Reactions of Dihydroquinolines and Dihydroisoquinolines with Arenesulphonyl Azides

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Tosyl azide reacts with 1,4-dihydro-1-methylquinoline-4-carbonitrile in ethyl acetate solution to form 1.2.3,4-tetrahydro-1-methyl-2-*p*-tolylsulphonyliminoquinoline-4-carbonitrile; in methanol. 1.2-dihydro-1-methyl-2-*p*-tolylsulphonyliminoquinoline-4-carbonitrile is also formed. 1.2-Dihydro-2-methylisoquinoline-1-carbonitrile reacts with tosyl azide yielding a mixture of 2.3-dihydro-2-methyl-3-*p*-tolylsulphonyliminoisoquinoline and the corresponding 1-carbonitrile.

THE reactions of a variety of indoles with arenesulphonyl azides have been examined;[1-3] we now report the reactions of some derivatives of quinoline and of isoquinoline with azides.

Indoles are attacked by azides at the 'enamine' 2,3-bond with ensuing 1,3-dipolar addition; it seemed unlikely that such an attack could occur on a quinoline

[1] A. S. Bailey and J. J. Merer, *J. Chem. Soc.* (*C*), 1966, 1345; A. S. Bailey, P. A. Hill, and J. F. Seager, *J.C.S. Perkin I*, 1974, 967.

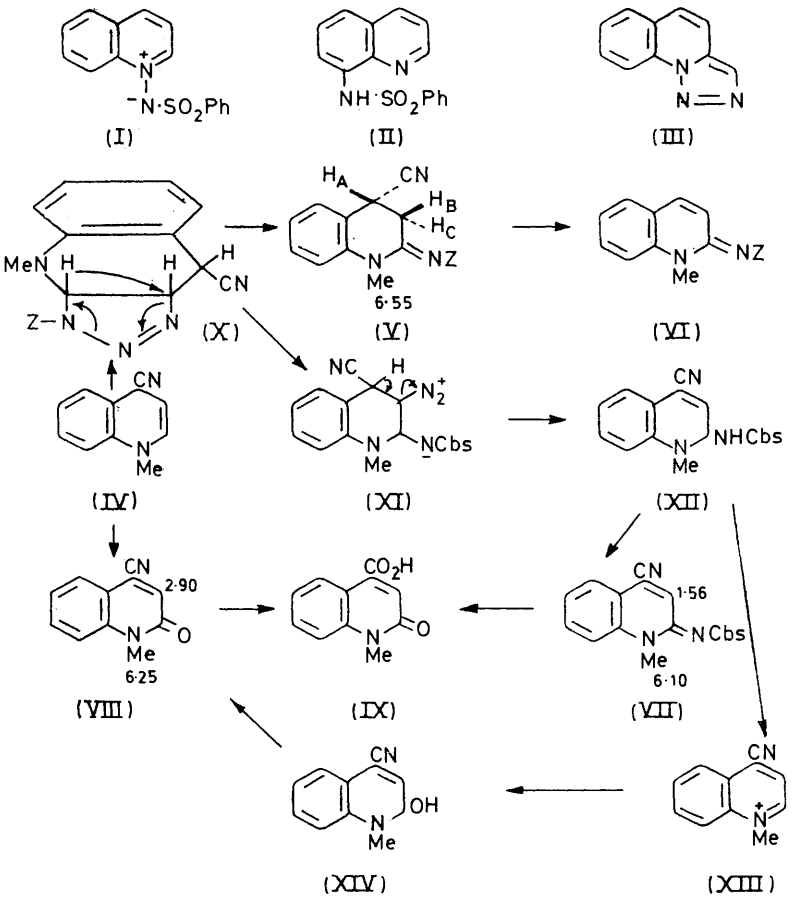
[2] A. S. Bailey, C. J. Barnes, and P. A. Wilkinson, *J.C.S. Perkin I*, 1974, 1321.

[3] A. S. Bailey, J. F. Seager, and Z. Rashid, *J.C.S. Perkin I*, 1974, 2384.

nucleus. Indeed quinoline is reported to react with benzenesulphonyl azide at 125° to give small yields of compounds (I) and (II), which are formed by nitrene attack, and 2-methylquinoline yields the triazoloquinoline (III) by diazo-transfer.[4] We, therefore, decided to examine derivatives of dihydroquinoline and dihydroisoquinoline which contained a good leaving group.

