Some Derivatives of 5,6,11,12-Tetrahydrodibenzo[*b*,*f*][1,4]diazocine

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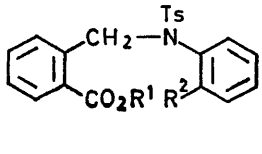
The synthesis of 5,6,11,12-tetrahydro-12-*p*-tolylsulphonyldibenzo[*b*,*f*][1,4]diazocin-6-one and a number of 5-alkyl derivatives is described. Removal of the *p*-tolylsulphonyl group from these compounds with sulphuric acid was accompanied by a ring contraction, the products being phthalimidines. The 5-methyl derivative (IIb) also gave a phthalimidine when treated with phenyl-lithium. The reduction of the dibenzodiazocines was investigated. An authentic sample of 5,6,11,12-tetrahydro-5-methyldibenzo[*b*,*f*][1,4]diazocine was prepared, and a compound to which this structure was previously assigned [1] was shown to be the bis-(12-methyldiazocin-5-yl)-methane (XVII). In an attempted synthesis of 11-substituted 5,6-dihydrodibenzo[*b*,*f*][1,4]diazocines the only products obtained were substituted benzimidazoles.

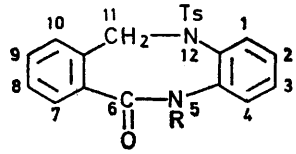
A PREVIOUS paper [1] has described the preparation of 5,6,11,12-tetrahydrodibenzo[*b*,*f*][1,4]diazocine (XIVc) and its reaction with aldehydes to give bridged-ring compounds (XVI); the synthesis of *N*-alkyl derivatives of the dibenzodiazocine (XIVc) was also investigated. Ring-substituted derivatives of compounds (XIVc) and (XVI) have also been prepared.[2] This paper describes the synthesis and reactions of certain derivatives of the dibenzodiazocine (XIVc) in which the eight-membered ring is substituted.

Ethyl 2-(chloromethyl)benzoate [3] reacted with the sodium salt of 2-(*p*-tolylsulphonylamino)nitrobenzene to give compound (Ia). Catalytic reduction of this compound (Ia) gave the amine (Ib) which underwent cyclis-



(I)

	R^1	R^2
a;	Et	NO_2
b;	Et	NH_2
c;	H	NO_2
d;	H	NH_2



(II)

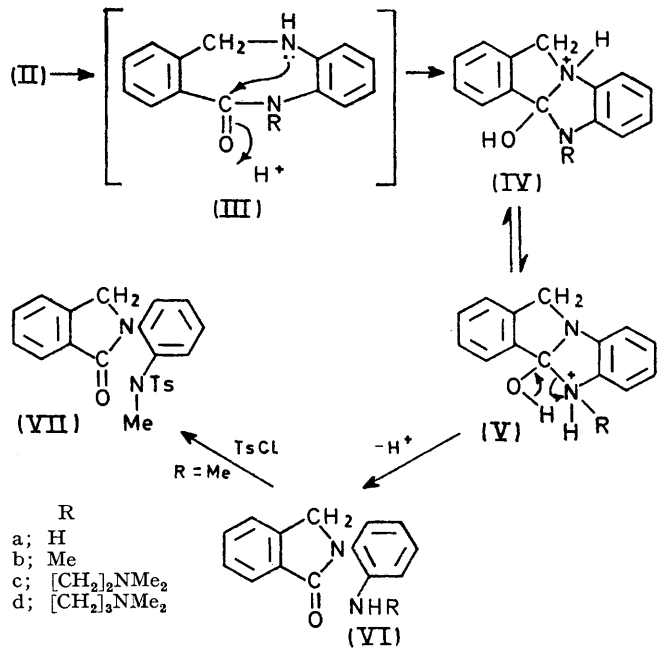
	R
a;	H
b;	Me
c;	$[CH_2]_2NMe_2$
d;	$[CH_2]_3NMe_2$

Ts = *p*-tolylsulphonyl

ation to 5,6,11,12-tetrahydro-12-*p*-tolylsulphonyldibenzo[*b*,*f*][1,4]diazocin-6-one (IIa) in good yield when treated with sodium hydride in dioxan. The dibenzodiazocine (IIa) was also obtained by hydrolysis of the nitro-ester (Ia) to the nitro-acid (Ic), reduction to the amino-acid (Id), and subsequent ring closure, effected with either dicyclohexylcarbodi-imide in ethyl acetate or ethyl 2-ethoxy-1,2-dihydroquinoline-1-carboxylate in tetrahydrofuran.

The sodio-derivative of the amide (IIa), prepared using sodium hydride in dioxan, reacted with alkyl halides to give the 5-alkyl derivatives (IIb—d). The 5-methyl compound (IIb) was also prepared by the interaction of 2-(bromomethyl)benzoyl bromide and *N*-methyl-*N'*-*p*-tolylsulphonyl-*o*-phenylenediamine, the latter compound being obtained by treatment of *N*-methyl-*o*-phenylenediamine with toluene-*p*-sulphonyl chloride.

Attempts were made to remove the *p*-tolylsulphonyl group from the dibenzodiazocines (IIa—d) by treatment with sulphuric acid monohydrate at room temperature. However, although these conditions did effect hydrolysis of the sulphonamide group it became apparent that a ring contraction had occurred in the formation of the products, which were not the desired dibenzodiazocines (IIIa—d) but the isomeric phthalimidines (VIa—d). Thus the



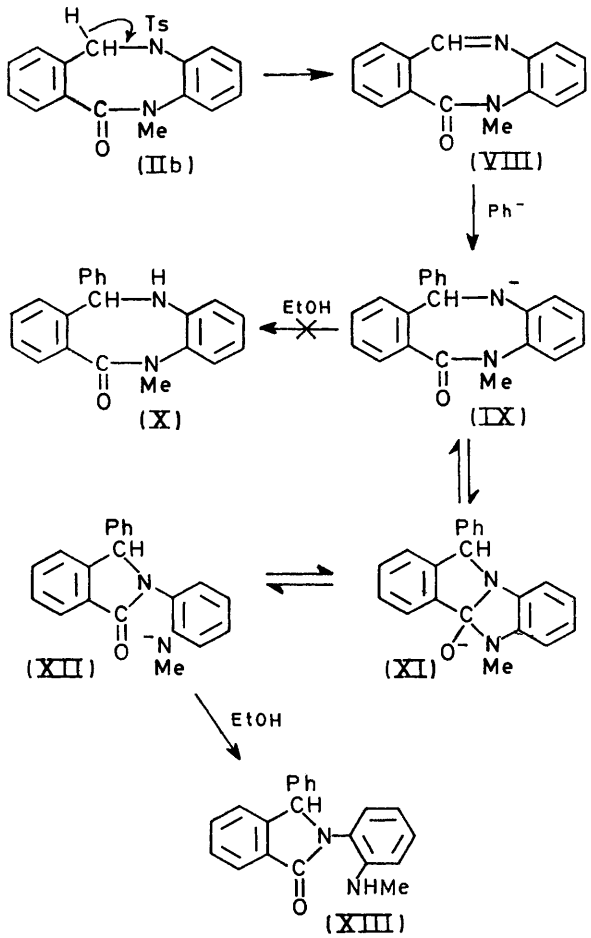
SCHEME 1

i.r. spectra of the products showed a carbonyl absorption in the region 1695—1670 cm^{-1}, whereas in the starting materials (IIa—d) this was in the region 1660—1645 cm^{-1}; in addition, the spectrum of the product obtained from the dibenzodiazocine (IIa) showed absorptions typical of a primary amine. Furthermore, when the compound obtained from the 5-methyldibenzodiazocine (IIb) was treated with toluene-*p*-sulphonyl chloride the product obtained was not identical to the dibenzodiazocine (IIb), and is assigned the structure (VII). Babichev and his co-workers [4] obtained a compound, to which they assigned the structure of 2-(2-methylaminophenyl)phthalimidine (VIb), by treating salts of 5-methyl-11*H*-isoindolo[2,1-*a*]benzimidazole with alkali. A sample of their compound was identical to that obtained from the dibenzodiazocine (IIb).

