

Novel Aspects in the Synthesis and Acid-promoted Cyclisation of Some 2-Diazo-2'-(*p*-tolylsulphonylamino)acetophenones: Electrophilic Displacement of an Arylsulphonyl Group from a Sulphonamide

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Under conditions where 2-(*p*-tolylsulphonylamino)benzoyl chloride (VIa) and diazomethane gave the expected diazo-ketone (VIIIa) in high yield, use of diazoethane gave only a low yield of the corresponding diazopropiophenone (VIIIb), contaminated by 2-methyl-*N*-(*p*-tolylsulphonyl)indoxyl (Xa). In contrast, 2-(*N*-methyl-*p*-tolylsulphonyl)benzoyl chloride (VIb) reacted with both diazoalkanes to give high yields of the expected diazo-ketones (VIIIe and f). 2-Diazo-2'-(*N*-methyl-*p*-tolylsulphonylamino)acetophenone (VIIIe) in acetic acid-acetic anhydride provided 3-acetoxy-2-acetyl-1-methylindole (XII) and toluene-*p*-sulphonic acid *via* novel electrophilic displacement of an arylsulphonyl group from the sulphonylamino-substituent; similar displacement from 2-diazo-2'-(*p*-tolylsulphonyloxy)acetophenone (Ih) was much more difficult.

We and others have recently shown that 2-diazoacetophenones with an *ortho*-substituent possessing lone-pair electrons in either the α - (Ia—c)¹ or the β - (Id and e)² position readily undergo acid-promoted cyclisation (Scheme 1) *via* their respective diazonium ions (IIa—e) to give five- and six-membered fused heterocycles, (IVa and b) and (Va and b), respectively. Our finding that a comparable reaction may be effected with 2-diazo-2'-(*p*-tolylsulphonylamino)acetophenone [(If) \rightarrow (IVc)] was anticipated by Hampel,³ and we now report an extension of those parts of our work not covered by him.

When 2-(*p*-tolylsulphonylamino)benzoyl chloride (VIa) was treated with diazoethane under conditions where diazomethane gave a high yield of the diazo-ketone (VIIIa), the product was much more complex (Scheme 2). The expected diazo-ketone (VIIIb) was not isolated but

its presence in the crude product was inferred from spectroscopic evidence (i.r. and n.m.r.) and the yield was estimated at 30% by the amount of nitrogen evolved when it was treated with acid; 2-methyl-*N*-(*p*-tolylsulphonyl)indoxyl (Xa) was isolated in 25% yield. Prior mixing of the diazoethane with triethylamine (1 mol. equiv.) had little influence on the yield of the diazo-ketone (VIIIb), but significantly increased that of the indoxyl (Xa), which became the major product (40%) when the amount of amine was increased (2 mol. equiv.); the presence of the tertiary base also led to the formation in low yield of the cyclic sulphonamide (XIV) by the known self-condensation⁴ of the acid chloride.