Z = Ts).[6] This sequence of reactions has been repeated with *p*-chlorobenzenesulphonyl (Cbs) azide, giving compounds (V; Z = Cbs) and (VI; Z = Cbs).

When the dihydro-compound (IV) was treated with Cbs azide in methanol, compound (V) did not crystallise out, but a solid to which we assign structure (VII) was isolated. The i.r. spectrum contained a weak C≡N band;



The numbers on the formulae are τ values

1,4-Dihydro-1-methylquinoline-4-carbonitrile (IV) [5] reacted vigorously with tosyl azide in ethyl acetate solution affording 1,2,3,4-tetrahydro-1-methyl-2-*p*-tolylsulphonyliminoquinoline-4-carbonitrile (V; Z = Ts) in high yield. The spectroscopic properties of the material supported its identification. In the n.m.r. spectrum the signal from H_C was obscured by the NCH_3 signal and the signals from H_A and H_B appeared as a multiplet, τ 5·75—6·2, at 100 MHz. This portion of the spectrum, examined at 270 MHz, showed τ(H_A) 5·89 (J_{AB} 4·5, J_{AC} 9·5 Hz) and τ(H_B) 6·03 (J_{BC} 16·5 Hz). The structure was confirmed by treating the compound with 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), affording 1,2-dihydro-1-methyl-2-*p*-tolylsulphonyliminoquinoline (VI; this band can be very weak and sometimes may not be detected.[7] The u.v. spectrum was similar to that of (VI) [6b] but with $\lambda_{max.}$ moved to longer wavelength. Brief treatment of the compound with sodium hydroxide solution afforded 1,2-dihydro-1-methyl-2-oxoquinoline-4-carboxamide, and prolonged hydrolysis gave the corresponding acid (IX), identical with a sample obtained [5] by hydrolysis of (VIII). In the n.m.r. spectrum of (VIII) the signal from C(3)H appears at τ 2·90, whereas in that of (VII) the C(3)H signal appears further downfield at τ 1·56, indicating that the Cbs group in (VII) is *anti* to the NMe group.[6b] At first we assumed that compound (VII) was formed from (V; Z = Cbs) either by

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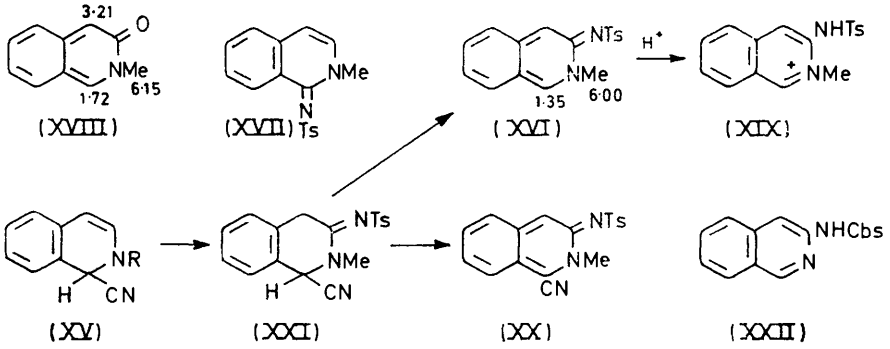
[6] (*a*) M. Regitz and G. Himbert, *Annalen*, 1970, **734**, 70; (*b*) A. S. Bailey, R. Scattergood, and W. A. Warr, *J. Chem. Soc.* (*C*), 1971, 2479.

[7] L. J. Bellamy, 'The Infra-red Spectra of Complex Molecules,' Methuen, London, 1958, p. 265; A. S. Bailey and C. R. Worthing, *J. Chem. Soc.*, 1956, 4535; K. T. Potts and Sir Robert Robinson, *ibid.*, 1955, 2466.