[1] N. J. Harper and J. M. Sprake, *J. Chem. Soc.* (*C*), 1969, 882.
[2] A. Saunders and J. M. Sprake, *J. Chem. Soc.* (*C*), 1970, 1161.
[3] I. G. Hinton and F. G. Mann, *J. Chem. Soc.*, 1959, 599.
[4] F. S. Babichev, L. G. Khilko, and N. V. Melnichenko, *Ukrain. khim. Zhur.*, 1969, **35**, 615.

A mechanism which would account for the ring contraction observed is shown in Scheme 1. The initial hydrolysis of the *p*-tolylsulphonyl group in the dibenzodiazocine (II) gives the expected product (III). Although the amino-nitrogen atom in the intermediate (III) would be largely protonated in the strong acid used, it might be expected that, for the small amount of free amine present, nucleophilic attack on the protonated carbonyl group would occur. The cation produced (IV) is interconvertible with the isomer (V), which can rearrange to the phthalimidine (VI).

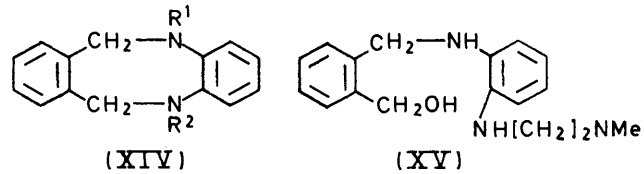
Treatment of the 5-methyldibenzodiazocine (IIb) with phenyl-lithium was expected, by analogy with the work of Negishi and Day,[5] to give the 11-phenyldibenzodiazocine (X). However, the product obtained appears, on the basis of the position of the carbonyl absorption in the i.r. spectrum, to be the isomeric phthalimidine (XIII). An attempt was made to prepare an authentic



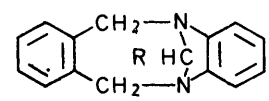
SCHEME 2

sample of the *p*-tolylsulphonyl derivative of 2-(2-methylaminophenyl)-3-phenylphthalimidine (XIII) by an extension of Meyer's route,[6] starting from 2-benzoylbenzoic acid and *N*-methyl-*N*-*p*-tolylsulphonyl-*o*-phenylenediamine, but this was unsuccessful. No pure compounds could be isolated from reactions involving the other dibenzodiazocines (IIa, c, and d) and phenyl-lithium. A mechanism for the formation of the phthalimidine (XIII), based on that of Negishi and Day and Scheme 1, is shown in Scheme 2.

Reduction of the dibenzodiazocines (IIa and b) with lithium aluminium hydride gave the expected products



	R^1	R^2
a;	Ts	H
b;	Ts	Me
c;	H	H
d;	H	Me
e;	Ac	Me
f;	NO	Me

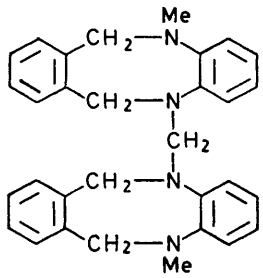


(XIVa and b). The compound (XIVa) was identical to a sample prepared by treating 5,6,11,12-tetrahydrodibenzo[*b*,*f*][1,4]diazocine[1] (XIVc) with one equivalent of toluene-*p*-sulphonyl chloride. Reduction of the dimethylaminoethyl compound (IIc), however, gave a compound which, on spectroscopic evidence, is formulated as *N*-(2-dimethylaminoethyl)-*N'*-(2-hydroxymethylbenzyl)-*o*-phenylenediamine (XV). Thus the molecular formula was found by mass spectrometry to be $C_{18}H_{25}N_3O$, and the i.r. spectrum indicated the presence of an NH group ($\nu_{max.}$ 3400 cm^{-1}), and a bonded OH or NH group ($\nu_{max.}$ 3400—2400 cm^{-1}), and the absence of a carbonyl group. The n.m.r. spectrum showed two singlets at τ 5·37 and 5·73, each integrating for a methylene group, and the two NH protons and the OH proton appeared together in a broad exchangeable peak at τ 5·88. The reductive cleavage of amides to aldehydes or alcohols and the amine component is well documented,[7] and reductive cleavages of sulphonamides have also been reported.[8]

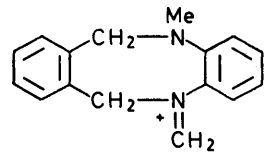
Hydrolysis of the *p*-tolylsulphonyl compounds (XIVa and b) with sulphuric acid gave the dibenzodiazocines (XIVc and d). The former compound (XIVc) was identical to an authentic sample,[1] but the latter (XIVd) was not identical to the compound previously[1] assigned this structure. This compound was obtained by treating the *endo*-methanodibenzodiazocine (XVI; R = H) with dimethyl sulphate and sodium hydroxide, and it was assigned the methyldibenzodiazocine structure (XIVd) by analogy with the products of similar reactions involving bridged dibenzo[*b*,*f*][1,5]diazocines.[9] This assignment has now proved incorrect, and the compound is reformulated as the bis-(12-methyldiazocin-5-yl)methane

[5] E. Negishi and A. R. Day, *J. Org. Chem.*, 1965, **30**, 43.
[6] H. Meyer, *Monatsh*, 1907, **28**, 1211, 1226, and 1235.
[7] N. G. Gaylord in 'Reduction with Complex Metal Hydrides,' Interscience, New York, 1956, 544.
[8] D. Klamann and G. Hofbauer, *Chem. Ber.*, 1953, **86**, 1246.
[9] (*a*) F. C. Cooper and M. W. Partridge, *J. Chem. Soc.*, 1957, 2888; (*b*) M. Häring, *Helv. Chim. Acta*, 1963, **46**, 2970.

(XVII). Thus although the elemental analysis reported[1] satisfies both structures (XIVd) and (XVII), the molecular formula as determined by mass spectrometry is $C_{31}H_{32}N_4$, and the fragmentation pattern is also consistent with the suggested structure. The base peak at *m/e* 237 can be rationalised as arising from a fission at the methylene bridge to give the ion (XVIII) and the rest of the fragmentation pattern is in accordance with that observed in other dibenzo[*b*,*f*][1,4]diazocines.[10] The n.m.r. spectra of the two compounds (XIVd) and (XVII) are very similar, the main difference being that that of the former (XIVd) shows a broad exchangeable singlet at τ 6·1—6·7 corresponding to the NH proton, whilst that of the latter (XVII) shows a sharp singlet at τ 5·36 due to the methylene bridge. The i.r. spectrum of the bisdiazocinylmethane (XVII) shows a weak absorption at 3415 cm^{-1}; this was assigned originally[1] as an NH stretching frequency, but is evidently due to an overtone. The spectrum of the dibenzodiazocine (XIVd) shows an NH stretching absorption at 3330 cm^{-1} typical of a secondary amine. The u.v. spectra of the two compounds are very similar.