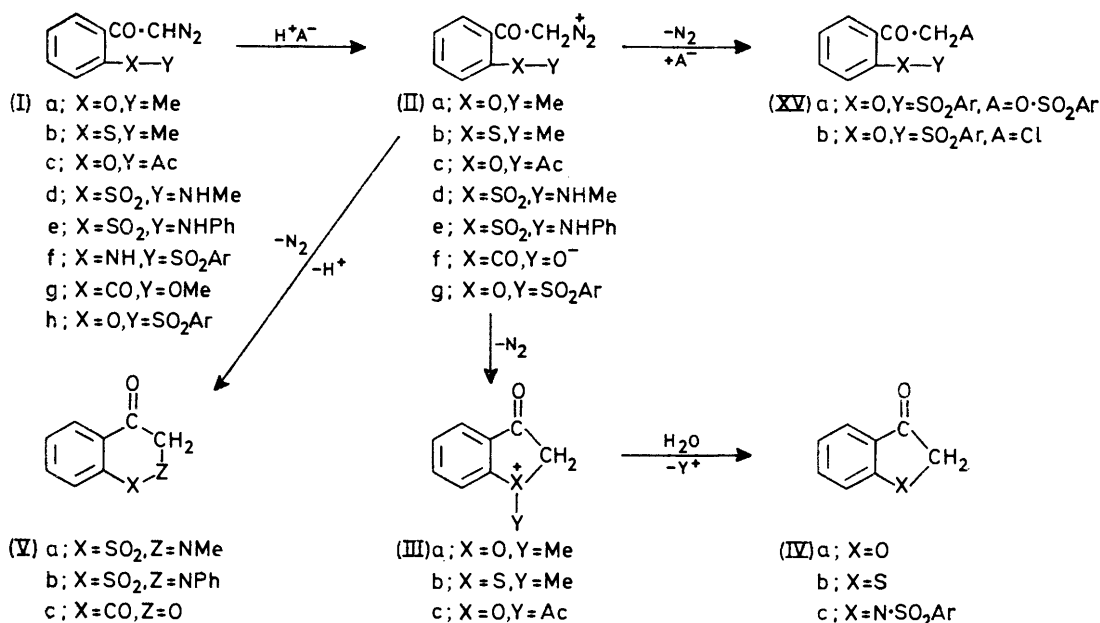
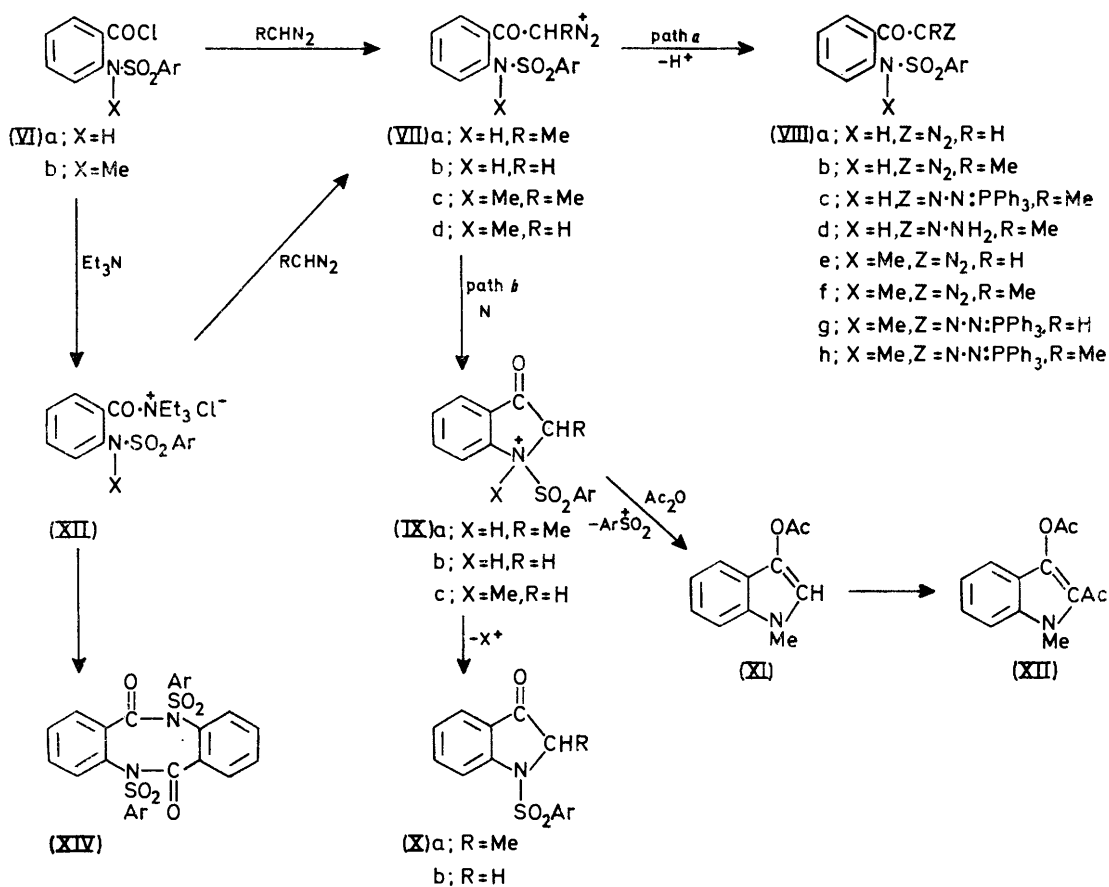
The desired diazo-ketone (VIIIb) was ultimately isolated from the crude product as its triphenylphosphine

² G. Heyes, G. Holt, and A. Lewis, *J.C.S. Perkin I*, 1972, 2351.

³ W. Hampel, *J. prakt. Chem.*, 1969, **311**, 78.

⁴ G. Schroefler and O. Eisleb, *Annalen*, 1909, **367**, 101.

¹ W. T. Flowers, G. Holt, and M. A. Hope, *J.C.S. Perkin I*, 1974, 1116, and references therein.

