Cyclisation of *ortho*-Substituted *N*-Arylbenzimidoyl Nitrenes. Part 2.[1] Preferential Cyclisations at an *ortho*-Position Bearing a Methoxycarbonyl Group

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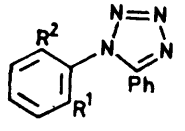
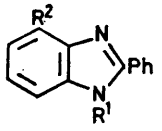
The 1-aryl-5-phenyltetrazoles (1), in which the 1-aryl group bears an *ortho*-methoxycarbonyl, nitro-, carboxamido-, or cyano-group, have been prepared and photolysed. The products are 2-phenylbenzimidazoles (2), which, it is suggested, result from two types of ring-closure of the intermediate benzimidoyl nitrenes : cyclisation at the free *ortho*-position, or cyclisation at the blocked *ortho*-position, followed by migration of the substituent from carbon to nitrogen. When the *ortho*-substituent is a methoxycarbonyl group, the second type of process competes effectively with the first.

A minor product of the photolysis of these tetrazoles in acetonitrile is the corresponding 1-aryl-5-methyltetrazole (3) in which a mole of the solvent has been incorporated.

In the preceding paper[1] we described the reaction products derived from *N*-arylbenzimidoyl nitrenes in which the *ortho*-positions of the aryl group are blocked by alkyl substituents. We suggested that 3a*H*-



(1)



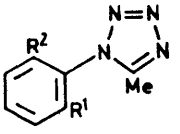
(2)

a; $R^1 = CO_2H$, $R^2 = Me$
b; $R^1 = CO_2Me$, $R^2 = Me$
c; $R^1 = CO_2H$, $R^2 = H$
d; $R^1 = CO_2Me$, $R^2 = H$
e; $R^1 = NO_2$; $R^2 = H$
f; $R^1 = CONH_2$, $R^2 = H$
g; $R^1 = CO\cdot N\cdot[CH_2]_3\cdot CH_2$, $R^2 = H$
h; $R^1 = CN$, $R^2 = H$

a; $R^1 = CO_2Me$, $R^2 = Me$
b; $R^1 = H$, $R^2 = Me$
c; $R^1 = CO_2Me$, $R^2 = H$
d; $R^1 = R^2 = H$
e; $R^1 = H$, $R^2 = CO_2Me$
f; $R^1 = H$, $R^2 = NO_2$
g; $R^1 = H$, $R^2 = CONH_2$
h; $R^1 = H$, $R^2 = CO\cdot N\cdot[CH_2]_3\cdot CH_2$
j; $R^1 = H$, $R^2 = CN$

benzimidazoles are the key intermediates in these reactions, the products being derived from these intermediates by way of sigmatropic skeletal migrations or, at high temperatures, sigmatropic alkyl shifts. In order to test this hypothesis further, we set out to investigate compounds in which the *ortho*-substituent was one which would migrate much more readily than do alkyl groups. The compound chosen for the preliminary investigation was the tetrazole ester (1b). Since this tetrazole bears two quite different *ortho*-substituents, its decomposition products were also expected to show whether there was any preference in the direction of cyclisation of the nitrene. If the nitrene were to cyclise at the carbon bearing the methoxycarbonyl group, it was predictable that this group would migrate: alkoxycarbonyl groups are known to undergo sigmatropic shifts very readily.[2,3]

The tetrazoles used in our earlier study[1] were all prepared by a standard route which involves the conversion of the appropriate aniline into its benzoyl derivative, the reaction of this amide with phosphorus pentachloride to give the imidoyl chloride, and then reaction with sodium azide. This route is inappropriate for the preparation of the tetrazole (1b) and similar compounds because the *ortho*-methoxycarbonyl group is nucleophilic and interferes in the preparation of the imidoyl chloride. A modification was therefore adopted (Scheme 1) in which the amide was converted into the tetrazole acid (1a) *via* an intermediate benzoxazinone, the ester being prepared from the acid by its reaction with diazomethane.