(XVII)



m/e 237

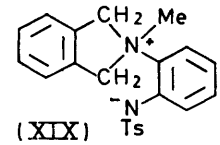
(XVIII)

Reaction of the bisdiazocinylmethane (XVII) with acetic anhydride and with nitrous acid was reported[1] to give the compounds (XIVe and f). These compounds proved to be identical to authentic samples prepared from the methyldibenzodiazocine (XIVd), and it was also found that the bisdiazocinylmethane (XVII) would react with toluene-*p*-sulphonyl chloride to give the 5-methyl-12-*p*-tolylsulphonyldibenzodiazocine (XIVb). In these reactions the bisdiazocinylmethane (XVII) therefore behaves similarly to the *endo*-methanodibenzodiazocine (XVI; R = H), which also loses the methylene bridge to form the diacetyl- (XIV; $R^1 = R^2 = Ac$) and dinitroso- (XIV; $R^1 = R^2 = NO$) dibenzodiazocines.[1]

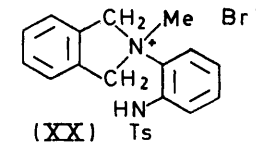
As a final proof of structure, the bisdiazocinylmethane (XVII) was synthesised by condensation of the 5-methyldibenzodiazocine (XIVd) with formaldehyde.

Attempts were made to alkylate the 5-methyldibenzodiazocine (XIVd) by treatment with sodium hydride or sodamide and an alkyl halide, but only unchanged starting material was recovered from these reaction mixtures.

The reaction between αα′-dibromo-*o*-xylene and *N*-methyl-*N*′-*p*-tolylsulphonyl-*o*-phenylenediamine was investigated as a prospectively more convenient synthesis of the 5-methyl-12-*p*-tolylsulphonyldibenzo[*b*,*f*][1,4]diazocine (XIVb). However, the product obtained was not identical to an authentic sample, although it possessed the expected molecular formula of $C_{22}H_{22}N_2O_2S$ and had an identical mass spectrum. On the basis of the mass and n.m.r. spectra the compound is assigned the dipolar ion structure (XIX). The n.m.r. spectrum shows



(XIX)

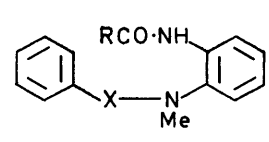


(XX)

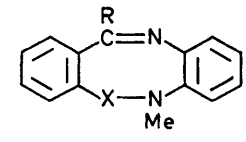
an AB quartet integrating for 4 protons, which is to be expected if the two methylene groups are equivalent but the geminal protons of each are not, and a methyl signal at τ 6·44, suggestive of the presence of a $\overset{+}{N}Me$ group. In contrast, the methylene groups of the dibenzodiazocine (XIVb) appear in the spectrum as two singlets; here, the methylene groups are not themselves equivalent, but the geminal protons of each are. In addition, the methyl signal occurs at appreciably higher field (τ 7·24).

Treatment of the dipolar ion (XIX) with hydrobromic acid gave a salt (XX), this being accompanied by changes in the positions of the sulphonamide absorptions in the i.r. spectrum.

A prospective synthesis, by means of the Bischler–Napieralski reaction, of 11-alkyl- or 11-aryl-5,6-dihydrodibenzo[*b*,*f*][1,4]diazocines of the type (XXII) was investigated. Acylation of *N*-benzoyl-*N*-methyl-*o*-phenylenediamine[11] with acetic anhydride or benzoyl chloride gave the *N*-acyl-*N*′-benzoyl-*N*′-methyl-*o*-phenylenediamines (XXIa and b). The dibenzoyl compound (XXIb) was also obtained by the interaction of *N*-methyl-*o*-phenylenediamine and benzoyl chloride. When the cyclisation of these compounds (XXIa and b) was attempted by heating with polyphosphoric acid at 150°

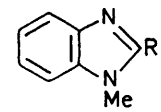


(XXI)



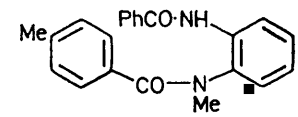
(XXII)

	R	X
a;	Me	CO
b;	Ph	CO
c;	Me	CH_2
d;	Ph	CH_2



(XXIII)

R
a; Ph
b; *p*-Tolyl
c; Me



(XXIV)

[10] B. J. Millard, A. Saunders, and J. M. Sprake, unpublished results.

[11] R. A. Heacock and D. H. Hey, *J. Chem. Soc.*, 1952, 1508.

for 2 h, they both afforded 1-methyl-2-phenylbenzimidazole (XXIIIa) with the loss of, respectively, the acetyl group or one of the benzoyl groups. That either benzoyl group can be eliminated is indicated by the behaviour of *N*-benzoyl-*N'*-methyl-*N'*-*p*-toluoyl-*o*-phenylenediamine (XXIV), which, when heated in polyphosphoric acid, afforded a mixture of 1-methyl-2-phenyl- and 1-methyl-2-*p*-tolyl-benzimidazole (XXIIIa and b) in the ratio of approximately 1 : 1·9. The composition of the mixture was determined by subjecting the reaction product to preparative t.l.c., eluting the band containing the benzimidazoles, and comparing the integral heights of the CMe and NMe peaks in the n.m.r. spectrum. Authentic 1-methyl-2-*p*-tolylbenzimidazole (XXIIIb) was prepared by treating *N*-methyl-*N*-*p*-toluoyl-*o*-phenylenediamine with polyphosphoric acid.

N-Benzyl-*N*-methyl-*o*-phenylenediamine [12] reacted with acetic anhydride and with benzoyl chloride to give the *N*-acyl-*N'*-benzyl-*N'*-methyl-*o*-phenylenediamines (XXIc and d). The acetyl compound (XXIc) was recovered unchanged after being heated in polyphosphoric acid at 150° for 2 h, but after 16 h at 180°, 1,2-dimethylbenzimidazole (XXIIIc) was obtained. The *N*-benzoyl-*o*-phenylenediamine (XXId) similarly gave 1-methyl-2-phenylbenzimidazole (XXIIIa).

The formation of the benzimidazoles (XXIIIa and c) from the substituted *o*-phenylenediamines (XXIa—d), with the concurrent loss of an acyl or a benzyl group, finds a precedent in a reaction described by Wunsch and his co-workers.[13] They found that when *N*-benzoyl-*N'*-benzyl-*N'*-phenylethylenediamine was heated in polyphosphoric acid, it gave 1,2-diphenyl-4,5-dihydroimidazole, with the loss of the benzyl group, instead of the desired benzo[1,4]diazepine. The mechanism which they suggested for this reaction can be extended to the reactions described above.

EXPERIMENTAL

U.v. spectra were recorded for solutions in absolute ethanol with Unicam SP 800 and 500 spectrophotometers. I.r. spectra were recorded for Nujol mulls with a Unicam SP 200 spectrophotometer. ^{1}H N.m.r. spectra were recorded for solutions in deuteriochloroform, with tetramethylsilane as internal standard, with a Perkin-Elmer R 12 (60 MHz) instrument. Mass spectra were recorded with an AEI MS 902 spectrometer operating at 70 eV. Preparative t.l.c. was conducted on 100 cm plates with 1 mm Kieselgel PF_{254} (Merck) layers.