SCHEME 1 Ar = *p*-MeC₆H₄SCHEME 2 Ar = *p*-MeC₆H₄

adduct (VIIIc). Diazoketones may frequently be regenerated from their triphenylphosphine adducts by treatment with methyl iodide,⁵ but, in the present case, this procedure failed. Accordingly, the adduct was 'hydrolysed' in 80% methanol to give triphenylphosphine oxide and the oxo-hydrazone (VIIId); oxidation of the separated hydrazone with activated manganese dioxide gave the diazo-ketone (VIIIb), contaminated by a small amount of the indoxyl (Xa).

The above results suggest that the acyldiazonium ion (VIIa) resulting from the action of diazoethane on the acid chloride (VIa) may suffer deprotonation at the diazo-carbon atom, thus providing the diazo-ketone (path *a*), or cyclise to give (IXa) with subsequent loss of a proton from the sulphonamide nitrogen atom (path *b*). The reported⁶ formation of the diazo-ketone (Ig) together with the oxo-lactone (Vc) when phthalic anhydride is treated with diazomethane has been ascribed to a similar duality in behaviour of the intermediate acyldiazonium ion (IIIf).

The influence of triethylamine on the reaction of (VIa) may be interpreted on the basis that the first-formed complex (XIII) can, as a minor reaction, dimerize to give the cyclic sulphonamide (XIV); alternatively it may react with diazoethane to give the acyldiazonium ion (VIIa), which, in addition to the duality in behaviour discussed above, may undergo deprotonation of the sulphonylamino-nitrogen atom, thus facilitating formation of the indoxyl (Xa).

The differing behaviour of diazomethane and diazoethane with the sulphonylamino-acid chloride (VIa) suggests that proton removal from the secondary acyldiazonium ion (VIIa) takes place less readily than from the primary acyldiazonium ion (VIIb); the latter therefore has less opportunity to cyclise to give (Xb), but careful examination of the product from diazomethane and the acid chloride (VIa) showed that here too there were traces of the cyclisation product (Xb).

Support for the above was obtained by studying the action of diazomethane and of diazoethane on the *N*-methylated acid chloride (VIb); in both instances the expected diazo-ketone (VIIIe or f) was obtained in high yield, as might be expected, since cyclisation even of the secondary acyldiazonium ion (VIIc) would involve displacement of either the methyl or the sulphonyl group from the sulphonylamino-nitrogen atom, both of which processes would be more difficult than loss of a proton from the unmethylated intermediates (VIIb and a).

When the diazo-ketone (VIIIe) was treated with toluene-*p*-sulphonic acid in acetic anhydride, nitrogen was rapidly evolved and the major product was the diacetyl derivative (XII). Such a process involves displacement of the arylsulphonyl group from the sulphonylamino-nitrogen atom: further evidence was obtained for this by carrying out the cyclisation with

acetic acid, when, after aqueous work-up, toluene-*p*-sulphonic acid was isolated in 55% yield.

One explanation of this result is that the acyldiazonium ion (VIIId) cyclises to give the quaternary cation (IXc), the enolic form of which is acetylated by acetic anhydride to give the β -acetoxy-derivative (XI) while the arylsulphonyl group is removed by acetic anhydride to give the mixed anhydride, acetyl toluene-*p*-sulphonate, which would then provide the observed diacetyl derivative (XII). The second acetylation is not brought about simply with acetic anhydride, as shown by the fact that the final stage in the literature preparation of the monoacetyl derivative (XIa) involves heating with acetic anhydride; in a separate experiment, however, the monoacetyl derivative (XI) was successfully acetylated with preformed mixed anhydride. When the reaction was carried out in acetonitrile as solvent, thereby excluding acetylation, the only identifiable product was *NN*-dimethylindigo; desulphonation of the quaternary cation (IXc) would give *N*-methylindoxyl which, it is known, undergoes oxidation to the indigo.⁷

In the cyclisation of *ortho*-substituted α -diazoacetophenones, displacement of an alkyl group from an alkoxy- (Ia) or an alkylthio- (Ib) substituent and of acetyl from an acetoxy- (Ic) substituent is familiar,^{1,8} but we believe this to be the first recorded example of the displacement of a sulphonyl group from a nitrogen atom in such reactions. With the corresponding diazoethyl ketone (VIIc) and toluene-*p*-sulphonic acid only tars were obtained.

