o-Nitroaniline Derivatives. Part III.[1] Cyclisation of *N*-*p*-Nitrobenzyl-*N*-*p*-tolylsulphonyl-*o*-nitroaniline by Sodium Methoxide: Formation of an *N*-Methoxybenzimidazole Derivative

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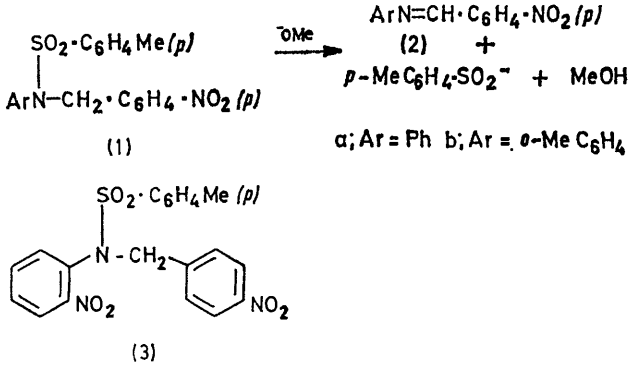
The reaction of the title sulphonamide with sodium methoxide gives a mixture of 1-hydroxy- and 1-methoxy-2-*p*-nitrophenylbenzimidazole, the latter apparently being formed by *in situ* methylation of the former. One step in the proposed mechanism involves the formation of methyl toluene-*p*-sulphonate: this compound is the most likely methylating agent in the reaction.

THE *N*-arylsulphonyl derivatives of secondary amines which possess an acidic hydrogen atom α to the nitrogen undergo elimination reactions when treated with base,[2,3] the products being azomethines and arenesulphinate ion. For example, *N*-*p*-nitrobenzyl-*N*-*p*-tolylsulphonylaniline (1a) gives *N*-*p*-nitrobenzylideneaniline (2a) by reaction with sodium methoxide in toluene.[2]

Our interest in the preparation and reactions of *ortho*-nitro-anils [1,4] led us to investigate the reaction of *N*-*p*-nitrobenzyl-*N*-*p*-tolylsulphonyl-*o*-nitroaniline (3) with sodium methoxide. Although in this case the elimination product, *N*-*p*-nitrobenzylidene-*o*-nitroaniline, would be highly reactive, it was expected that its *o*-nitroaniline adduct [4] or its methanol adduct † might be obtained. Since sodium methoxide in methanol was just as effective as, and more convenient than, sodium methoxide in toluene [2] for bringing about the elimination of toluene-*p*-sulphinic acid from compounds (1a and b),

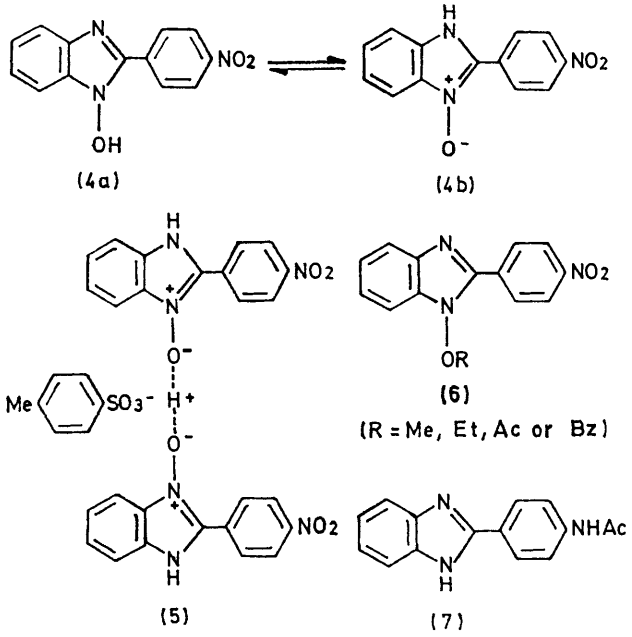


the reaction of *N*-*p*-nitrobenzyl-*N*-*p*-tolylsulphonyl-*o*-nitroaniline (3) with methanolic sodium methoxide solution was investigated.