attack of a second molecule of azide [yielding (VII) + N_2 + $CbsNH_2$] or by oxidation by air, since compound (VIII) is produced [5] from (IV) by aerial oxidation. However compound (V; Z = Cbs) was unaffected by treatment with Cbs azide in hot methanol and in pyridine, by nitric acid in acetic acid, and by shaking with air and platinum in methanol [conditions used for the transformation (IV) ⟶ (VIII) [5]]. The reaction between compound (IV) and Cbs azide was examined under different conditions (see Experimental section) and the crude solid which separated was examined by n.m.r. spectroscopy, the three NMe signals of compounds (V; Z = Cbs), (VII), and (VIII) being far enough apart for analytical use, and the intensities of the signals at τ 1·56 and 2·90 providing further confirmation of the composition of the mixtures. The addition of lithium perchlorate to the ethyl acetate solution resulted in formation of a mixture of compounds (V) and (VII), and when

Tosyl azide reacted smoothly with 1,2-dihydro-2-methylisoquinoline-1-carbonitrile (XV; R = Me) giving two major products which could only be separated by p.l.c. To the yellow-coloured compound, $C_{17}H_{16}N_2O_2S$, we assign structure (XVI). The compound did not contain an NH group (i.r.) and the NMe signal in the n.m.r. spectrum came at rather low field (τ 6·00) [in starting material, τ(NMe) = 7·05] and there was a sharp singlet (1H) at τ 1·35 showing that the =NTs group was attached to C(3) and not to C(1) since in the alternative structure (XVII) the protons at C(3) and C(4) would be strongly coupled. We assign the signal at τ 1·35 to C(1)H rather than C(4)H by comparison with the n.m.r. spectrum of (XVIII).[10] In compound (XVI) the signal associated with C(4)H appears further downfield in the aromatic region [*cf.* the positions of the signals from C(3)H in (VII) and (VIII)]; the n.m.r. spectrum of a solution in trifluoroacetic acid [ion (XIX)] contained a very low-field



the reaction was carried out under nitrogen the solid consisted mainly of (VIII). The effects of solvent polarity and of lithium perchlorate on the reactions of cyanogen azide with olefins have been examined [8] and it was suggested that in non-polar media the decomposition of the intermediate triazoline follows a concerted route but that in a polar medium the ionic intermediates are stabilized, allowing other reaction pathways. Our results suggest that in a non-polar medium the triazoline (X) breaks down as shown giving rise to compound (V) in high yield, whereas under polar conditions the most acidic proton, that at C-4, is lost, yielding the 1,2-dihydroquinoline (XII) *via* (XI); compound (XII) could either disproportionate or be oxidized forming (VII); alternatively it could lose sulphonamide to form (XIII) which would yield (VIII) *via* the pseudo-base (XIV) either by disproportionation or by oxidation.[9] It appears unlikely that compound (VIII) is formed in these reactions by hydrolysis of (VII), and (VII) is recovered unchanged after recrystallisation from boiling chloroform–methanol. Treatment of compound (IV) in methanolic solution with tosyl azide leads to the formation of (VII; Ts replacing Cbs) showing that this reaction is not confined to Cbs azide.

singlet (τ 0·46) [C(1)H of isoquinoline methiodide in $CF_3{\cdot}CO_2H$ shows τ 0·16]. The u.v. spectrum (ethanol) of (XVI) was similar to that of (XVIII); addition of acid caused a hypsochromic shift which could be reversed by adding triethylamine. The second (red) product did not give satisfactory analytical results, although pure by t.l.c. It appeared to hold traces of water tenaciously; we assign structure (XX) to this compound. The i.r. spectrum showed the presence of a C≡N group and the absence of NH. In the n.m.r. spectrum the NMe signal (5·8) is downfield of that in (XVI) and the signal of C(4)H appears further downfield at τ 1·65; a cyano-group in the 2-position of pyridine moves the signal of C(5)H downfield by 0·6 p.p.m.[11] The u.v. spectrum of (XX) is similar to that of (XVI) but the bands have moved to longer wavelength [*cf.* the relationship between the u.v. spectra of (VI) and (VII)], addition of acid producing a hypsochromic shift. Compounds (XVI) and (XX) are probably formed *via* the intermediate (XXI), loss of HCN affording (XVI) and oxidation yielding (XX).

In an attempt to extend these reactions the Reissert compound [12] (XV; R = Bz) was treated with Cbs azide

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[9] 'Heterocyclic Compounds,' vol. 4, ed. R. C. Elderfield, Wiley, New York, 1952, pp. 232 and 473.

[10] D. A. Evans, G. F. Smith, and M. A. Wahid, *J. Chem. Soc.* (*B*), 1967, 590; D. W. Jones, *J. Chem. Soc.* (*C*), 1969, 1729.