Ethyl 2-[N-(2-*Nitrophenyl*)-N-p-*tolylsulphonylaminomethyl*]*benzoate* (Ia).—*N*-*p*-Tolylsulphonyl-2-nitroaniline (73·4 g), 50% sodium hydride in oil (12·15 g), and dimethylformamide (250 ml) were heated together on a steam-bath for 30 min. Sodium bromide (26 g) was added to the solution, and then a solution of ethyl 2-(chloromethyl)-benzoate [3] (50 g) in dimethylformamide (150 ml) was added dropwise with stirring. The mixture was heated for 3 h on a steam-bath. The solvent was removed under reduced pressure, and the residue was shaken with a mixture of water (500 ml) and benzene (500 ml). The aqueous layer was extracted with benzene (2 × 500 ml) and the combined benzene extracts were dried ($MgSO_4$). Removal of the solvent and crystallisation of the residue from methanol gave the *nitro-ester* (74·8 g, 65%) as pale yellow needles, m.p. 106° (Found: C, 61·0; H, 4·95; N, 6·3. $C_{23}H_{22}N_2O_6S$ requires C, 60·75; H, 4·9; N, 6·15%), $\nu_{max.}$ 1710 (C=O), 1535 and 1355 (NO_2), and 1360 and 1165 (S=O) cm^{-1}.

Ethyl 2-[N-(2-*Aminophenyl*)-N-p-*tolylsulphonylaminomethyl*]*benzoate* (Ib).—The foregoing nitro-ester (Ia) (50 g) was reduced with hydrogen over 10% palladium–charcoal (5 g) in methanol (100 ml) and dimethylformamide (100 ml) at 5 atm. for 3 h. Removal of the catalyst and evaporation of the solvent under reduced pressure gave a solid which, on crystallisation from ethanol, afforded the *amino-ester* (35 g, 76%) as needles, m.p. 133° (Found: C, 64·95; H, 5·85; N, 6·7. $C_{23}H_{24}N_2O_4S$ requires C, 65·05; H, 5·7; N, 6·6%), $\nu_{max.}$ 3510 and 3410 (NH_2), 1705 (C=O), and 1370 and 1160 (S=O) cm^{-1}.

2-[N-(2-*Nitrophenyl*)-N-p-*tolylsulphonylaminomethyl*]-*benzoic Acid* (Ic).—The nitro-ester (Ia) (25 g) was dissolved in boiling ethanol (200 ml), and sodium hydroxide (5 g) in water (15 ml) was added. The mixture was refluxed for 15 min. The warm solution was then stirred vigorously as hydrochloric acid (13·5 ml) and water (100 ml) were added rapidly, followed by water (250 ml). Stirring was maintained as the mixture was cooled. Crystallisation of the precipitate from ethanol afforded the *nitro-acid* (20·6 g, 88%) as prisms, m.p. 194—195° (Found: C, 59·25; H, 4·45; N, 6·6. $C_{21}H_{18}N_2O_6S$ requires C, 59·15; H, 4·25; N, 6·55%), $\nu_{max.}$ 3400—2500 (bonded OH), 1680 (C=O), 1540 and 1350 (NO_2), and 1370 and 1160 (S=O) cm^{-1}.

2-[N-(2-*Aminophenyl*)-N-p-*tolylsulphonylaminomethyl*]-*benzoic Acid* (Id).—The foregoing nitro-compound (Ic) (20 g) was reduced with hydrogen over 10% palladium–charcoal (2 g) in a mixture of methanol (100 ml) and dimethylformamide (100 ml) at 5 atm. for 2 h. Crystallisation of the product from ethanol yielded the *amino-acid* as the *mono-ethanolate* (16·8 g, 81%), prisms, m.p. 89—90° (Found: C, 62·6; H, 6·1; N, 6·15. $C_{23}H_{26}N_2O_5S$ requires C, 62·4; H, 5·95; N, 6·35%). Crystallisation from benzene afforded the free *amino-acid* as prisms, m.p. 142° (Found: C, 63·2; H, 5·2; N, 6·8. $C_{21}H_{20}N_2O_4S$ requires C, 63·6; H, 5·1; N, 7·05%), $\nu_{max.}$ 3400 and 3300 (NH_2), 3300—2200 (bonded OH), 1690 (C=O), and 1345 and 1150 (S=O) cm^{-1}.

5,6,11,12-*Tetrahydro*-12-p-*tolylsulphonyldibenzo*[b,f][1,4]-*diazocin*-6-*one* (IIa).—(*a*) The amino-ester (Ib) (25 g), 50% sodium hydride in oil (3·12 g), and dry dioxan (250 ml) were heated together under reflux for 4 h. The solution was poured into water (2·5 l) and the precipitate was crystallised from n-butanol to give the *dibenzodiazocine* (16·3 g, 73%) as needles, m.p. 200—201° (Found: C, 66·5; H, 4·8; N, 7·6. $C_{21}H_{18}N_2O_3S$ requires C, 66·6; H, 4·8; N, 7·4%), $\nu_{max.}$ 3160 (NH), 1645 (C=O), and 1340 and 1155 (S=O) cm^{-1}.

(*b*) The amino-acid (Id) (2 g) was dissolved in dry tetrahydrofuran (5 ml), ethyl 2-ethoxy-1,2-dihydroquinoline-1-carboxylate (1·37 g) was added, and the mixture was stirred at room temperature for 24 h. The solvent was removed under reduced pressure and the residue was crystallised from n-butanol to yield the dibenzodiazocine (1·23 g, 64%), m.p. and mixed m.p. 200—201°.

This cyclisation was also effected in 40% yield with *NN'*-dicyclohexylcarbodi-imide in dry ethyl acetate.

N-*Methyl*-N'-p-*tolylsulphonyl*-o-*phenylenediamine*.— *N*-Methyl-*o*-phenylenediamine (61 g) was dissolved in dry

[12] Ger.P. 1,078,132/1960.

[13] K. H. Wunsch, H. Dettman, and S. Schonberg, *Chem. Ber.*, 1969, **102**, 3891.

pyridine (175 ml), and a solution of toluene-*p*-sulphonyl chloride (96 g) in dry pyridine (200 ml) was added slowly with stirring, the temperature of the mixture being kept below 60°. After 3 h the product was poured into water (1·2 l) and sodium hydroxide solution (5N; 260 ml) was added. The mixture was extracted with benzene (2 × 500 ml), and the aqueous layer was heated to boiling, charcoaled, and filtered. The solution was then acidified with hydrochloric acid, and again boiled, charcoaled, and filtered. To the cooled filtrate was added, with stirring, 5% sodium hydroxide solution until no further precipitation was apparent. Crystallisation of the product from benzene–light petroleum (b.p. 60—80°) gave N-*methyl*-N′-p-*tolylsulphonyl*-o-*phenylenediamine* (70 g, 51%) as needles, m.p. 117—118° (Found: C, 60·9; H, 5·8; N, 10·3. $C_{14}H_{16}N_2O_2S$ requires C, 60·85; H, 5·85; N, 10·15%), $\nu_{max.}$ 3440 (NH), 3370 (NH), and 1330 and 1155 (S=O) cm^{-1}.