† Addition of methanol to *N*-benzylidene-*o*-nitroaniline gives *o*-$O_2N{\cdot}C_6H_4{\cdot}NH{\cdot}CH(OMe)Ph$.[5]

[1] Part II, R. Marshall and D. M. Smith, *J. Chem. Soc.* (*C*), 1971, 3510.
[2] W. Paterson and G. R. Proctor, *J. Chem. Soc.*, 1965, 485.
[3] E. Negishi and A. R. Day, *J. Org. Chem.*, 1965, **30**, 43.
[4] R. Marshall, D. J. Sears, and D. M. Smith, *J. Chem. Soc.* (*C*), 1970, 2144.
[5] R. Marshall and D. M. Smith, unpublished work.

In this reaction, however, neither the product of elimination nor either of its adducts was obtained. The mixture of products was separated by partition between benzene and water: acidification of the aqueous layer with sulphuric acid gave 1-hydroxy-2-*p*-nitrophenylbenzimidazole (4a) [which is tautomeric with 2-*p*-nitrophenyl-1*H*-benzimidazole 3-oxide (4b)],[6] and evaporation of the benzene layer gave a non-acidic compound, $C_{14}H_{11}N_3O_3$.



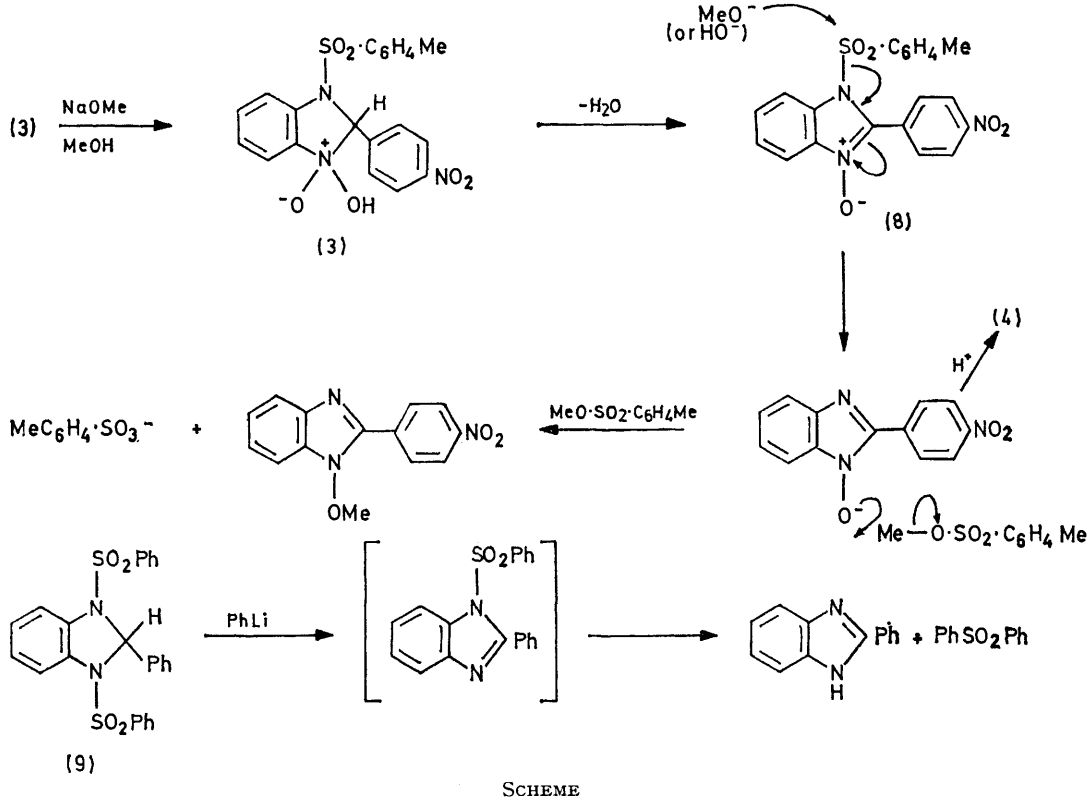
The position of the equilibrium (4a) ⇌ (4b) was not established, but the presence of the *N*-oxide tautomer (4b) under mass spectral conditions may be inferred from the high intensity of the $(M - 16)^+$ fragment ion [6,7] in the mass spectrum of (4). The *N*-oxide tautomer may also be involved in the formation of a 2 : 1 adduct with toluene-*p*-sulphonic acid; this was the major product isolated from the reaction of (3) with sodium methoxide when the aqueous layer was acidified with hydrochloric instead of sulphuric acid, and is possibly a basic salt (5) similar to those already observed in other series of *N*-oxides.[8] On the other hand, alkylation and acylation of (4) occurred on oxygen and gave derivatives of the *N*-hydroxy-tautomer (4a), *viz.* (6). The correctness of structures (6), as opposed to the alternative 1-alkyl- or 1-acyl-benzimidazole 3-oxide structures, is established not only by analogy with the corresponding reactions of benzimidazole *N*-oxide [9] and its 2-phenyl derivative,[10] but also, in the case of the alkyl derivatives, by the chemical shift of the alkyl protons and the absence of the $(M - 16)^+$ ion from the mass spectra, and in the case of the acyl derivatives by the exceptionally high frequency of the i.r. carbonyl absorption.[11]