It was then appreciated that desulphonylation may also occur in the reaction of the unmethylated acid chloride (VIa) with diazoethane, since the combined yields of diazoketone (VIIIb) and cyclisation product (Xa) amounted to little more than 50% and experiments showed that neither of these reacted further with diazoethane. Pure products were not isolated from the residual material, but its spectroscopic characteristics suggested the presence of *N*-ethyl, *O*-ethyl, and *C*-methyl groups, as would be expected from cyclisation of the acyldiazonium ion (VIIa) with elimination of the sulphonyl group followed by reaction with diazoethane to give 3-ethoxy-*N*-ethyl-2-methylindole.

The above described displacement of a tolylsulphonyl group from nitrogen prompted us to attempt a similar displacement from oxygen. 2-Diazo-2'-(*p*-tolylsulphonyloxy)acetophenone (Ih) was prepared in high yield from the corresponding acyl chloride; no evidence for cyclisation of the intermediate diazonium ion (IIg) was obtained. Treatment of (Ih) with toluene-*p*-sulphonic acid or with a catalytic amount of hydrochloric acid, under conditions which brought about displacement of the methyl group from the *ortho*-methoxy-diazoketone (Ia), gave only acyclic products in amounts proportional to the quantity of acid employed. Since such displacements are believed to proceed *via* an 'onium salt, this

⁵ H. J. Bestmann, H. Buckshewski, and H. Leube, *Chem. Ber.*, 1959, **92**, 1345.

⁶ P. McC. Duggleby and G. Holt, *J. Chem. Soc.*, 1962, 3579.

⁷ L. Ettinger and P. Friedlander, *Ber.*, 1912, **45**, 2074.

⁸ E. R. Marshall, J. A. Kuck, and R. C. Elderfield, *J. Org. Chem.*, 1942, **7**, 444.

result presumably reflects the greater stability of quaternary nitrogen over oxonium oxygen. When however, perchloric acid was gradually added to the diazoketone (Ih) in acetic anhydride, the acyclic toluene-*p*-sulphonate (XVa) resulted. This result may be rationalised by postulating cyclisation of the acyldiazonium ion (IIg) to give benzofuranone (IVa), while the arylsulphonyl group is removed by acetic anhydride as discussed above. The resultant acetyl toluene-*p*-sulphonate may then act as an acetylating agent with concomitant liberation of toluene-*p*-sulphonate ion. Attack of the latter on the acyldiazonium ion (IIg) will then provide the observed bis-(*p*-tolylsulphonyloxy)-derivative (XVa). Support for this view is obtained by spectroscopic examination of the reaction mixture which, in addition to the bis-(*p*-tolylsulphonyloxy)-derivative (XVa), contained benzofuranone (IVa), together with its mono- and di-acetylation products.

EXPERIMENTAL

I.r. spectra were recorded with a Perkin-Elmer 257 instrument, ¹H n.m.r. spectra with Perkin-Elmer R20A and Varian HA100 spectrometers, and mass spectra with an A.E.I. MS902 spectrometer. Gas volumes have been reduced to S.T.P. All the known compounds gave satisfactory analytical and spectroscopic data. For products marked with an asterisk, further spectral data are available in Supplementary Publication No. SUP 21790 (4 pp.).†

Diazoketones.—Prepared from diazomethane or diazoethane and the corresponding acid chloride by standard procedures,⁹ these were characterised as their triphenylphosphine adducts.⁵