(3)

a; $R^1 = CO_2Me$, $R^2 = Me$
b; $R^1 = CO_2Me$, $R^2 = H$
c; $R^1 = CONH_2$, $R^2 = H$
d; $R^1 = CO\cdot N\cdot[CH_2]_3\cdot CH_2$, $R^2 = H$
e; $R^1 = CN$, $R^2 = H$

The tetrazole ester (1b) was photolysed in acetonitrile as solvent and the products were isolated in moderate yield. Two of these were identified as benzimidazoles, the structures (2a) and (2b) being assigned to them by comparison with independently synthesised specimens. The ester (2a) has not previously been reported: a specimen was prepared by the reaction of 4-methyl-2-phenylbenzimidazole (2b) with methyl chloroformate. It was also shown that the ester (2a) could be converted into compound (2b) during the chromatographic work-up of the photolysis products; hence it is likely that (2a) is the primary product, and (2b) is derived from it. The third product, which was obtained in 10% yield, was identified as the 5-methyltetrazole (3a), the structure being established by comparison of the product with an authentic sample prepared by a route analogous to that of Scheme 1.

The origin of the tetrazole (3a), in which a mole of the solvent, acetonitrile, has been incorporated, is under in-

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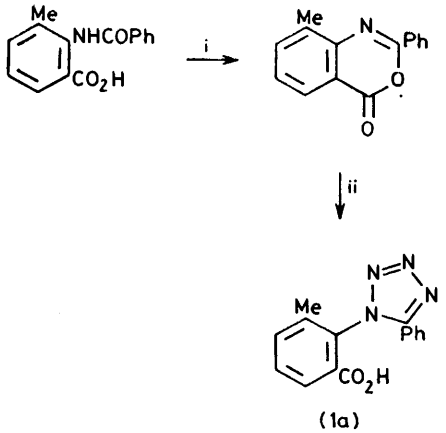
vestigation. The benzimidazole (2a) is most simply accounted for by postulating that the nitrene closes on to the carbon bearing the methoxycarbonyl group, and that this group then migrates, by a [1,5]sigmatropic shift, to the adjacent nitrogen atom (Scheme 2). It has been noted before that alkoxycarbonyl groups, and other groups which migrate easily, tend to move to an adjacent nitrogen rather than to an adjacent carbon atom.[3]



(1a)

SCHEME 1 Reagents: i, Ac_2O, heat; ii, NaN_3 in dimethylformamide, heat

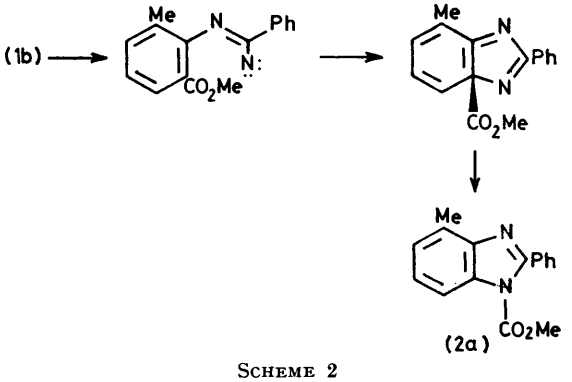
Surprisingly, no products were detected which could have come from closure of the nitrene on to the methyl-bearing carbon atom. This encouraged us to investigate the analogous photolysis of the tetrazole (1d), in which only one of the *ortho*-positions of the aryl group is blocked, in the hope that the tendency of the nitrene to close on to the carbon atom bearing the alkoxycarbonyl group would still be maintained in competition with closure at the unblocked position. The ester (1d) was prepared, by a route analogous to that of Scheme 1, *via* the acid (1c). Photolysis of the ester gave a mixture from which four compounds were isolated in high yield (85%). Three of the products were benzimidazoles: the methyl esters (2c) (29%) and (2e) (41%), and 2-phenylbenzimidazole (2d) (10%).* The fourth product was identified as the 5-methyltetrazole (3b) by comparison with an independently synthesised specimen.