Catalytic hydrogenolysis of the *O*-acetyl derivative (6; R = Ac) furnished conclusive proof of the structure (4) assigned to the acidic reaction product. Acetylation of the crude hydrogenolysis product gave 2-*p*-acetamidophenylbenzimidazole (7), identical with a specimen prepared from 2-*p*-nitrophenylbenzimidazole hydrochloride [12] by reduction followed by acetylation.

The non-acidic product, $C_{14}H_{11}N_3O_3$, obtained along with (4) from the reaction of the sulphonamide (3) with sodium methoxide, was identical with the product of methylation of (4), *i.e.* it was 1-methoxy-2-*p*-nitrophenylbenzimidazole (6; R = Me). Although the formation of a heterocyclic *N*-oxide or *N*-hydroxy-compound by base-induced cyclisation of an *ortho*-substituted nitrobenzene is not unexpected, especially if, as in (3), the *ortho*-substituent has a nucleophilic centre β to the ring,[13] the formation of an *N*-alkoxy-compound in such a reaction is entirely novel. We believe that it is produced in this case by *in situ* methylation of compound (4), and that methyl toluene-*p*-sulphonate, which may be generated as shown in the Scheme, is the effective methylating agent. The step in the Scheme which leads to methyl toluene-*p*-sulphonate, *viz.* nucleophilic displacement at the sulphur atom of the intermediate (8), is similar to that already proposed [3] to explain the formation of diphenyl sulphone in the reaction of phenyllithium with the disulphonamido-compound (9).

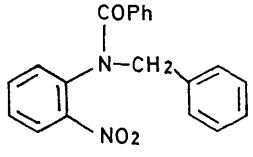
Evidence in support of the proposed mechanism is also provided by the following experimental observations. (i) Toluene-*p*-sulphonate ions were detected among the water-soluble reaction products. (ii) The *N*-methoxy-compound (6; R = Me) was the only product isolated when methyl toluene-*p*-sulphonate was added to the reaction mixture prior to work-up. (iii) When the reaction was carried out in the presence of 1 mol. equiv. of sodium 2-naphtholate, the naphtholate ion underwent methylation in preference to the anion of (4), and 2-methoxynaphthalene was formed instead of the *N*-methoxybenzimidazole. (iv) The use of an increased amount of sodium methoxide led to a marked decrease in the proportion of the methoxybenzimidazole produced. When equimolar amounts of sulphonamide and sodium methoxide were used, the yields of the hydroxy- and methoxy-benzimidazoles were 29 and 23%, respectively, whereas in the presence of an additional 1 equiv. of methoxide the corresponding yields were 38 and 10%. In the latter case the excess of methoxide would be expected to undergo methylation in competition with the anion of (4).