5,6,11,12-*Tetrahydro*-5-*methyl*-12-p-*tolylsulphonyldibenzo*[b,f][1,4]*diazocin*-6-*one* (IIb).—(*a*) The dibenzodiazocine (IIa) (0·5 g) and 50% sodium hydride in oil (0·07 g) were heated under reflux in dry dioxan (5 ml) for 1 h. Methyl iodide (0·23 g) in dry benzene (1 ml) was added, and the mixture was refluxed for 1 h, and filtered hot. On cooling, the filtrate deposited a solid which, on crystallisation from 2-ethoxyethanol, afforded the 5-*methyldibenzodiazocine* (0·47 g, 91%) as prisms, m.p. 243—244° (Found: C, 67·1; H, 5·3; N, 7·4. $C_{22}H_{20}N_2O_3S$ requires C, 67·3; H, 5·15; N, 7·15%), $\nu_{max.}$ 1645 (C=O), and 1355 and 1165 (S=O) cm^{-1}.

(*b*) *N*-Methyl-*N*′-*p*-tolylsulphonyl-*o*-phenylenediamine (5 g) was dissolved in water (60 ml) containing potassium hydroxide (2·25 g). 2-(Bromomethyl)benzoyl bromide [14] (5 g) in benzene (20 ml) was added, and the mixture was stirred at room temperature for 1 h, and then heated under reflux for 8 h. The mixture was cooled, and the solid was collected and crystallised from 2-ethoxyethanol to yield the 5-methyldibenzodiazocine (5·03 g, 71%), m.p. and mixed m.p. 243—244°.

5-(3-*Dimethylaminopropyl*)-5,6,11,12-*tetrahydro*-12-p-*tolylsulphonyldibenzo*[b,f][1,4]*diazocin*-6-*one* (IId).—The dibenzodiazocine (IIa) (10 g), 50% sodium hydride in oil (1·4 g), and dry dioxan (100 ml) were heated under reflux for 1 h. 3-Dimethylaminopropyl chloride (4 g) in dry benzene (10 ml) was added and the mixture was heated under reflux for 16 h. The solvent was removed under reduced pressure and the residue was shaken with water (200 ml) and benzene (200 ml). The aqueous layer was extracted with benzene (2 × 200 ml) and the combined organic extracts were dried ($MgSO_4$) and the solvent removed. Crystallisation of the residue from benzene–cyclohexane gave the 5-(3-*dimethylaminopropyl*)*dibenzodiazocine* (7·92 g, 65%) as prisms, m.p. 140° (Found: C, 67·45; H, 6·3; N, 8·95. $C_{26}H_{29}N_3O_3S$ requires C, 67·35; H, 6·3; N, 9·05%), $\nu_{max.}$ 1660 (C=O), and 1360 and 1165 (S=O) cm^{-1}.

5-(2-*Dimethylaminoethyl*)-5,6,11,12-*tetrahydro*-12-p-*tolylsulphonyldibenzo*[b,f][1,4]*diazocin*-6-*one* (IIc) (74%) was prepared as above, using 2-dimethylaminoethyl chloride, and was obtained as prisms from benzene–cyclohexane, m.p. 159—160° (Found: C, 67·05; H, 6·25; N, 9·3. $C_{25}H_{27}N_3O_3S$ requires C, 66·75; H, 6·05; N, 9·35%), $\nu_{max.}$ 1650 (C=O), and 1355 and 1160 (S=O) cm^{-1}.

Hydrolysis of the Diazocines (IIa, b, *and* d).—A solution of the 12-*p*-tolylsulphonyldibenzodiazocine in sulphuric acid monohydrate (5 g per g of diazocine) was allowed to stand at room temperature for 7 days. The solution was poured onto crushed ice and made alkaline with 5N-sodium hydroxide solution, and the product was worked up as described below.

(*a*) 2-(2-*Aminophenyl*)*phthalimidine* (VIa). The dibenzodiazocine (IIa) gave a solid which, on crystallisation from ethyl acetate, gave 2-(2-*aminophenyl*)*phthalimidine* (71%) as plates, m.p. 159—160° (Found: C, 74·85; H, 5·3; N, 12·35. $C_{14}H_{12}N_2O$ requires C, 75·0; H, 5·4; N, 12·5%), $\lambda_{max.}$ 232, 272, 279, and 298 nm (log ε 4·35, 3·67, 3·67, and 3·69), $\nu_{max.}$ 3450, 3340 and 3220 (NH_2), and 1670 (C=O) cm^{-1}, τ 1·93—3·29 (8H, m, aromatic), 5·19 (2H, s, CH_2), and 5·97—6·32 (2H, exchangeable, s, NH_2).

(*b*) 2-(2-*Methylaminophenyl*)*phthalimidine* (VIb). The 5-methyldibenzodiazocine (IIb) yielded a solid which, on crystallisation from carbon tetrachloride, gave 2-(2-methylaminophenyl)phthalimidine (86%) as plates, m.p. 169—170°, identical to an authentic sample.[4] The compound had $\lambda_{max.}$ 241, 279, and 307 nm (log ε 4·24, 3·47, and 3·56), $\nu_{max.}$ 3280 (NH) and 1665 (C=O) cm^{-1}, τ 2·02—3·39 (8H, m, aromatic), 5·31 (2H, s, CH_2), 5·7—6·3 (1H, exchangeable, s, NH), and 7·24 (3H, s, Me).

(*c*) 2-[2-(3-*Dimethylaminopropylamino*)*phenyl*]*phthalimidine* (VId). The 5-(3-dimethylaminopropyl)dibenzodiazocine (IId) gave an oil which was taken up in ether. The solution was dried ($MgSO_4$), and the solvent was removed. Crystallisation of the residue from cyclohexane gave 2-[2-(3-*dimethylaminopropylamino*)*phenyl*]*phthalimidine* (43%) as prisms, m.p. 91° (Found: C, 73·75; H, 7·35; N, 13·4. $C_{19}H_{23}N_3O$ requires C, 73·75; H, 7·5; N, 13·6%), $\nu_{max.}$ 3250 (NH) and 1695 (C=O) cm^{-1}.

Hydrolysis of 5-(2-*Dimethylaminoethyl*)-5,6,11,12-*tetrahydro*-12-p-*tolylsulphonyldibenzo*[b,f][1,4]*diazocin*-6-*one*.—2-[2-(2-*Dimethylaminoethylamino*)*phenyl*]*phthalimidine* (VIc). A solution of the 5-(2-dimethylaminoethyl)dibenzodiazocine (IIc) (4 g) in sulphuric acid monohydrate (20 g) was heated at 60° for 7 days. The mixture was poured onto crushed ice, and made alkaline with 5N-sodium hydroxide solution. The product was taken up in ether, the solution was dried ($MgSO_4$), and the solvent was removed. Crystallisation of the residue from benzene–light petroleum (b.p. 60—80°) gave 2-[2-(2-*dimethylaminoethylamino*)*phenyl*]*phthalimidine* (1·45 g, 55%) as needles, m.p. 80—81° (Found: C, 73·25; H, 7·05; N, 14·0. $C_{18}H_{21}N_3O$ requires C, 73·2; H, 7·2; N, 14·2%), $\nu_{max.}$ 3380 (NH) and 1690 (C=O) cm^{-1}.