The ester (2c), which was also identified by independent synthesis, was shown to give 2-phenylbenzimidazole in the conditions required for work-up of the reaction products, so the latter is probably an artefact. The esters (2c) and (2e) were also irradiated independently in control experiments designed to establish whether they could be interconverted. The 4-methoxycarbonyl compound (2e) was recovered after irradiation, but the 1-methoxycarbonyl compound (2c) did give some of the ester (2e) (17%) when subjected to the conditions of the original photolysis. A similar migration of an alkoxycarbonyl group from nitrogen to carbon has previously been observed in the photolysis of ethyl indole-1-carboxylate.[4]

There are, therefore, two independent and competing processes in the photolysis of the tetrazole (1d) which lead respectively to the benzimidazoles (2c) and (2e). The first appears to involve closure at the *ortho*-blocked position and subsequent migration of the methoxycarbonyl group, in a sequence analogous to that of Scheme 2; the other, to involve closure at the unblocked position and subsequent hydrogen shift. Assuming that all the 2-phenylbenzimidazole comes from the ester (2c) during the work-up and that some of the ester (2e) could have come by photoinduced rearrangement of (2c), the two processes are occurring to an approximately equal extent: that is, the nitrene does not discriminate between an *ortho*-position occupied by a hydrogen atom or by a methoxycarbonyl group. On the other hand, we had previously found that with one *ortho*-methyl or chloro-substituent, cyclisation occurred exclusively at the unblocked position.[5]

In order to establish whether this directing effect of the methoxycarbonyl group applied to other substituents as well, we prepared other tetrazoles (1e)—(1h) with one *ortho*-substituent in the *N*-aryl ring. The nitro-derivative (3e) was prepared from 2-nitroaniline by the route we used in the earlier work,[1] and the amides (1f) and (1g) and the nitrile (1h) were derived from the acid (1c) by standard transformations. This selection of *ortho*-substituents was designed to show whether the directing effect applied to all conjugatively electron-withdrawing groups, or whether there was some ' through space ' interaction between the electrophilic nitrene and the nucleophilic atoms of the substituents. Thus, all the substituents should be capable of producing the same directing effect as the methoxycarbonyl group if the former factor is dominant, but if a ' through space ' interaction is important the linear cyano-group should be a much less effective directing substituent than the others.

A summary of the products obtained when these tetrazoles were photolysed is given in the Table. It is reasonable to assume that 2-phenylbenzimidazole is



SCHEME 2

derived from the appropriate 1-substituted-2-phenylbenzimidazole by the loss of the substituent during work-up, and that the 4-substituted-2-phenylbenzimidazoles (2f)—(2j) are formed by closure of the nitrene at the unblocked position. None of the other experiments provide substantial evidence that cyclisation

* These yields varied considerably when a different photolysis apparatus was used.

TABLE

Products of photolysis of the tetrazoles (1)

Tetrazole (1)	Products (%) Benzimidazole (2)	Tetrazole (3)
(1b)	(2a) (19), (2b) (16)	(3a) (10)
(1d)	(2c) (29), (2d) (10), (2e) (41)	(3b) (5)
(1e)	(2f) (17)	
(1f)	(2g) (66)	(3c) (4)
(1g)	(2h) (53), (2d) (1.5)	(3d) (6)
(1h)	(2j) (62)	(3e) (7)

occurs at the blocked position. Neither the electron-withdrawing capacity of the substituent, nor its potential for ' through space ' interaction with the nitrene, satisfactorily accounts for these results.

The results are all consistent with our basic hypothesis that the *N*-arylbenzimidoyl nitrenes cyclise to 3a*H*-benzimidazole intermediates, which subsequently rearrange by way of sigmatropic shifts. The unexpected directing effect of the methoxycarbonyl group lacks a convincing explanation at present, but it bears further examination in that it may well apply to other substituents, and possibly to other types of cyclisation reaction involving substituted aromatic rings. Cyclisation onto a substituted position when an unsubstituted position is also available is certainly very rare; one example, involving thermal cyclisation of a (stable) side-chain onto a benzene ring, is provided by the Claisen rearrangement of an allyl phenyl ether where closure occurs at an acetylated, as well as unsubstituted *ortho*-position.[6]

The other unexpected feature of these photolyses was the formation of the 5-methyltetrazoles (3): these tetrazoles were isolated in low yields from all except the *ortho*-nitrotetrazole (1e). No close analogy for this reaction appears to exist. We considered the possibility that the tetrazoles (1) were undergoing a photoinduced retro-addition to give benzonitrile and the corresponding azides, which were then intercepted by the solvent, acetonitrile. In order to test this possibility, methyl 2-azidobenzoate was irradiated in acetonitrile but none of the tetrazole (3b) could be detected. It therefore seems unlikely that the tetrazoles dissociate to the azides, and the mechanism of this curious exchange reaction is under investigation.