[6] Tautomerism of this type is discussed by S. O. Chua, M. J. Cook, and A. R. Katritzky, *J. Chem. Soc.* (*B*), 1971, 2350.
[7] A. Tatematsu, H. Yoshizumi, E. Hayashi, and H. Nakata, *Tetrahedron Letters*, 1967, 2985.
[8] See A. R. Katritzky and J. M. Lagowski, 'Chemistry of the Heterocyclic *N*-Oxides,' Academic Press, London and New York, 1971, p. 144.
[9] S. Takahashi and H. Kano, *Chem. and Pharm. Bull.* (*Japan*), 1963, **11**, 1375; 1964, **12**, 282.
[10] G. W. Stacy, B. V. Ettling, and A. J. Papa, *J. Org. Chem.*, 1964, **29**, 1537.
[11] *Cf.* ref. 10; also J. D. Loudon and I. Wellings, *J. Chem. Soc.*, 1960, 3462.
[12] R. Weidenhagen, *Ber.*, 1936, **69**, 2263.
[13] J. D. Loudon and G. Tennant, *Quart. Rev.*, 1964, **18**, 389; P. N. Preston and G. Tennant, *Chem. Rev.*, 1972, **72**, 627.



SCHEME

An alternative mechanism, in which detosylation of the sulphonamide precedes cyclisation, appears less likely, since *N*-benzyl- and *N*-methyl-*N*-*p*-tolylsulphonyl-*o*-nitroanilines, which lack the reactive methylene group of (3) but have a similarly situated *p*-tolylsulphonyl group, are completely unreactive towards sodium methoxide in methanol. On the other hand, preliminary experiments by Mr. G. A. Reed indicate that in the corresponding series of carboxamides, *e.g.* (10) and (11),



(10) R = H
(11) R = NO2

deacylation may indeed precede cyclisation. These and related reactions will be reported later.

EXPERIMENTAL

' Light petroleum ' refers to the fraction of b.p. 40—60°. I.r. spectra were obtained for Nujol mulls, and n.m.r. spectra were recorded with tetramethylsilane as internal reference.

N-*p*-Tolylsulphonylaniline, m.p. 98—100° (from methanol–water) (lit.,[14] 103°), *N*-*p*-tolylsulphonyl-*o*-toluidine, m.p. 105—107° (from methanol–water) (lit.,[14] 110°) and *N*-*p*-tolylsulphonyl-*o*-nitroaniline, m.p. 111—113° (from ethanol) (lit.,[15] 112—114°) were obtained from the appropriate amines and toluene-*p*-sulphonyl chloride in pyridine.

N-Benzyl-*N*-*p*-tolylsulphonyl-*o*-nitroaniline,[15] m.p. 175—176° (from benzene–light petroleum) (lit.,[15] 175—176°), and *N*-methyl-*N*-*p*-tolylsulphonyl-*o*-nitroaniline,[16] m.p. 133—134° (from methanol) (lit.,[16] 134°), were prepared by established methods. 2-*p*-Nitrophenylbenzimidazole was prepared from *o*-phenylenediamine, *p*-nitrobenzaldehyde, and copper(II) acetate [12] and was isolated as its hydrochloride, m.p. 294—299° (lit.,[12] 307°).

2-*Methoxynaphthalene*.—A solution of 2-naphthol (2·88 g) in methanol (20 ml) was added to a solution of sodium methoxide [from sodium (0·46 g)] in methanol (50 ml). After a few minutes a solution of methyl toluene-*p*-sulphonate (3·72 g) in methanol (10 ml) was added; the mixture was heated under reflux for 1 h, then evaporated *in vacuo*. The residue was washed with water and recrystallised from methanol to give 2-methoxynaphthalene (1·70 g, 54%), m.p. 71—73° (lit.,[17] 71°).