2-[2-(N-*Methyl*-N-p-*tolylsulphonylamino*)*phenyl*]*phthalimidine* (VII).—Treatment of 2-(2-methylaminophenyl)-phthalimidine with toluene-*p*-sulphonyl chloride gave the p-*tolylsulphonyl derivative* (69%) as needles, m.p. 196° (from n-butanol) (Found: C, 67·4; H, 5·15; N, 7·15. $C_{22}H_{20}N_2O_3S$ requires C, 67·3; H, 5·15; N, 7·15%), $\lambda_{max.}$ 224 nm (log ε 4·21), $\nu_{max.}$ 1690 (C=O), and 1345 and 1150 (S=O) cm^{-1}.

Reactions of 5,6,11,12-*Tetrahydro*-12-p-*tolylsulphonyldibenzo*[b,f][1,4]*diazocin*-6-*ones with Phenyl-lithium*.—2-(2-*Methylaminophenyl*)-3-*phenylphthalimidine* (XIII).— The 5-Methyl-12-*p*-tolylsulphonyldibenzodiazocine (IIb) (5 g) in dry tetrahydrofuran (125 ml) was stirred under nitrogen, and 2M-phenyl-lithium solution (25·5 ml) was added. The mixture was stirred at room temperature for 3 days. The excess of phenyl-lithium was decomposed with ethanol (5 ml), the solvent was removed under reduced pressure, and the residue was extracted with hot benzene. The cooled extract was dried ($MgSO_4$) and evaporated to dryness. Trituration of the residual oil with ether gave a solid which, on crystallisation from benzene–cyclohexane, gave 2-(2-

[14] W. Davies and W. H. Perkin, *J. Chem. Soc.*, 1922, 2207.

methylaminophenyl)-3-*phenylphthalimidine* (1·87 g, 47%) as prisms, m.p. 165° (Found: C, 80·25; H, 5·8; N, 8·8. $C_{21}H_{18}N_2O$ requires C, 80·2; H, 5·8; N, 8·9%), $\lambda_{max.}$ 230 and 241 nm (log ε 4·31 and 4·30), $\nu_{max.}$ 3410 (NH) and 1670 (C=O) cm^{-1}, τ 1·82—3·55 (13H, m, aromatic), 4·04 (1H, s, CH), 5·6—6·2 (1H, exchangeable, s, NH), and 7·31 (3H, s, Me).

Similar treatment of 5,6,11,12-tetrahydro-12-*p*-tolylsulphonyldibenzo[*b,f*][1,4]diazocin-6-one (IIa), and of the dimethylaminoethyl and dimethylaminopropyl derivatives (IIc and d) with phenyl-lithium gave products which could not be purified.

N-*Methyl*-N-p-*tolylsulphonyl*-o-*phenylenediamine*.— *N*-Methyl-*N*-*p*-tolylsulphonyl-2-nitroaniline (40 g) was reduced with hydrogen over 10% palladium–charcoal (4 g) in methanol (100 ml) and dimethylformamide (100 ml) at 5 atm. for 3 h. Crystallisation of the product from ethanol gave N-*methyl*-N-p-*tolylsulphonyl*-o-*phenylenediamine* (29·3 g, 81%), as needles, m.p. 104—105° (Found: C, 60·85; H, 5·85; N, 10·15. $C_{14}H_{16}N_2O_2S$ requires C, 61·1; H, 5·55; N, 10·15%), $\nu_{max.}$ 3520, 3430, and 3360 (NH_2), and 1340 and 1150 (S=O) cm^{-1}.

Attempted Synthesis of 2-[2-(N-*Methyl*-N-p-*tolylsulphonylamino*)*phenyl*]-3-*phenylphthalimidine*.— 2-Benzoylbenzoic acid (0·57 g, 1 mol. equiv.) was heated with *N*-methyl-*N*-*p*-tolylsulphonyl-*o*-phenylenediamine (2·07 g, 3 mol. equiv.) at 180° for 8 h. Trituration of the cooled mixture with ethanol afforded the unchanged phenylenediamine (1·9 g), m.p. and mixed m.p. 103—105°.

Reduction of the Diazocines (IIa—d).—A solution of the dibenzodiazocine (5 g) in dry tetrahydrofuran (250 ml) was added slowly to a stirred suspension of lithium aluminium hydride (1·5 g) in tetrahydrofuran (50 ml) under nitrogen. The mixture was heated under reflux for 12 h. To the reaction mixture was added, with cooling, water (2·5 ml), sodium hydroxide solution (10%; 2·5 ml), and water (7·5 ml). The mixture was filtered, and the collected solid was extracted with boiling ether (100 ml). The combined ethereal solutions were dried ($MgSO_4$), and the solvent was removed. The residue was treated as described below.

(*a*) 5,6,11,12-*Tetrahydro*-5-p-*tolylsulphonyldibenzo*[b,f][1,4]*diazocine* (XIVa). (i) The product obtained on reduction of the dibenzodiazocine (IIa) crystallised from ethanol to give the 5-p-*tolylsulphonyldibenzodiazocine* (42%) as prisms, m.p. 169—170° (Found: C, 69·2; H, 5·45; N, 7·8. $C_{21}H_{20}N_2O_2S$ requires C, 69·2; H, 5·55; N, 7·7%), $\nu_{max.}$ 3370 (NH), and 1350 and 1160 (S=O) cm^{-1}. (ii) Treatment of 5,6,11,12-tetrahydrodibenzo[*b,f*][1,4]diazocine [1] with toluene-*p*-sulphonyl chloride (1 mol. equiv.) gave the same compound (56%), m.p. and mixed m.p. 169—170°.

(*b*) 5,6,11,12-*Tetrahydro*-5-*methyl*-12-p-*tolylsulphonyldibenzo*[b,f][1,4]*diazocine* (XIVb). The product obtained on reduction of the dibenzodiazocine (IIb) was triturated with methanol, and the resulting solid was crystallised from carbon tetrachloride to yield the 5-*methyl*-12-p-*tolylsulphonyldibenzodiazocine* (54%) as prisms, m.p. 130—131° (Found: C, 70·05; H, 5·8; N, 7·4%; M^+, 378·1400. $C_{22}H_{22}N_2O_2S$ requires C, 69·8; H, 5·85; N, 7·4%; *M*, 378·1402), $\nu_{max.}$ 1345 and 1155 (S=O) cm^{-1}, τ 2·50—3·30 (12H, m, aromatics), 5·06 (2H, s, CH_2), 5·97 (2H, s, CH_2), 7·24 (3H, s, NMe), and 7·65 (3H, s, CMe), *m/e* 378 (M^+, 7%), 224(76), 223(100), 207(48), 105(43), 91(29), 77(27), and 65(20).

(*c*) N-(2-*Dimethylaminoethyl*)-N′-(2-*hydroxymethylbenzyl*)-o-*phenylenediamine* (XV). The product obtained on reduction of the dibenzodiazocine (IIc) crystallised from carbon tetrachloride to give the *substituted* o-*phenylenediamine* (70%) as prisms, m.p. 129—130° (Found: C, 71·8; H, 8·15; N, 13·75%; M^+, 299·2004. $C_{18}H_{25}N_3O$ requires C, 72·2; H, 8·45; N, 14·05%); *M*, 299·1998), $\nu_{max.}$ 3400 (NH) and 3400—2400 (bonded OH and NH) cm^{-1}, τ 2·69 (4H, s, C–C_6H_4–C), 3·22 (4H, s, N–C_6H_4–N), 5·37 (2H, s, CH_2OH), 5·73 (2H, s, CH_2N), 5·88 (3H, exchangeable, s, OH and 2 × NH), 6·91 and 7·04 (4H, 2t, *J* 9 Hz, $NCH_2{\cdot}CH_2N$), and 7·85 (6H, s, NMe_2).