EXPERIMENTAL

^{1}H N.m.r. spectra were obtained on a Perkin-Elmer R 34 instrument operating at 220 MHz, with $CDCl_3$ as solvent, except where indicated otherwise. Mass spectra were recorded at 70 eV, using a direct-insertion probe. Melting points are uncorrected. Preparative-layer chromatography was carried out using silica gel PF_{254} (Merck) as the stationary phase. Photochemical reactions were carried out in a Rayonet R100 reactor with lamps of 253.7 nm, and with dry acetonitrile as solvent, the concentration of the solutions being *ca.* 2 mmol/100 cm^3.

Preparation of the Tetrazoles (1).—(a) *3-Methyl-2-(5-phenyltetrazol-1-yl)benzoic acid* (1a). (i) 2-Benzamido-3-methylbenzoic acid [7] (2.20 g, 9.1 mmol) was heated in acetic anhydride (15 cm^3) under reflux for 1.5 h, to give *8-methyl-2-phenyl-3,1-benzoxazin-4-one* (1.52 g, 75%), m.p. 124—125 °C (from acetic anhydride) (Found: C, 75.5; H, 4.6; N, 6.0. $C_{15}H_{11}NO_2$ requires C, 75.9; H, 4.6; N, 5.9%); $\nu_{max.}$ 1 755 cm^{-1} (C=O); δ 2.64 (3 H) and 7.1—8.6 (8 H, m). (ii) The benzoxazinone (0.900 g, 4.05 mmol) was dissolved in dry dimethylformamide (40 cm^3) and the solution was stirred while finely ground sodium azide (0.300 g, 4.6 mmol) was added. The mixture was then heated to 100 °C and stirred for 20 h. It was cooled, poured into water (50 cm^3), and the solution was acidified to Congo Red with concentrated hydrochloric acid. Extraction with dichloromethane gave the *carboxylic acid* (1a) (0.800 g, 75%), m.p. 186—188 °C (from aqueous ethanol) (Found: C, 64.0; H, 4.5; N, 20.2. $C_{15}H_{12}N_4O_2$ requires C, 64.3; H, 4.3; N, 20.0%); $\nu_{max.}$ (KBr) 3 100—2 500 (OH) and 1 705 (C=O) cm^{-1}; δ[$(CD_3)_2SO$] 1.95 (3 H), 7.5—7.65 (5 H, m), 7.75—7.85 (2 H, m), and 8.05—8.10 (1 H, m); *m/e* 280 (M^+), 279, 251, and 77 (base).

(b) *Methyl 3-methyl-2-(5-phenyltetrazol-1-yl)benzoate* (1b). An excess of ethereal diazomethane was added to a solution of the tetrazole acid (1a) (0.500 g, 1.79 mmol) in methanol (20 cm^3) to give the *ester* (1b) (0.500 g, 95%), m.p. 94—96 °C (from methanol) (Found: C, 65.6; H, 4.8; N, 19.0. $C_{16}H_{14}N_4O_2$ requires C, 65.3; H, 4.8; N, 19.0%); $\nu_{max.}$ (Nujol) 1 710 cm^{-1} (C=O); δ 2.02 (3 H), 3.67 (3 H), and 7.3—8.4 (8 H, m); $\lambda_{max.}$ (EtOH) 235 and 277 nm; *m/e* 294 (M^+) and 266.