N-p-*Nitrobenzyl*-N-p-*tolylsulphonylaniline Derivatives* (with H. M. JONES).—The following procedure is typical. A solution of sodium ethoxide [from sodium (1·5 g)] in ethanol (30 ml) was added to a warm solution of *N*-*p*-tolylsulphonyl-*o*-nitroaniline (20·0 g) in ethanol (160 ml), and to the resulting red solution was added *p*-nitrobenzyl bromide (16·0 g; 10% excess). The mixture was heated under reflux for 30 min, then cooled to 0°; the crystalline product was filtered off and washed well with water. N-p-*Nitrobenzyl*-N-p-*tolylsulphonyl*-o-*nitroaniline* (3) (23·4 g, 80%) had m.p. 192—194° (from acetic acid) (Found: C, 56·1; H, 3·85; N, 9·5. $C_{20}H_{17}N_3O_6S$ requires C, 56·2; H, 4·0; N, 9·8%), $\nu_{max.}$ 1510 (NO_2), 1340br (NO_2 and SO_2), and 1160 (SO_2) cm^{-1},

[14] A. I. Vogel, ' Practical Organic Chemistry,' Longmans, London, 3rd edn., 1956, p. 656.
[15] J. L. Huppatz and W. H. F. Sasse, *Austral. J. Chem.*, 1963, **16**, 417.
[16] E. H. Usherwood and M. A. Whiteley, *J. Chem. Soc.*, 1923, **123**, 1085.
[17] G. S. Hiers and F. D. Hager, *Org. Synth.*, 1932, Coll. Vol. I, p. 51.

τ ($CDCl_3$) 1·8—3·2 (12H, m, aromatic), 5·12 (2H, s, $ArCH_2$·N), and 7·56 (3H, s, $ArCH_3$).

N-p-Nitrobenzyl-*N-p*-tolylsulphonylaniline (1a), m.p. 126—128° (from methanol) (lit.,[2] 122°), and N-p-*nitrobenzyl*-N-p-*tolylsulphonyl*-o-*toluidine* (1b), m.p. 155—157° (from acetic acid–ethanol) (Found: C, 63·4; H, 5·2. $C_{21}H_{20}N_2O_4S$ requires C, 63·6; H, 5·1%), were similarly prepared in yields of 78 and 72%, respectively.

Reactions of the Sulphonamides with Sodium Methoxide.—(i) N-p-*Nitrobenzyl*-N-p-*tolylsulphonylaniline* (1a) (*cf.* ref. 2). A solution of sodium methoxide [from sodium (0·13 g)] in methanol (13 ml) was added to a suspension of *N-p*-nitrobenzyl-*N-p*-tolylsulphonylaniline (1·91 g) in methanol (50 ml). The mixture was heated under reflux for 2 h, then evaporated *in vacuo*, and the residue was washed with water (to extract sodium toluene-*p*-sulphinate) and recrystallised from ethanol, giving *N-p*-nitrobenzylideneaniline (2a) (0·80 g, 71%), m.p. and mixed m.p. 88—89° (lit.,[2] 92°); τ (CCl_4) 1·53 (1H, s, CH=N) and 1·6—2·9 (9H, m, aromatic). Addition of sodium nitrite (0·35 g) to the water washings followed by acidification gave *NN*-bis-*p*-tolylsulphonylhydroxylamine (0·58 g, 68%), m.p. and mixed m.p. 115—119° (decomp.) (from methanol–water) (lit.,[18] 120—122°).

(ii) (with H. M. Jones) N-p-*Nitrobenzyl*-N-p-*tolylsulphonyl*-o-*toluidine* (1b). This was similarly converted, almost quantitatively, into *N-p*-nitrobenzylidene-*o*-toluidine (2b),[19] m.p. and mixed m.p. 84—86° (from methanol) (lit.,[19] 89°).

(iii) N-*Benzyl- and* N-*methyl*-N-p-*tolylsulphonyl*-o-*nitroaniline*. These compounds underwent no reaction when treated with sodium methoxide in methanol under conditions similar to the above.