[11] W. Bruegel, *Z. Electrochem.*, 1962, **66**, 159; T. J. Batterham, 'N.M.R. Spectra of Simple Heterocycles,' Wiley, New York, 1973, p. 31.

[12] F. D. Popp, *Adv. Heterocyclic Chem.*, 1968, **9**, 1.

under a variety of conditions; at room temperature no reaction occurred and at 100° only polymeric materials and *p*-chlorobenzenesulphonamide were obtained. However when ethyl 1-cyano-1,2-dihydroisoquinoline-2-carboxylate [13] (XV; R = CO_2Et) was boiled with Cbs azide in ethyl propionate for several days a small quantity of 3-*p*-chlorophenylsulphonylaminoisoquinoline (XXII) was isolated, identical with material obtained by treating 3-aminoisoquinoline [14] with Cbs chloride. Hence it appears that compounds of type (XV) only react smoothly with azides when R = alkyl.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. I.r. spectra were obtained with a Perkin-Elmer 257 instrument for Nujol mulls unless otherwise stated. U.v. spectra were measured for solutions in ethanol with a Cary 14M spectrometer and n.m.r. spectra with either a Perkin-Elmer R14 or R32 instrument for solutions in $CDCl_3$ unless otherwise stated. Mass spectra were recorded with either an A.E.I. MS9 or a CH7 spectrometer (direct inlet systems).

1,2,3,4-*Tetrahydro*-1-*methyl*-2-p-*tolylsulphonyliminoquinoline*-4-*carbonitrile* (V; Z = Ts).—1,4-Dihydro-1-methylquinoline-4-carbonitrile [5] (1·69 g) in ethyl acetate (10 ml) was added to tosyl azide (1·94 g) in ethyl acetate (5 ml). After the vigorous reaction had ceased the mixture was cooled in ice and the solid collected (2·57 g, 90% yield; m.p. 212—214°). The *compound* formed pale yellow prisms, m.p. 213—214° (from acetonitrile) (Found: C, 63·8; H, 5·2; N, 12·3; S, 9·2. $C_{18}H_{17}N_3O_2S$ requires C, 63·7; H, 5·0; N, 12·4; S, 9·4%); $\lambda_{max.}$ 216sh and 280 nm (ε 24,800 and 22,800); $\nu_{max.}$ 1550 and 2240 cm^{-1}; τ 2·15 (2H, d, *J* 8 Hz, low-field half of tosyl signal), 2·5—2·9 (6H, m, Ar), 5·8—6·2 (2H, m, H_A and H_B), 6·4—6·6 (1H, m, H_C), 6·50 (3H, s, NMe), and 7·60 (3H, s, CMe); *m/e* 339 (M^+, 34%) and 184 (100).

1,2-*Dihydro*-1-*methyl*-2-p-*tolylsulphonyliminoquinoline* (VI; Z = Ts).—Compound (V; Z = Ts) (340 mg) and DBN (125 mg) were boiled (5 h) in benzene (10 ml) and half the solvent was removed. The solid was collected (150 mg) and recrystallised (acetonitrile); the product had m.p. 213° (lit.,[6] 211°) (Found: C, 65·2; H, 5·0; N, 8·9. Calc. for $C_{17}H_{16}N_2O_2S$: C, 65·4; H, 5·1; N, 9·0%) and was identical (i.r.) with an authentic sample.

