); $\nu_{max.}$ (N) 1512, 1572br,s, 1600w, 1617w, and 3160 cm^{-1}; $\lambda_{max.}$ ($CHCl_3$) 241 and 284 nm (24,900 and 22,700); τ [$(CD_3)_2SO$] 7·72 (6H, s, tosyl Me), 6·73 (6H, s, NMe), 6·24 (3H, s, OMe), 4·26 (1H, s, H_b), 2·6—3·4 (16H, m, Ar), 2·35 (4H, d, *J* 8 Hz, low-field half of tosyl signals), and 0·58 (2H, s, NH, exchanged D_2O); *m/e* (molecular ion not detected) 418 [(X; R^1 = R^2 = H, R^3 = OMe, Z = Ts), 0·7%], 300 [(II; R = Ts), 28%], 263 (418 — Ts, 10%), and 145 (300 — Ts, 100%).

Benzaldehyde and (II; R = Ts) gave *bis*-1-*methyl*-2-p-

tolylsulphonylaminoindol-3-yl(phenyl)methane (XI; R^1 = R^2 = H, Z = Ts), microcrystalline powder, m.p. 199—200° (yield 80%) (from benzene) (Found: C, 67·8; H, 5·2; N, 8·4; S, 9·3. $C_{39}H_{36}N_4O_4S_2$ requires C, 68·0; H, 5·2; N, 8·2; S, 9·3%); $\nu_{max.}$ (N) 1565, 1598, and 3195 cm^{-1}; $\lambda_{max.}$ 223 and 283 nm (ε 57,000 and 28,200); *m/e* (molecular ion not detected) 388 [(X; R^1 = R^2 = R^3 = H, Z = Ts), 4%], 300 [(II; Z = Ts), 45%], 233 (388 — Ts, 70%), 145 (71%), and 91 (100%). *p*-Nitrobenzaldehyde and (II; R = Cbs) gave *bis*-2-p-*chlorophenylsulphonylamino*-1-*methylindol*-3-*yl*-(p-*nitrophenyl*)*methane* (XI; R^1 = H, R^2 = NO_2, Z = Cbs), pale yellow crystals [from chloroform–methanol (1 : 1)] (yield 33%), m.p. 225—227° (Found: C, 57·5; H, 4·0; Cl, 9·0; N, 8·9; S , 8·1. $C_{37}H_{29}Cl_2N_5O_6S_2$ requires C, 57·3; H, 3·7; Cl, 9·2; N, 9·0; S, 8·3%); $\nu_{max.}$ (N) 1560br,s, 1600w, and 3115w cm^{-1}; $\lambda_{max.}$ 223 and 280 nm (ε 23,200 and 11,900); $\lambda_{max.}$ ($CHCl_3$) 241 and 282 nm (ε 33,000 and 33,500); τ [$(CD_3)_2SO$] 6·70 (6H, s, NMe), 4·00 (1H, s, H_b), 2·4—3·2 (14H, m, Ar), 2·20 (4H, d, *J* 8 Hz, low-field half of Cbs signal), 1·92 (2H, d, *J* 8 Hz, protons *ortho* to NO_2), and 0·06 (2H, NH, exchanged D_2O). Piperonal (0·56 g) and (II; R = Ts) (1 g) in pyridine (20 ml) gave *bis*-1-*methyl*-2-p-*tolylsulphonylaminoindol*-3-*yl*-(3,4-*methylenedioxyphenyl*)-*methane* (XI; R^1R^2 = O·CH_2·O, Z = Ts) (1·1 g). Recrystallisation from pyridine–methanol gave crystals, m.p. 218—219° (Found: C, 66·1; H, 5·1; N, 7·6; S, 9·0. $C_{40}H_{36}N_4O_6S_2$ requires C, 65·6; H, 4·9; N, 7·6; S, 8·7%); $\nu_{max.}$ (N) 1570br,s, 1600w, and 3160 cm^{-1}; $\nu_{max.}$ ($CHCl_3$) 1590br,s and 3200w cm^{-1}; $\lambda_{max.}$ 223 and 280 nm (ε 50,300 and 27,200); $\lambda_{max.}$ ($CHCl_3$) 242 and 288 (ε 24,900 and 25,900); τ [$(CD_3)_2SO$] 7·69 (6H, s, tosyl Me), 6·73 (6H, s, NMe), 4·27 (1H, s, H_b), 4·02 (2H, O·CH_2·O), 2·6—3·7 (16H, m, Ar), 2·32 (4H, d, *J* 8 Hz, low-field half of tosyl signals), and 0·52 (2H, NH, exchanged D_2O); *m/e* (molecular ion not detected) 432 (0·5%), 300 (72%), 277 (432 — Ts, 72%), and 145 (300 — Ts, 100%). Compound (XI; R^1R^2 = O·CH_2O·, Z = Ts) (0·5 g) was dissolved in chlorobenzene and the solution boiled for 1 h. On cooling the yellow solution starting material separated. This was removed and the solvent was evaporated off. The residue was chromatographed on silica; elution with benzene–ethyl acetate mixtures yielded yellow crystals of (*E*)-1-methyl-3-(3,4-methylenedioxybenzylidene)-2-*p*-tolylsulphonyliminoindoline (X; R^1 = H, R^2R^3 = O·CH_2·O, Z = Ts) (30 mg), m.p. 218—219°; $\nu_{max.}$ (N) 1575br,s and 1620 cm^{-1}; $\lambda_{max.}$ 210 and 325 nm (ε 45,000 and 6000). The second fraction from the column was (II; R = Ts) (22 mg), and starting material (50 mg) was recovered. Compound (XI; R^1R^2 = O·CH_2·O, Z = Ts) (0·5 g) was dissolved in hot acetic acid (50 ml) and conc. hydrochloric acid (1 ml) was added. After 1 h the solvent was removed and the residue chromatographed on 1 m prep. t.l.c. plates (four elutions with chloroform), yielding starting material (210 mg), compound (II; R = Ts) (100 mg), and (E)-1-*methyl*-3-(3,4-*methylenedioxybenzylidene*)-2-p-*tolylsulphonyliminoindoline* (160 mg), identical with the sample just described; *m/e* 432 (M^+, 3%), 277 (*M* — Ts, 100%), and 145 (63%). The molecular ion was too weak for high resolution mass determination so that was performed on *m/e* 277 (*M* — Ts) (Found: *m/e* 277·0972. $C_{17}H_{13}N_2O_2$ requires *m/e* 277·09769); τ ($CDCl_3$) 7·60 (3H, s, tosyl Me), 6·54 (3H, s, NMe), 3·82 (2H, s, O·CH_2·O), 2·2—3·4 (9H, m, Ar), 2·10 (low-field half of tosyl signal), and 1·95 (1H, s, H_a).