(iv) N-p-*Nitrobenzyl*-N-p-*tolylsulphonyl*-o-*nitroaniline* (3). A solution of sodium methoxide [from sodium (0·23 g, 0·01 mol)] in methanol (25 ml) was added to a suspension of the sulphonamide (3) (4·27 g, 0·01 mol) in methanol (100 ml); the mixture was heated under reflux for 2 h, then evaporated *in vacuo*. The dark red residue was shaken with a mixture of equal volumes of benzene and water (*ca.* 100—150 ml of each).

The benzene layer was separated, washed with water, dried (Na_2SO_4), and evaporated, and the residue was extracted with methanol. The methanol-insoluble fraction (0·40 g) was identified (m.p. and mixed m.p.) as unchanged sulphonamide (3) (recovery 9%). The methanol-soluble product was purified with charcoal, recovered by re-evaporation, and recrystallised from propan-2-ol, giving 1-*methoxy*-2-p-*nitrophenylbenzimidazole* (6; R = Me) (0·63 g, 23%), identical (mixed m.p.; i.r. and n.m.r. spectra) with an authentic sample (see later).

The aqueous layer was acidified with dilute sulphuric acid, and the precipitated solid filtered off and recrystallised from dimethylformamide–water to give 1-*hydroxy*-2-p-*nitrophenylbenzimidazole* (4) (0·78 g, 29%), m.p. 243—246° (decomp.) [Found: C, 56·6; H, 3·7; N, 15·2%; *M*, 255. $C_{13}H_9N_3O_3,H_2O$ requires C, 57·1; H, 4·1; N, 15·4%; *M*(anhydrous), 255]; $\nu_{max.}$ 1515 and 1330 cm^{-1} (NO_2); τ [$(CD_3)_2SO$] *ca.* 1·50 and 1·60 (4H, AA'BB', *p*-$O_2N{\cdot}C_6H_4$) and 2·1—2·7 (4H, m, benzimidazole ring), *m/e* 255 (31%), 239 (100), 193 (70), and 150 (59).

(v) *Variations of procedure* (iv). (*a*) Acidification of the aqueous layer with hydrochloric acid instead of sulphuric acid gave compound (4) as its *toluene*-p-*sulphonic acid adduct* (5), m.p. 264—266° (decomp.) (from dimethylformamide–acetic acid) (Found: C, 57·7; H, 3·8; N, 12·25; S, 4·6. $C_{33}H_{26}N_6O_9S$ requires C, 58·05; H, 3·8; N, 12·3; S, 4·7%); $\nu_{max.}$ 1520, 1335 (NO_2), and 1170 (SO_2) cm^{-1}; τ [$(CD_3)_2SO$] 1·35br (2H, s, NH), 1·55 (8H, s, *p*-$O_2N{\cdot}C_6H_4$), 2·1—2·7 (10H, m, aromatic), 2·94 (2H, part of AA'BB' system, *o*- to Me), and 7·72 (3H, s, Me); *m/e* 255 (52%), 239 (100), 193 (63), 172 (14), and 150 (20).

(*b*) Repetition of procedure (iv) with 2 equiv. of sodium methoxide gave 1-hydroxy- and 1-methoxy-2-*p*-nitrophenylbenzimidazole in 38 and 10% yield, respectively.

(*c*) Repetition of procedure (iv) with 2 equiv. of sodium methoxide and 1 equiv. of sodium 2-naphtholate gave 1-hydroxy-2-*p*-nitrophenylbenzimidazole in 51% yield; chromatography of the non-acidic reaction products on silica gel and elution with benzene gave 2-methoxynaphthalene (11%), identical (mixed m.p.; i.r., n.m.r., and mass spectra) with an authentic sample. 1-Methoxy-2-*p*-nitrophenylbenzimidazole was not isolated, nor was it detected by t.l.c.