1,4-Dihydro-1-methylquinoline-4-carbonitrile reacted with Cbs azide in ethyl acetate affording 2-p-*chlorophenylsulphonylimino*-1,2,3,4-*tetrahydro*-1-*methylquinoline*-4-*carbonitrile* (V; Z = Cbs) (93%) as pale yellow prisms, m.p. 187—188° (from propan-1-ol) (Found: C, 56·9; H, 4·1; N, 11·7; S, 8·7. $C_{17}H_{14}ClN_3O_2S$ requires C, 56·7; H, 3·9; N, 11·7; S, 8·9%); $\lambda_{max.}$ 280 nm (ε 18,600); $\nu_{max.}$ 1555 and 2240 cm^{-1}; τ 2·1 (2H, s, *J* 9 Hz, low-field half of Cbs signal), 2·5—2·9 (6H, m, Ar), 5·75—6·2 (2H, m), 6·4—6·6 (1H, m), and 6·55 (3H, s, NMe). Boiling this material with DBN in benzene gave 2-p-*chlorophenylsulphonylimino*-1,2-*dihydro*-1-*methylquinoline* (VI; Z = Cbs) (75%) as prisms, m.p. 201—202° (from acetonitrile) (Found: C, 57·7; H, 4·3; N, 8·3; S, 9·5. $C_{16}H_{13}ClN_2O_2S$ requires C, 57·7; H, 3·9; N, 8·4; S, 9·6%); $\lambda_{max.}$ ($CHCl_3$) 256, 264, 293sh, 340sh, 354, and 366sh nm (ε 20,800, 20,800, 5100, 8800, 10,400, and 7200); $\nu_{max.}$ 1625 and 1570 cm^{-1}; τ 1·95—2·7 (10H, m) and 6·11 (3H, s).

Reaction between 1,4-*Dihydro*-1-*methylquinoline*-4-*carbonitrile and Cbs Azide in Methanol.*—The azide (2·18 g) in methanol (8 ml) was added to a solution of the nitrile (IV) (1·7 g) in methanol (5 ml). After 2 h effervescence ceased and the solid (0·83 g) was collected (m.p. 207—209°). Recrystallisation (chloroform–methanol) afforded 2-p-*chlorophenylsulphonylimino*-1,2-*dihydro*-1-*methylquinoline*-4-*carbonitrile* (VII), yellow plates, m.p. 230—232° (Found: C, 56·8; H, 3·4; N, 11·4; S, 9·0. $C_{17}H_{12}ClN_3O_2S$ requires C, 57·1; H, 3·4; N, 11·7; S, 9·0%); $\lambda_{max.}$ ($CHCl_3$) 260, 308, 390, and 406sh nm (ε 30,800, 38,500, 12,200, and 8750); $\nu_{max.}$ 1570, 1630, and 2220 cm^{-1}; τ 1·56 [1H, s, C(3)H], 1·9—2·6 (8H, m), and 6·10 (3H, s); *m/e* 357 (M^+, 13%), 293 (12, *m** 241·5), 182 (100, *m** 92·5), and 153 (19). Compound (VII) (0·52 g) was dissolved in ethanol (5 ml) and sodium hydroxide solution (2 ml; 2M) was added. The mixture was boiled (10 min) and cooled and the solid (starting material) which separated was filtered off. Addition of chloroform (10 ml) to the filtrate yielded 1,2-*dihydro*-1-*methyl*-2-*oxoquinoline*-4-*carboxamide*, needles, m.p. 256—257° (0·15 g) (Found: C, 64·1; H, 5·1; N, 13·5. $C_{11}H_{10}N_2O_2$ requires C, 65·3; H, 5·0; N, 13·9%); $\lambda_{max.}$ 231, 275, and 336 nm (ε 31,800, 5600, and 5500); $\nu_{max.}$ 1590, 1645vbr, 3200, and 3325 cm^{-1}; τ [$(CD_3)_2SO$] 1·8 (2H, NH, exchanged in D_2O), 2·0—2·8 (4H, m), 3·34 [1H, s, C(3)H], and 6·35 (3H, s, NMe); *m/e* 202 (M^+, 100%) 158 (M − $CONH_2$, 46%), and 130 (15%). The above hydrolysis was repeated and the time of heating increased to 2 h. The solution was then acidified (2M-sulphuric acid) and the solid collected (yield 58%). The material was recrystallised from acetic acid–water (50%) yielding 1,2-dihydro-1-methyl-2-oxoquinoline-4-carboxylic acid (IX), needles, m.p. 252—253°, identical (i.r.) with an authentic sample (see below). Oxidation of the nitrile (IV) in methanolic solution with oxygen in the presence of platinum [5] gave 1,2-*dihydro*-1-*methyl*-2-*oxoquinoline*-4-*carbonitrile*, needles, m.p. 170—171° (lit.,[5] 165—166°); $\lambda_{max.}$ 208, 236, 290, and 361 nm (ε 38,800, 20,700, 5050, and 4750); $\nu_{max.}$ 1590, 1660br, and 2220w cm^{-1}; τ 2·2—2·7 (4H, m), 2·90 [1H, s, C(3)H], and 6·25 (3H, s, NMe). Hydrolysis [5] gave 1,2-dihydro-1-methyl-2-oxoquinoline-4-carboxylic acid (IX), m.p. 253—254° (lit.,[5] 242—243°), $\nu_{max.}$ 1580, 1660br, 1720, and 2400—2600br,w cm^{-1}; τ [$(CD_3)_2SO$] 1·78 [1H, d, *J* 9 Hz, C(5)H], 2·25—2·8 (4H, m), 3·05 [1H, s, C(3)H], and 6·34 (3H, s, NMe).