(a) 2-(*N*-Methyl-*p*-tolylsulphonylamino)benzoyl chloride* (VIb) (76%) (Found: C, 55.6; H, 4.5; N, 4.4. C₁₅H₁₄ClNO₃ requires C, 55.6; H, 4.3; N, 4.3%), m.p. 88—90° (from carbon tetrachloride), ν_{\max} . 1748s (CO), 1348s (SO₂), and 1149s cm⁻¹ (SO₂), τ (CDCl₃) 1.90—3.25 (8 H, aromatic), 6.8 (3 H, NCH₃), and 7.6 (3 H, CH₃), prepared from the corresponding acid with phosphorus pentachloride and toluene, provided 2-diazo-2'-(*N*-methyl-*p*-tolylsulphonylamino)acetophenone* (VIIIf) (88%) (Found: C, 57.8; H, 4.7; N, 10.6. C₁₆H₁₅N₃O₃S requires C, 58.3; H, 4.5; N, 12.7%), m.p. 88—90° (decomp.) (from ether), ν_{\max} . 2101s (diazo), 1620s (CO), 1361s (SO₂), and 1170s cm⁻¹ (SO₂), τ (CDCl₃) 2.15—3.40 (8 H, aromatic), 3.98 (1 H, CO·CHN₂), 6.78 (3 H, NCH₃), and 7.55 (3 H, *p*-CH₃). 2'-(*N*-Methyl-*p*-tolylsulphonylamino)-2-(triphenylphosphoranylidenehydrazono)acetophenone* (VIIIf) (90%) (Found: C, 68.9; H, 5.3; N, 7.2. C₃₄H₃₀N₃O₃PS requires C, 69.0; H, 5.1; N, 7.1%) had m.p. 148—150° (decomp.) (from methanol), ν_{\max} . 1645s (CO), 1351s (SO₂), and 1156s cm⁻¹ (SO₂), τ (CDCl₃) 2.1 (1 H, COCH=N-N=P, *J* 2.3 Hz). The acid chloride and diazoethane gave 2-diazo-2'-(*N*-methyl-*p*-tolylsulphonylamino)propiofenone (VIIIf) (70%), ν_{\max} . 2105s (diazo), 1615s (CO), 1358s (SO₂), and 1163s cm⁻¹ (SO₂), τ (CDCl₃) 1.85—3.35 (8 H, aromatic), 6.80 (3 H, NCH₃), 7.55 (3 H, CO·CMeN₂), and 7.65 (3H, *p*-CH₃). 2'-(*N*-Methyl-*p*-tolylsulphonylamino)-2-(triphenylphosphoranylidenehydrazono)propiofenone* (VIIIf) (88%) (Found: C, 65.2; H, 5.2; N, 6.6; S, 5.0;

P, 4.8. C₃₅H₃₂N₃O₃PS requires C, 69.4; H, 5.3; N, 6.9; S, 5.3; P, 5.1%) had m.p. 190—192° (decomp.) (from methanol), ν_{\max} . 1626s (CO), 1360s (SO₂), and 1176s cm⁻¹ (SO₂), τ (CDCl₃) 2.27 (1 H, COCH=N-N=P, *J* 2.3 Hz), 2.3—3.1 (23 H, aromatic), and 7.62 (3 H, *p*-CH₃).

(b) 2-(*p*-Tolylsulphonyloxy)benzoyl* chloride (80%) (Found: C, 53.9; H, 3.7; S, 10.0. C₁₄H₁₁O₄Cl requires C, 54.1; H, 3.5; S, 10.3%), m.p. 94—95° (from carbon tetrachloride), ν_{\max} . 1179s (CO), 1370s (SO₂), and 1176s cm⁻¹ (SO₂), τ (CDCl₃) 1.85—2.85 (8 H, aromatic), 7.58 (3 H, *p*-CH₃), and diazomethane gave 2-diazo-2'-(*p*-tolylsulphonyloxy)acetophenone* (Ih) (83%) (Found: C, 56.7; H, 4.0; S, 8.8. C₁₅H₁₂N₂O₄S requires C, 56.9; H, 3.8; S, 8.9%), m.p. 81—83° (decomp.) (from ether), ν_{\max} . 2119s (diazo), 1610s (CO), 1357s (SO₂), and 1167 cm⁻¹ (SO₂), τ (CDCl₃) 2.25—3.05 (8 H, aromatic), 4.2 (1 H, CO·CHN₂) and 7.58 (3 H, *p*-CH₃). 2'-(*p*-Tolylsulphonyloxy)-2-(triphenylphosphoranylidenehydrazono)acetophenone* (82%) (Found: C, 67.0; H, 4.4; N, 5.0; S, 6.4. C₃₃H₂₇N₂O₄PS requires C, 68.5; H, 4.7; N, 4.8; S, 5.5%) had m.p. 113—115° (from ethanol), ν_{\max} . 1626s (CO), 1360s (SO₂), and 1167s cm⁻¹ (SO₂), τ (CDCl₃) 2.27 (1 H, COCH=N-N=P, *J* 2.3 Hz), 2.3—3.1 (23 H, aromatic), and 7.62 (3 H, *p*-CH₃).

2-(*p*-Tolylsulphonylamino)benzoyl chloride and diazoethane. A suspension of the acid chloride*,¹⁰ (VIa) (15.45 g, 0.05 mol) in dry ether (300 ml) was added to a stirred solution of diazoethane (7 g, 0.125 mol) in dry ether (1.2 l) at -20 °C during 30 min. After a further 1 h the filtered solution was evaporated under reduced pressure to provide an oil (A) (16.4 g) which could not be induced to crystallize; ν_{\max} . 3333m (NH), 2092s (diazo), and 1613s cm⁻¹ (CO), τ (CDCl₃) 1.1 (NH), 5.64 (N·CH₂·C, *J* 6.75 Hz), 6.05 (CO·CHN, *J* 7 Hz), 6.3 (C=C·OCH₂, *J* 7.25 Hz), 7.55 (CO·CMeN₂), 8.12 (C=C·CH₃), 8.35 (CO·CMeN), 8.6 (OC·CH₃, *J* 7.25 Hz), and 8.85 (N·C·CH₃, *J* 6.75 Hz). Portions of (A) were treated as follows.