(*d*) Repetition of procedure (iv) with 2 equiv. of sodium methoxide, with the addition of 1 equiv. of methyl toluene-*p*-sulphonate to the mixture after 1 h, gave 1-methoxy-2-*p*-nitrophenylbenzimidazole (38%) as the only isolated product.

Identification of Toluene-p-*sulphonate Ions in Reaction* (iv) (*with Miss* E. A. Smith).—The aqueous filtrate, obtained in reaction (iv) by removal of 1-hydroxy-2-*p*-nitrophenylbenzimidazole, was carefully neutralised with sodium hydroxide, filtered again, and evaporated to dryness *in vacuo*. The finely ground residue was mixed with phosphorus pentachloride (3·5 g), and the mixture was heated at 150° for 30 min, cooled, and extracted with dry benzene. The extract was added slowly, with stirring, to aqueous ammonia (*d* 0·880): the organic layer was separated, dried (Na_2SO_4), and concentrated, giving toluene-*p*-sulphonamide (0·28 g), identical (mixed m.p.; i.r. and mass spectra) with an authentic sample.

1-*Methoxy*-2-p-*nitrophenylbenzimidazole* (6; R = Me) (*with Miss* E. A. Smith).—A suspension of 1-hydroxy-2-*p*-nitrophenylbenzimidazole (4) (1·0 g) in warm sodium hydroxide solution (2M; 10 ml) was treated, dropwise and with vigorous stirring, with a mixture of dimethyl sulphate (2 ml) and methanol (1 ml). After a few minutes, the semi-solid product was added to sodium hydroxide solution (2M; 20 ml) and water (20 ml). The mixture was stirred for 30 min, then filtered, and the residue was washed with water. 1-*Methoxy*-2-p-*nitrophenylbenzimidazole* (0·57 g, 54%) had m.p. 154—156° (from propan-2-ol) (Found: C, 62·0; H, 4·2; N, 15·4. $C_{14}H_{11}N_3O_3$ requires C, 62·4; H, 4·1; N, 15·6%); $\nu_{max.}$ 1510 and 1340 (NO_2) cm^{-1}; $\lambda_{max.}$ (EtOH) 240 and 339 nm (ε 11,720 and 17,140); τ ($CDCl_3$) 1·61 (4H, AA'BB' pattern, almost a singlet at 60 MHz, *p*-$O_2N{\cdot}C_6H_4$), 2·1—2·8 (4H, m, benzimidazole ring), and 5·98 (3H, s, OMe); *m/e* 269 (100%), 254 (4), 239 (15), 238 (36), 193 (7), 192 (14), and 150 (76).

The methoxy-compound (6; R = Me) was also obtained in 62% yield by the addition of compound (4) (1 mol. equiv.) to a solution of sodium hydroxide (2 mol. equiv.) in methanol and treatment of the resulting sodium salt with methyl toluene-*p*-sulphonate (2 mol. equiv.) at room temperature.

1-*Ethoxy*-2-p-*nitrophenylbenzimidazole* (6; R = Et), m.p. 107—109° (from ethanol), was similarly obtained (73% yield) from the hydroxy-compound (4) by treatment with diethyl sulphate and sodium hydroxide (Found: C, 63·5; H, 4·8; N, 15·05. $C_{15}H_{13}N_3O_3$ requires C, 63·6; H, 4·6;

[18] J. D. Loudon and D. M. Smith, *J. Chem. Soc.*, 1964, 2806; *cf.* E. von Meyer, *J. prakt. Chem.*, 1901, **63**, 167.

[19] A. Lowy and C. G. King, *J. Amer. Chem. Soc.*, 1921, **43**, 625.

N, 14·8%); τ ($CDCl_3$) 1·60 and 1·70 (4H, AA'BB' pattern, *p*-$O_2N{\cdot}C_6H_4$), 2·1—2·8 (4H, m, benzimidazole), 5·82 (2H, q, *J* 7 Hz, $O{\cdot}CH_2$), and 8·65 (3H, t, *J* 7 Hz, CH_3); *m/e* 283 (50%), 255 (5), 239 (7), 238 (17), 193 (7), 192 (10), 151 (15), and 150 (100%).