Tosyl azide (2·1 g) in methanol (8 ml) was added to a solution of the nitrile (IV) (1·67 g) in methanol (6 ml). After 4 h the solid (0·756 g; m.p. 230—233°) was collected. Recrystallisation from chloroform–methanol gave 1,2-*dihydro*-1-*methyl*-2-p-*tolylsulphonyliminoquinoline*-4-*carbonitrile*, yellow prisms, m.p. 244—246° (Found: C, 63·8; H, 4·6; N, 12·2; S, 9·4. $C_{18}H_{15}N_3O_2S$ requires C, 64·1; H, 4·5; N, 12·5; S, 9·5%); $\lambda_{max.}$ 218, 258, 308, and 389 nm (ε 34,200, 20,400, 4150, and 7200); $\nu_{max.}$ 1570 and 1630 cm^{-1}; τ 1·54 [1H, s, C(3)H], 1·9—2·8 (8H, m), 6·12 (NMe), and 7·60 (CMe). Compound (IV) was treated with Cbs azide under various conditions. After effervescence ceased the mixture was cooled to 0°, the solid collected and washed with a little cold methanol, and the composition of the mixture determined by n.m.r. spectroscopy.

Reaction of 1,2-*Dihydro*-2-*methylisoquinoline*-1-*carbonitrile with Tosyl Azide.*—Compound (XV; R = Me) [5] (0·85 g) was dissolved in ethyl acetate (10 ml) and tosyl azide (1·08 g) added. After 12 h t.l.c. (silica; 80% chloroform–benzene), showed the presence of three materials, pink (R_F 0·18), red

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(R_F 0·15), and yellow (R_F 0·1). Preparative t.l.c. (5 × 1 m plates; 75% chloroform–benzene; 3 elutions) separated the mixture. The yellow band gave golden-yellow needles

Reaction between 1,4-dihydro-1-methylquinoline-4-carbonitrile (IV) and Cbs azide

Wt. of (IV) (g)	Wt. of azide (g)	Solvent (14 ml)	Wt. of product (g)	Product ratio (VII) : (V) : (VIII)
1·67	2·12	MeOH	0·96	4 : 1 : 0
1·01	1·40	MeOH [a]	0·58	9 : 2 : 0
1·77	2·21	MeOH [b]	0·93	3 : 1 : 1
2·13	2·73	MeOH [c]	1·72	1 : 0 : 5
1·86	2·30	EtOAc [d]	1·06	3 : 2 : 0
1·86	2·30	EtOAc [e]	1·23	2 : 1 : 3

[a] Contains pyridine (1 ml). [b] Contains lithium perchlorate (0·40 g in 10 ml). [c] Carried out under nitrogen. [d] Contains lithium perchlorate (0·16 g in 10 ml). [e] As *d* + pyridine (1 ml).