(a) The sample (A) (4 g) was treated with absolute ethanol at 0—5 °C until all the oily material passed into solution. The residual material (0.66 g, m.p. 119—121°, was separated; crystallisation from ethanol provided 2-methyl-*N*-*p*-tolylsulphonylindoxyl* (Xa) (18%) (Found: C, 64.0; H, 5.3; N, 4.7. C₁₆H₁₅NO₃S requires C, 63.8; H, 5.0; N, 4.7%), m.p. 122—124° (from ethanol), ν_{\max} . 1709s (CO), 1366s (SO₂), and 1168s cm⁻¹ (SO₂), τ (CDCl₃) 1.88—1.94 (8 H, aromatic) and 6.04 (1 H, q, CO·CHN, *J* 7 Hz).

(b) The sample (A) (4 g) in acetonitrile (40 ml) was treated with toluene-*p*-sulphonic acid monohydrate (0.7 g) in acetonitrile (20 ml). The nitrogen evolved (79 ml) corresponded to a 30% yield of diazo-ketone. The solvent was removed under reduced pressure and the residual dark green oil was shaken with ether (100 ml) and water (50 ml). The ether layer was separated, washed with water until no longer acidic, dried (Na₂SO₄), and evaporated. The oil obtained was treated as in (a) to provide 2-methyl-*N*-(*p*-tolylsulphonyl)indoxyl (0.97 g, 25%), identical with that described above.

(c) The oil (A) (4 g) and triphenylphosphine (2.2 g) in dry ether (50 ml) were stirred at 18—24 °C for 12 h, and the mixture was stored at 0 °C for 6 h. The solid (1.92 g, 89%) based on the diazo-ketone [m.p. 158—161° (decomp.)],

⁹ See W. E. Bachmann and W. S. Struve, *Org. Reactions*, 1942, **1**, 38, for compilation of references.

¹⁰ H. J. Scheifele, jun., and D. F. De Tar, *Org. Synth.*, 1952, **32**, 8.

† For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1975, Index issue.

recrystallised from ethanol, proved to be 2'-(*p*-tolylsulphonylamino)-2-(triphenylphosphoranylidenehydrazono)propio-phenone* (VIIIc) (78%) (Found: C, 68.8; H, 5.2; N, 7.1. $C_{34}H_{30}N_2O_3PS$ requires C, 69.0; H, 5.1; N, 7.1%), m.p. 160—163° (decomp.), ν_{\max} 3 247m (NH), 1 592s (CO), 1 364s (SO₂), and 1 160s cm⁻¹ (SO₂), τ (CDCl₃) 0.87 (1 H, NH), 2.32—3.65 (23 H, aromatic), 7.90 (3 H, CO-CMeN₂), and 7.95 (3 H, *p*-CH₃). Chromatography of the residue from which the adduct (VIIIc) had been separated provided, as the only identified products, triphenylphosphine oxide and 2-methyl-*N*-(*p*-tolylsulphonyl)indoxyl. In a repeat experiment, the yield of adduct (VIIIc) was not increased by doubling the quantity of triphenylphosphine. When a suspension of the acid chloride (VIa) (9.27 g, 0.03 mol) in dry ether (100 ml) was added gradually to diazoethane (2.52 g, 0.045 mol) and triethylamine (3.03 g, 0.03 mol) in ether (500 ml), a white solid (B) (5.28 g) separated. This was stirred with hot water (50 ml) and the resulting solid was separated and washed with water until the washings no longer responded to a test for triethylamine hydrochloride. The dried solid was washed with a little ethanol and with ether and dried again (yield 1.31 g, 16%) to give *NN'*-bis-(*p*-tolylsulphonyl)dibenzo[*b,f*][1,5]diazocine-6,12(5*H*,11*H*)-dione (XIV).⁵ The main ethereal solution from which the latter and triethylamine hydrochloride had been separated was worked up as in previous experiments; it proved to contain the diazo-ketone (30%) and 2-methyl-*N*-(*p*-tolylsulphonyl)indoxyl (2.29 g, 28%). When a double quantity of triethylamine was employed, the yields of diazo-ketone (VIIIb), indoxyl derivative (Xa), and cyclic amide (XIV) were, respectively, 27, 40, and 18%.