1-*Acetoxy*-2-p-*nitrophenylbenzimidazole* (6; R = Ac).—1-Hydroxy-2-*p*-nitrophenylbenzimidazole (4) (1·0 g) was heated with acetic anhydride (5 ml) for 15 min at 100°; the solution was then poured onto crushed ice. The *acetoxy-compound* (6; R = Ac) was filtered off and recrystallised from methanol (yield 0·77 g, 66%): it had m.p. 145—147° (Found: C, 60·25; H, 3·5; N, 14·3. $C_{15}H_{11}N_3O_4$ requires C, 60·6; H, 3·7; N, 14·1%); $\nu_{max.}$ 1800 cm^{-1} (C=O), $\lambda_{max.}$ (EtOH) 368 nm (ε 18,100), τ ($CDCl_3$) 1·65 and 1·83 (4H, AA'BB' pattern, *p*-$O_2N{\cdot}C_6H_4$), 2·0—2·8 (4H, m, benzimidazole ring), and 7·60 (3H, s, OAc).

1-*Benzoyloxy*-2-p-*nitrophenylbenzimidazole* (6; R = Bz).—A suspension of 1-hydroxy-2-*p*-nitrophenylbenzimidazole (0·2 g) in sodium hydroxide solution (2M; 4 ml) and dimethylformamide (2 ml) was shaken with benzoyl chloride (0·5 ml) until the orange-red colour of the solution had disappeared. The yellow solid was filtered off and recrystallised from dimethylformamide–ethanol, giving the *benzoyl compound* (6; R = Bz) (0·13 g, 46%), m.p. 204—205° (decomp.) (Found: C, 66·8; H, 3·7; N, 12·0. $C_{20}H_{13}N_3O_4$ requires C, 66·9; H, 3·65; N, 11·7%); $\nu_{max.}$ 1770 cm^{-1} (C=O).

2-p-*Acetamidophenylbenzimidazole* (7).—(*a*) A solution of 1-acetoxy-2-*p*-nitrophenylbenzimidazole (0·30 g) in ethanol (25 ml) was hydrogenated over 10% palladium–charcoal (0·20 g); uptake of hydrogen (4 mol. equiv.) was complete in 1·5 h. The catalyst was filtered off and the solution evaporated, giving a gum: this was dissolved in aqueous ethanol and shaken with acetic anhydride to give the acetamido-compound (7).

(*b*) 2-*p*-Nitrophenylbenzimidazole hydrochloride [12] (0·27 g), dissolved in ethanol (25 ml), was hydrogenated over 10% palladium–charcoal (0·20 g); uptake of hydrogen (3 mol. equiv.) was complete in 1 h. Removal of the catalyst and the solvent left a solid (presumably 2-*p*-aminophenylbenzimidazole hydrochloride) which was acetylated, in aqueous ethanolic solution, by shaking with acetic anhydride. Basification of this solution with dilute potassium hydroxide solution gave the acetamido-compound (7), identical with the product from (*a*).

2-p-*Acetamidophenylbenzimidazole* had m.p. 313—314° (decomp.) (from ethanol) (Found: C, 68·4; H, 6·5; N, 14·2. $C_{15}H_{13}N_3O,C_2H_5OH$ requires C, 68·7; H, 6·4; N, 14·1%); $\nu_{max.}$ *ca.* 3000br (NH + solvent) and 1670 (C=O) cm^{-1}, τ [$(CD_3)_2SO$] — 0·28br (1H, s, NH), 1·7—3·0 (8H, m, aromatic), and 7·89 (3H, s, Ac); *m/e* 251 (50%), 210 (17), 209 (100),* 208 (14), 182 (7), 181 (8), 118 (8), and 43 (28).

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* The $(M - 42)^+$ ion also gives rise to the base peak in the mass spectrum of acetanilide.[20]

[20] J. L. Cotter, *J. Chem. Soc.*, 1964, 5477.