(c) *2-(5-Phenyltetrazol-1-yl)benzoic acid* (1c). 2-Phenyl-3,1-benzoxazin-4-one [8] (5.00 g, 22.4 mmol) and sodium azide (1.60 g, 24.6 mmol) in dimethylformamide (100 cm^3) gave, by the method described for the tetrazole (1a), the *carboxylic acid* (1c) (5.04 g, 85%), m.p. 157—159 °C (from dichloromethane–hexane) (Found: C, 63.0; H, 3.7; N, 21.35. $C_{14}H_{10}N_4O_2$ requires C, 63.2; H, 3.8; N, 21.05%); $\nu_{max.}$ (KBr) 3 100—2 200 (OH) and 1 690 (C=O) cm^{-1}; δ 7.3—7.4 (2 H, m), 7.4—7.5 (4 H, m), 7.75—7.81 (2 H, m), and 8.20—8.25 (1 H, m); *m/e* 266 (M^+), 237, and 146 (base).

(d) *Methyl 2-(5-phenyltetrazol-1-yl)benzoate* (1d). The carboxylic acid (1c) (5.04 g, 19.0 mmol) gave, with an excess of diazomethane, the *ester* (1d) (5.00 g, 95%), m.p. 96—98 °C (Found: C, 64.4; H, 4.3; N, 20.3. $C_{15}H_{12}N_4O_2$ requires C, 64.3; H, 4.3; N, 20.0%); $\nu_{max.}$ (KBr) 1 715 cm^{-1} (C=O); δ 3.60 (3 H), 7.30—7.55 (6 H, m), 7.7—7.8 (2 H, m), and 8.1—8.2 (1 H, m); *m/e* 280 (M^+), 252, and 251 (base).

(e) *1-(2-Nitrophenyl)-5-phenyltetrazole* (1e). 2'-Nitrobenzanilide (4.84 g, 20.0 mmol) was stirred in a mixture of benzene (16 cm^3) and acetonitrile (4 cm^3), and phosphorus pentachloride (4.16 g, 20.0 mmol) was added during 15 min. The reaction mixture was stirred for 4 h and the solvent was then removed. The residue was dissolved in dimethylformamide (70 cm^3) and sodium azide (1.30 g, 20.0 mmol) was added. The mixture was stirred at 100 °C for 20 h, cooled, poured into water (200 cm^3), and the solution was stirred for a further 0.5 h. The precipitate was filtered off, dried, and recrystallised twice to give the *tetrazole* (1e) (2.67 g, 50%), m p. 167—168.5 °C (from ethanol) (lit.,[9] m.p. 168—169 °C).

(f) *2-(5-Phenyltetrazol-1-yl)benzamide* (1f). The carboxylic acid (1a) (5.00 g, 18.7 mmol) was converted into the acid chloride by treatment with an excess of thionyl chloride for 5 h. The solid acid chloride was finely ground

and then added to an excess of concentrated aqueous ammonia to give the *amide* (1f) (4.45 g, 89%), m.p. 187—189 °C (from ethanol) (Found: C, 63.3; H, 3.95; N, 26.6. $C_{14}H_{11}N_5O$ requires C, 63.4; H, 4.15; N, 26.4%); $\nu_{max.}$ (KBr) 3 460, 3 340 (NH), and 1 680 (C=O) cm^{-1}; δ[$(CD_3)_2SO$] 7.4—7.9 (10 H, m) (reduced to 8 H, m, by shaking with D_2O), and 8.10 (1 H); *m/e* 265 (M^+), 237, and 236 (base).

(g) 1-[2-(5-*Phenyltetrazol*-1-*yl*)*benzoyl*]*pyrrolidine* (1g). The acid (1a) (5.00 g, 18.7 mmol) was converted into its acid chloride, which was added to pyrrolidine (2.60 g, 36.6 mmol) in aqueous sodium hydroxide (20 cm^3, 10%). After 2 h, the suspended solid was filtered off and crystallised to give the *pyrrolidine* (1g) (5.50 g, 92%), m.p. 161—162 °C (from ethanol) (Found: C, 67.8; H, 5.4; N, 21.8. $C_{18}H_{17}N_5O$ requires C, 67.7; H, 5.3; N, 21.9%); $\nu_{max.}$ (KBr) 1 630 cm^{-1} (C=O); δ 1.80—1.90 (4 H, m), 3.30—3.40 (4 H, m), and 7.2—7.7 (9 H, m); *m/e* 319 (M^+), 290, and 119 (base).