2-Diazo-2'-(p-tolylsulphonylamino)propio-phenone. The adduct (VIIIc) (11.3 g, 0.02 mol) was heated in refluxing methanol (150 ml) until the solution became clear. After 12 h at 0 °C, the precipitated hydrazone (3 g) (m.p. 128—131°) was separated. The solvent was removed from the filtrate, and by following the general procedure of Bestmann,⁵ a further crop of hydrazone (1.79 g) (m.p. 129—131°) was isolated. The combined products on recrystallization from toluene provided 2-hydrazone-2'-(*p*-tolylsulphonylamino)propio-phenone* (VIIId) (75%) (Found: C, 58.3; H, 5.2; N, 12.6. $C_{18}H_{17}N_3O_3S$ requires C, 58.0; H, 5.1; N, 12.7%), m.p. 134—135° (from toluene), ν_{\max} 3 425s (NH₂), 3 333m (NH₂), 3 205s (NH), 1 639s (CO), 1 330s (SO₂), and 1 163s cm⁻¹ (SO₂), τ (CDCl₃) 0.53 (1 H, NH), 2.2—3.5 (8 H, aromatic), 3.85 (2 H, C=N-NH₂), 7.67 (3 H, *p*-CH₃), and 8.10 (3 H, CO-CMe=N). The hydrazone (3.31 g, 0.01 mol) in chloroform (30 ml) was stirred with activated manganese dioxide¹¹ (4.35 g, 0.05 mol) for 2 h at 0 °C. The filtered solution was concentrated under reduced pressure to provide a yellow oil (A) (13 g), the i.r. spectrum of which indicated that it was the diazo-ketone (VIIIb) contaminated with a much smaller amount of the indoxyl derivative (Xa). The oil (A) (1 g) and triphenylphosphine (0.60 g, 0.0023 mol) under standard conditions provided an adduct (0.75 g, 63% based on the hydrazone), identical (mixed m.p. and spectra) with (VIIIc). The oily diazo-ketone (VIIIb) (1 g) in acetonitrile (20 ml) was treated with toluene-*p*-sulphonic acid (0.50 g); nitrogen (48 ml, 70% based on diazo-ketone) was evolved. Work-up of the green solution as in (b) above gave 2-methyl-*N*-(*p*-tolylsulphonyl)indoxyl (Xa) (0.35 g, 55% based on the hydrazone).

¹¹ H. Morrison, S. Danishefsky, and P. Yates, *J. Org. Chem.*, 1961, **26**, 2617.

Cyclisation of 2-Diazo-2'-(N-methyl-p-tolylsulphonylamino)-acetophenone (VIIIe).—When the diazo-ketone (VIIIe) (6.58 g, 0.02 mol) in acetic anhydride (100 ml) was treated with acetic acid (2.4 g, 0.004 mol) at 18—20 °C, nitrogen (248 ml) was evolved over 40 min. Evaporation under reduced pressure at 60 °C gave a viscous oil which on stirring with water (50 ml) solidified; the cream solid (Y) (3.74 g, 81%), m.p. 118—121° was separated and washed with a little water. The combined filtrate and washings were concentrated to low bulk under reduced pressure to precipitate toluene-*p*-sulphonic acid (1.88 g, 55%), m.p. 102—104° (lit.,¹² 105—106°), *m/e* 172 (*M*⁺, 66.4%), 108 (29.3), 107 (40.1), 91 (100), 65 (41.9), and 64 (5.5). The solid (Y) after recrystallization from ethanol (charcoal) gave white needles of 3-acetoxy-2-acetyl-1-methylindole* (XII) (72%) (Found: C, 67.2; H, 5.7; N, 5.8. $C_{13}H_{13}NO_3$ requires C, 67.5; H, 5.7; N, 6.0%), m.p. 127—129° (from ethanol), ν_{\max} 1 761s (OAc) and 1 667s cm⁻¹ (Ac), τ (CDCl₃) 2.2—2.9 (4 H, aromatic), 5.97 (3 H, NCH₃), 7.42 (3 H, Ac), and 7.52 (3 H, OAc). When the above experiment was repeated with toluene-*p*-sulphonic acid monohydrate (3.8 g, 0.02 mol) in place of acetic acid, the diazo-nitrogen was quantitatively evolved during 10 min and the diacetyl compound (XII) was obtained (3.23 g, 70%), identified by m.p., mixed m.p., and i.r. spectrum. From the aqueous layer was isolated toluene-*p*-sulphonic acid (5.67 g, 0.033 mol). When the diazo-ketone in acetic anhydride was treated with a catalytic quantity (0.1 mol) of acetic or toluene-*p*-sulphonic acid, nitrogen (100%) was evolved during 90 and 30 min, respectively; both reaction mixtures however developed a deep green colour and no identified products were isolated. A similar result was obtained when acetonitrile was used in place of acetic anhydride as solvent; even when an equimolar amount of acid was employed, in the latter case the only identifiable product was one having the same m.p. and spectroscopic characteristics as reported for *NN'*-dimethylindigo.⁷ The structure of the diacetyl derivative (XII) was confirmed by its identity (m.p., mixed m.p., and spectroscopic data) with the product obtained when the known* 3-acetoxy-1-methylindole (XI) (1.89 g, 0.02 mol) and acetyl toluene-*p*-sulphonate (2.15 g, 0.01 mol) were mixed in acetic anhydride (250 ml). T.l.c. indicated that the reaction was complete after 10 min at 18—20 °C and after a further 20 min the solvent was removed under reduced pressure. Treatment of the residual oil with water, as described above, gave the diacetyl derivative (XII).