(*d*) Reduction of the dimethylaminopropyldibenzodiazocine (IId) gave no identifiable product.

5,6,11,12-*Tetrahydrodibenzo*[b,f][1,4]*diazocine* (XIVc).— The 5-*p*-tolylsulphonyldibenzo[*b,f*][1,4]diazocine (XIVa) (1 g) and 90% (v/v) sulphuric acid (10 ml) were heated together on a steam-bath for 3 h. The reaction mixture was poured onto crushed ice and made alkaline with 5N-sodium hydroxide solution. Crystallisation of the precipitate from toluene gave 5,6,11,12-tetrahydrodibenzo[*b,f*][1,4]diazocine (0·36 g, 62%) as prisms, m.p. and mixed m.p. 190—192°.

5,6,11,12-*Tetrahydro*-5-*methyldibenzo*[b,f][1,4]*diazocine* (XIVd).—The 5-methyl-12-*p*-tolylsulphonyldibenzodiazocine (XIVb) was treated with 90% (v/v) sulphuric acid as described above. The product crystallised from light petroleum (b.p. 60—80°) to give the 5-*methyldibenzodiazocine* (75%) as needles, m.p. 84° (Found: C, 80·55; H, 7·05; N, 12·25%; M^+, 224·1309. $C_{15}H_{16}N_2$ requires C, 80·3; H, 7·2; N, 12·5%; *M*, 224·1313), $\lambda_{max.}$ 228, 268, and 307 nm (log ε 4·51, 3·82, and 3·74), $\nu_{max.}$ 3340 (NH) cm^{-1}, τ 2·73—3·50 (8H, m, aromatic), 5·53 (2H, s, CH_2), 5·66 (2H, s, CH_2), 6·1—6·7 (1H, exchangeable, s, NH), and 7·18 (3H, s, Me).

The acetyl derivative (XIVe) (83%), prepared by heating the base (XIVd) under reflux with acetic anhydride, crystallised from benzene–light petroleum (b.p. 60—80°) as prisms, m.p. 109°.

The *N*-nitroso-derivative (XIVf) was prepared by addition of sodium nitrite (0·2 g) in water (7·5 ml) dropwise at 0° to a solution of the base (XIVd) (0·5 g) in 10N-hydrochloric acid (1 ml). After 15 min, the precipitate was collected and crystallised from ethanol to give the *N*-nitroso-derivative (0·46 g, 82%) as pale yellow plates, m.p. 146°.

No reaction occurred when the 5-methyldibenzodiazocine (XIVd) was treated with alkyl halides in dioxan or xylene in the presence of sodium hydride or sodamide.

Bis-(5,6,11,12-*tetrahydro*-12-*methyldibenzo*[b,f][1,4]*diazocin*-5-*yl*)*methane* (XVII).—(*a*) Treatment of the 5,12-*endo*-methanodibenzodiazocine (XVI; R = H) with dimethyl sulphate and alkali, as described in an earlier paper,[1] afforded the *bisdiazocinylmethane* (Found: M^+, 460·2628, $C_{31}H_{32}N_4$ requires *M*, 460·2627), τ 2·60—3·65 (16H, m, aromatic), 5·36 (2H, s, NCH_2N), 5·80 (4H, s, 2 × CH_2), 6·18 (4H, s, 2 × CH_2), and 7·25 (6H, s, 2 × Me).

This compound was originally [1] assigned the incorrect structure of 5,6,11,12-tetrahydro-5-methyldibenzo[*b,f*][1,4]-diazocine (XIVd). The analytical figures quoted [1] (C, 80·95; H, 6·8; N, 12·45%) are in accordance with the molecular formula $C_{31}H_{32}N_4$ (which requires C, 80·8; H, 7·0; N, 12·15%).

(*b*) The 5-methyldibenzodiazocine (XIVd) (0·224 g) and paraformaldehyde (0·12 g) were heated together under reflux in dry xylene (10 ml) for 16 h. The solvent was removed under reduced pressure, and the residue was crystallised from light petroleum (b.p. 100—120°) to give the bisdiazocinylmethane (0·02 g, 9%) as needles, m.p. and mixed m.p. 192—194°.

As previously described,[1] the bisdiazocinylmethane reacts with acetic anhydride and with nitrous acid to give the 12-acetyl- and 12-nitroso-5-methyldibenzodiazocines (XIVe and f). These compounds were identical to authentic samples prepared from the 5-methyldibenzodiazocine (XIVd).

When treated with toluene-*p*-sulphonyl chloride in pyridine, the bisdiazocinylmethane gave the 5-methyl-12-*p*-tolylsulphonyldibenzodiazocine (XIVb) (50%), identical to an authentic sample.

Reaction between N-*Methyl*-N′-p-*tolylsulphonyl*-o-*phenylenediamine and* αα′-*Dibromo*-o-*xylene*.—*N*-Methyl-*N*′-*p*-tolylsulphonyl-*o*-phenylenediamine (1·38 g, 1 mol. equiv.) was dissolved in water (15 ml) containing potassium hydroxide (0·84 g, 3 mol. equiv.). αα′-Dibromo-*o*-xylene (1·32 g, 1 mol. equiv.) in benzene (5 ml) was added and the mixture was stirred at room temperature for 1 h, and then heated under reflux for 8 h. The mixture was cooled and the precipitate was crystallised from dimethylformamide–ethanol to give N-[o-(N-*methylisoindolinio*)*phenyl*]*toluene*-p-*sulphonamidate* (XIX) (0·72 g, 38%) as prisms, m.p. 237° (decomp.) (Found: C, 69·9; H, 5·85; N, 7·55. $C_{22}H_{22}N_2O_2S$ requires C, 69·8; H, 5·85; N, 7·4%), $\nu_{max.}$ 1310 and 1130 (S=O) cm^{-1}, τ 2·20—3·08 (12H, m, aromatic), 4·60 (4H, AB q, 2 × CH_2), 6·44 (3H, s, $\overset{+}{N}$Me), and 7·82 (3H, s, CMe).

Treatment of the dipolar ion with hydrobromic acid gave N-*methyl*-N-[2-(p-*tolylsulphonylamino*)*phenyl*]*isoindolinium bromide* (XX), which crystallised from ethanol as prisms, m.p. 157—158° (Found: C, 57·8; H, 5·1; N, 6·3; Br, 16·8. $C_{22}H_{23}BrN_2O_2S$ requires C, 57·5; H, 5·05; N, 6·1; Br, 17·4%), $\nu_{max.}$ 3370 (NH), and 1340 and 1160 (S=O) cm^{-1}.

N-*Acetyl*-N′-*benzoyl*-N′-*methyl*-o-*phenylenediamine* (XXIa) was obtained by acetylation of *N*-benzoyl-*N*-methyl-*o*-phenylenediamine,[11] and crystallised from ethanol as needles (66%), m.p. 188° (Found: C, 71·65; H, 5·95; N, 10·45. $C_{16}H_{16}N_2O_2$ requires C, 71·6; H, 6·0; N, 10·45%).

NN′-*Dibenzoyl*-N-*methyl*-o-*phenylenediamine* (XXIb).—(*a*) Benzoylation of *N*-benzoyl-*N*-methyl-*o*-phenylenediamine gave prisms (66%), m.p. 141° (from benzene–cyclohexane) (Found: C, 76·0; H, 5·7; N, 8·65. $C_{21}H_{18}N_2O_2$ requires C, 76·35; H, 5·5; N, 8·5%).