N.m.r. spectra of compounds (XI) in $CDCl_3$ (τ values)

(XI)	NH (s)	Protons *ortho* to SO_2 *	Aromatic H (m)	Aliphatic H (m) †	(d) ‡	NMe (s)	CMe (s)
R^1 = H, R^2 = OMe, Z = Ts	0·52	2·08	2·4—3·75	4·61	4·93	6·13 7·4	7·58 7·88
R^1R^2 = O·CH_2·O, Z = Ts §	0·52	2·07	2·3—3·6	4·64	4·93	6·13 7·4	7·58 7·79
R^1 = H, R^2 = NO_2, Z = Cbs	0·50	2·00	2·3—3·7 ¶	4·64	4·80	6·11 7·33	
R^1 = R^2 = H, Z = Ts	0·51	2·05	2·4—3·8	4·58	4·68	6·12 7·40	7·58 7·90
R^1 = R^2 = H, Z = Cbs	0·54	2·02	2·4—3·8	4·52	4·93	6·14 7·37	

* 2H, position suggests C=N·SO_2Ar. † Appearance of two overlapping doublets. ‡ *J* 8 Hz. § Determined at 220 Hz; O·CH_2·O signal at τ 3·90. ¶ Protons *ortho* to NO_2, τ 1·90 (d, *J* 8 Hz).

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