(from ethanol) of 2,3-*dihydro*-2-*methyl*-3-p-*tolylsulphonyliminoisoquinoline* (XVI), m.p. 212—214° (0·4 g) (Found: C, 64·9; H, 5·45; N, 8·7; S, 10·4. $C_{17}H_{16}N_2O_2S$ requires C, 65·4; H, 5·1; N, 9·0; S, 10·3%); $\lambda_{max.}$ 218, 251, 297, 308, and 412 nm (ε 39,800, 42,400, 15,100, 16,200, and 5700), $\lambda_{max.}$ (with added $HClO_4$) 240 and 345 nm (ε 54,000 and 6250); $\nu_{max.}$ 1605 and 1650 cm^{-1}; τ 1·35 (1H, s), 2·1—2·9 (9H, m, Ar), 6·00 (3H, s, NMe), and 7·65 (3H, s, CMe); τ ($CF_3{\cdot}CO_2H$) 0·46 (1H, s), 1·55—2·6 (9H, m), 5·45 (NMe), and 7·50 (CMe); *m/e* 312 (M^+, 43%), 248 (M — SO_2, 24%), 247 (52), 157 (M — Ts, 100), 130 (157 — HCN, 72), and 91 (72). The red band afforded 2,3-*dihydro*-2-*methyl*-3-p-*tolylsulphonyliminoisoquinoline*-1-*carbonitrile* (XX) (280 mg), red needles (from propan-2-ol), m.p. 220° (decomp.) (Found: C, 63·0, 62·2; H, 4·4, 4·5; N, 11·9, 12·0; S, 8·9. $C_{18}H_{15}N_3O_2S$ requires C, 64·1; H, 4·45; N, 12·5; S, 9·5%. $2C_{18}H_{15}N_3O_2S,H_2O$ requires C, 62·4; H, 4·6; N, 12·1; S, 9·3%); $\lambda_{max.}$ ($CHCl_3$) 271, 307sh, and 480 nm (ε 31,000, 10,000, and 4500); $\lambda_{max.}$ (with added $HClO_4$) 388 nm (ε 3500); $\nu_{max.}$ 1590, 1630, and 2210w cm^{-1} (there was also a broad weak band at 3600—3400 cm^{-1}); τ 1·65 (1H, s), 2·0—2·8 (8H, m, Ar), 5·80 (NMe), and 7·60 (CMe); *m/e* 337 (M^+, 23%), 273 (9), 272 (8), 182 (M — Ts, 44), 155 (24), 105 (40), and 91 (100). The pink band afforded a small quantity (32 mg) of an orange solid, m.p. 169—171°, which we have not identified (Found: C, 58·9; H, 4·8; N, 18·4%); $\nu_{max.}$ 1540, 1570, 1645, 2180, and 3490br cm^{-1}; n.m.r. showed no CMe group, τ (NMe) 6·3; *m/e* 183 (100%), 159 (51), 155 (36), and 129 (27%). In another experiment separation on a silica column was attempted but only toluene-*p*-sulphonamide (0·2 g) was isolated, the other components running very close together.

3-p-*Chlorophenylsulphonylaminoisoquinoline* (XXII).—Compound (XV; R = CO_2Et) [13] (2·8 g) and Cbs azide (2·61 g) were boiled in ethyl propionate for 8 days. Chromatography (silica; toluene–ethyl acetate) gave starting material and an oil to which was added benzene (2—3 ml). A crystalline solid (0·26 g) separated. Recrystallisation from benzene gave the *sulphonamide* (XXII), needles, m.p. 210—211° (Found: C, 56·5; H, 3·3; N, 8·5. $C_{15}H_{11}ClN_2O_2S$ requires C, 56·4; H, 3·4; N, 8·8%); $\nu_{max.}$ 1588, 1598, 1634, and 3100 cm^{-1}; τ [$(CD_3)_2SO$] — 1·2br (1H, s, NH), 1·0 [1H, s, C(1)H], and 1·9—2·5 (9H, m); *m/e* 318 (M^+, 8%), 254 (28), 253 (56), 143 (M — Cbs, 11), and 116 (143 — HCN 100). 3-Aminoisoquinoline, m.p. 176—178° (lit.,[14] 178—179°), was heated (80°; 6 h) with *p*-chlorobenzenesulphonyl chloride in pyridine, yielding the sulphonamide (XXII) (87%), m.p. 210—211°, identical (i.r.) with the compound isolated above. 3-p-*Tolylsulphonylaminoisoquinoline* formed needles, m.p. 207—208° (from benzene) (Found: C, 64·2; H, 4·8; N, 9·3. $C_{16}H_{14}N_2O_2S$ requires C, 64·4; H, 4·7; N, 9·4%) τ [$(CD_3)_2SO$] —1·05 (1H, s, NH), 0·94 [1H, s, C(1)H], 1·9—2·7 (9H, m), and 7·65 (3H, CMe); τ ($CF_3{\cdot}CO_2H$) 0·55 [1H, s, C(1)H], 1·5—2·7 (9H, m), and 7·58 (CMe) [this spectrum is very similar in appearance to that of the ion (XIX) formed by dissolving (XVI) in $CF_3{\cdot}CO_2H$].

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