(*b*) Benzoylation of *N*-methyl-*o*-phenylenediamine gave the same compound (40%), m.p. and mixed m.p. 141°.

N-*Methyl*-N-p-*toluoyl*-2-*nitroaniline*.— *N*-Methyl-2-nitroaniline (3·0 g) and *p*-toluoyl chloride (3·1 g) were warmed together on a steam-bath for 1 h. The product was crystallised from benzene–cyclohexane to give the *substituted* 2-*nitroaniline* (3·6 g, 68%) as yellow needles, m.p. 93—94° (Found: C, 66·55; H, 5·2; N, 10·25. $C_{15}H_{14}N_2O_3$ requires C, 66·65; H, 5·25; N, 10·35%), $\nu_{max.}$ 1645 (C=O), and 1530 and 1350 (NO_2) cm^{-1}.

N-*Methyl*-N-p-*toluoyl*-o-*phenylenediamine*.—*N*-Methyl-*N*-*p*-toluoyl-2-nitroaniline (3·0 g) was reduced with hydrogen over Raney nickel (3·0 g) in methanol at 1 atm. for 30 min. Crystallisation of the product from benzene gave the *amine* (2·2 g, 82%) as needles, m.p. 93° (Found: C, 75·0; H, 6·7; N, 11·4. $C_{15}H_{16}N_2O$ requires C, 75·0; H, 6·7; N, 11·65%), $\nu_{max.}$ 3400, 3420, and 3210 (NH_2) and 1620 (C=O) cm^{-1}.

N-*Benzoyl*-N′-*methyl*-N′-p-*toluoyl*-o-*phenylenediamine* (XXIV).—Benzoylation of *N*-methyl-*N*-*p*-toluoyl-*o*-phenylenediamine gave prisms (60%), m.p. 129° (benzene–cyclohexane) (Found: C, 76·9; H, 5·85; N, 7·95. $C_{22}H_{20}N_2O_2$ requires C, 76·7; H, 5·85; N, 8·15%), $\nu_{max.}$ 3220 (NH), 1680 (C=O), and 1630 (C=O) cm^{-1}.

Reactions of the Diamides (XXIa *and* b) *and* (XXIV) *with Polyphosphoric Acid*.—(*a*) *N*-Acetyl-*N*′-benzoyl-*N*′-methyl-*o*-phenylenediamine (XXIa) (0·25 g) and polyphosphoric acid (5 g) were heated together at 150° for 2 h. The mixture was poured onto crushed ice (20 g) and basified with concentrated ammonia solution. Crystallisation of the precipitate from cyclohexane gave 1-methyl-2-phenylbenzimidazole (0·18 g, 85%), m.p. 98°, identical to an authentic sample,[15] τ 2·05—2·85 (9H, m, aromatic), and 6·24 (3H, s, Me).

(*b*) *NN*′-Dibenzoyl-*N*-methyl-*o*-phenylenediamine (XXIb) similarly gave 1-methyl-2-phenylbenzimidazole (57%).

(*c*) *N*-Benzoyl-*N*′-methyl-*N*′-*p*-toluoyl-*o*-phenylenediamine (XXIV) (0·25 g) was treated similarly, and the product was taken up in ether. The ethereal solution was dried ($MgSO_4$) and evaporated to dryness, and the residue was taken up in acetone and subjected to preparative t.l.c. with ethyl acetate as solvent. Elution of the band (R_F 0·51) with acetone yielded a solid (0·055 g), τ 2·0—2·8 (m, aromatic), 6·19 (s, NMe), and 7·58 (s, CMe). The integrated peak heights at τ 6·19 (31·5 mm) and 7·58 (20·5 mm) showed that the mixture contained 1-methyl-2-phenylbenzimidazole and 1-methyl-2-*p*-tolylbenzimidazole in the ratio 1 : 1·9.

1-*Methyl*-2-p-*tolylbenzimidazole* (XXIIIb) (80%) was prepared by heating *N*-methyl-*N*-*p*-toluoyl-*o*-phenylenediamine in polyphosphoric acid as above, and crystallised from benzene–cyclohexane as plates, m.p. 117° (Found: C, 80·9; H, 6·3; N, 12·6. $C_{15}H_{14}N_2$ requires C, 81·0; H, 6·35; N, 12·6%), τ 2·0—2·94 (8H, m, aromatic), 6·33 (3H, s, NMe), and 7·64 (3H, s, CMe).

N-*Acetyl*-N′-*benzyl*-N′-*methyl*-o-*phenylenediamine* (XXIc).—Acetylation of *N*-benzyl-*N*-methyl-*o*-phenylenediamine [12] gave needles (73%), m.p. 56° [from light petroleum (b.p. 40—60°)] (Found: C, 75·2; H, 7·35; N, 11·3. $C_{16}H_{18}N_2O$ requires C, 75·6; H, 7·15; N, 11·05%), $\nu_{max.}$ 3240 (NH) and 1655 (C=O) cm^{-1}.

N-*Benzoyl*-N′-*benzyl*-N′-*methyl*-o-*phenylenediamine* (XXId).—Benzoylation of *N*-benzyl-*N*-methyl-*o*-phenylenediamine gave needles (60%), m.p. 72—73° (cyclohexane) (Found: C, 79·75; H, 6·6; N, 8·6. $C_{21}H_{20}N_2O$ requires C, 79·7; H, 6·4; N, 8·85%), $\nu_{max.}$ 3310 (NH) and 1645 (C=O) cm^{-1}.

Reaction of N-*Acyl*-N′-*benzyl*-N′-*methyl*-o-*phenylenediamines* (XXIc *and* d) *with Polyphosphoric Acid*.—(*a*) *N*-Acetyl-*N*′-benzyl-*N*′-methyl-*o*-phenylenediamine (XXIc) (0·5 g) and polyphosphoric acid (10 g) were heated together at 180° for 16 h. The mixture was poured onto crushed ice and basified with concentrated ammonia solution. Crystallisation of the precipitate from cyclohexane gave 1,2-dimethylbenzimidazole trihydrate (0·14 g, 29%), m.p. 64—65°, identical to an authentic sample,[16] $\nu_{max.}$ 3200br (bonded OH) cm^{-1}, τ 2·17—2·99 (4H, m, aromatic), 6·38 (3H, s, NMe), and 7·47 (3H, s, CMe).

No reaction occurred when the starting material was heated in polyphosphoric acid at 150° for 2 h.

(*b*) *N*-Benzoyl-*N*′-benzyl-*N*′-methyl-*o*-phenylenediamine (XXId) was treated as above. The product was taken up in ether, and the solution was dried ($MgSO_4$) and the solvent removed. The residue was dissolved in acetone (5 ml) and subjected to preparative t.l.c., with ethyl acetate–

[15] R. Weidenhagen, G. Train, H. Wegner, and L. Nordstrom, *Ber.*, 1942, **75**, 1936.
[16] M. A. Philips, *J. Chem. Soc.*, 1929, 2820.

benzene (1 : 1) as solvent. Elution of the band (R_F 0·51) with acetone gave 1-methyl-2-phenylbenzimidazole (0·18 g, 55%), m.p. 98° (cyclohexane), identical to an authentic sample,[15] with τ 2·06—2·75 (9H, m, aromatic), and 6·25 (3H, s, Me).

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