2-Diazo-2'-(p-tolylsulphonyloxy)acetophenone (Ih) with Acids.—When the diazo-ketone (Ih) (3.16 g, 0.01 mol) was treated with toluene-*p*-sulphonic acid monohydrate (1.90 g, 0.01 mol) in acetic anhydride as described above, the whole of the diazo-nitrogen (224 ml) was evolved over 10 min; work-up similar to that above provided 2,2'-bis-(*p*-tolylsulphonyloxy)acetophenone* (XVa) (88%) (Found: C, 57.4; H, 4.6; S, 14.1. $C_{22}H_{20}O_7S_2$ requires C, 57.4; H, 4.4; S, 13.9%), m.p. 86—87° (from ethanol), ν_{\max} 1 689s (CO), 1 360s (SO₂), and 1 160s cm⁻¹ (SO₂), τ (CDCl₃) 2.10—3.05 (12 H, aromatic), 4.95 (2 H, CO-CH₂-O-SO₂), and 1 755 (6 H, *p*-CH₃). When the toluene-*p*-sulphonic acid in the above experiment was replaced by perchloric acid, added over 15 min, nitrogen (223 ml) was evolved during 30 min. Removal of the solvent under reduced pressure gave a red oil which partly solidified; stirring the oil with ice-cold ethanol (20

¹² A. Vogel, 'Practical Organic Chemistry,' Longmans, London, 3rd edn., 1966, p. 552.

ml) and filtration gave 2,2'-bis-(*p*-tolylsulphonyloxy)acetophenone (1.5 g, 65% based on the diazoketone) identical (mixed m.p. and spectra) with that described above. The oil contained in the filtrate from which the toluenesulphonate had been separated was shown by t.l.c. to be a complex mixture, but i.r., n.m.r., and mass spectrometry indicated the presence of benzofuranone (IVa) together with 3-acetoxybenzo[*b*]furan and probably 3-acetoxy-2-acetylbenzo[*b*]furan; ν_{\max} . 1 694s (CO·CH₂), 1 744s (OAc), and 1 667s cm⁻¹ (Ac), τ (CDCl₃) 3.95 (C=CH-O-), 5.35 (CO·CH₂·O), 7.62 (C:C·COMe), 7.85 (OAc), and 7.95 (OAc), *m/e* 176

(C₁₀H₈O₃, 0.6%), 134 (C₈H₆O₂, 34.7), 133 (C₈H₅O₂, 61.1), and 43 (C₂H₃O, 100). Decomposition of the diazo-ketone could not be effected by catalytic quantities of perchloric toluene-*p*-sulphonic, or hydrochloric acid, but with 1 mol. equiv. of the last in aqueous 80% ethanol, there resulted 2-chloro-2'-(*p*-tolylsulphonyloxy)acetophenone* (XVb) (89%) (Found: C, 55.7; H, 4.1; S, 10.1. C₁₅H₁₃ClO₄S requires C, 55.5; H, 4.0; S, 9.9%), m.p. 82–83°, ν_{\max} . 1 700s (CO), 1 370s (SO₂), and 1 167s cm⁻¹ (SO₂), τ (CDCl₃) 2.25–3.10 (8 H, aromatic), 5.45 (2 H, CO·CH₂Cl), and 7.58 (3 H, *p*-CH₃).

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