(h) 2-(5-*Phenyltetrazol*-1-*yl*)*benzonitrile* (1h). The amide (1f) (3.25 g, 12.3 mmol) was heated in toluene (25 cm^3) under reflux with phosphoric oxide (3.61 g, 2.0 mmol). After 20 h, the solid was filtered off and washed with hot toluene. The filtrate and washings were combined and evaporated. Crystallisation of the solid residue gave the *nitrile* (1.67 g, 55%), m.p. 139—140 °C (from ethanol) (Found: C, 68.2; H, 3.6; N, 28.5. $C_{14}H_9N_5$ requires C, 68.0; H, 3.6; N, 28.3%); $\nu_{max.}$ (KBr) 2 220 cm^{-1} (C≡N); δ 7.3—7.95 (9 H, m); *m/e* 247 (M^+) and 219 (base).

Photolysis of Tetrazoles.—(a) *Methyl* 3-*methyl*-2-(5-*phenyltetrazol*-1-*yl*)*benzoate* (1b). A solution of the tetrazole (0.500 g, 1.7 mmol) in acetonitrile (100 cm^3) was irradiated for 11 h. Layer chromatography gave (with chloroform–ethyl acetate 50 : 1) (i) methyl 4-methyl-2-phenylbenzimidazole-1-carboxylate (2a) (84 mg, 19%), which was identical with independently synthesised material; (ii) 4-methyl-2-phenylbenzimidazole (2b) (56 mg, 16%), m.p. and mixed m.p. 250—251 °C (lit.,[10] 251—252 °C); and (iii) methyl 3-methyl-2-(5-methyltetrazol-1-yl)benzoate (3a) (39 mg, 10%) which was identical with independently synthesised material.

(b) *Methyl* 2-(5-*phenyltetrazol*-1-*yl*)*benzoate* (1d). The tetrazole (1.00 g, 3.5 mmol) in acetonitrile (200 cm^3) was irradiated for 12 h. Layer chromatography gave (i) the starting tetrazole (325 mg); (ii) methyl 2-phenylbenzimidazole-1-carboxylate (2c) (175 mg, 29%) which was identical with independently synthesised material; (iii) *methyl* 2-*phenylbenzimidazole*-4-*carboxylate* (2e) (250 mg 41%) m.p. 127 °C (from dichloromethane–hexane) (Found: C 71.4; H 4.9; N, 11.15. $C_{15}H_{12}N_2O_2$ requires C, 71.4; H, 4.8; N, 11.1%); $\nu_{max.}$ (KBr) 3 360 (NH) and 1 690 (C=O) cm^{-1}; δ 4.00 (3 H), 7.35 (1 H, t, *J* 7 Hz), 7.50—7.55 (3 H, m), 7.90 (1 H, d, *J* 7 Hz), 8.05 (1 H, d, *J* 7 Hz), and 7.10 (2 H, m); *m/e* 252 (M^+, base); (iv) 2-phenylbenzimidazole (2d) (50 mg, 10%), m.p. and mixed m.p. 286—289 °C (lit.,[10] 288 °C); and (v) methyl 2-(5-methyltetrazol-1-yl)benzoate (3b) (25 mg, 5%), which was identical with independently synthesised material.

(c) 1-(2-*Nitrophenyl*)-5-*phenyltetrazole* (1e). The tetrazole (0.400 g, 1.50 mmol) in acetonitrile (100 cm^3) was irradiated for 90 h and gave (i) the starting tetrazole (92 mg, 23% recovery); and (ii) 4-*nitro*-2-*phenylbenzimidazole* (2f) (59 mg, 17%), m.p. 194—196 °C (from dichloromethane–hexane) (Found: C, 65.4; H, 3.7; N, 17.8. $C_{13}H_9N_3O_2$ requires C, 65.3; H, 3.8; N, 17.6%); $\nu_{max.}$ (KBr) 3 380 cm^{-1} (NH); δ 7.40 (1 H, m), 7.45—7.50 (3 H, m), and 8.12—8.17 (4 H, m); *m/e* 239 (M^+, base).

(d) 2-(5-*Phenyltetrazol*-1-*yl*)*benzamide* (1f). The tetrazole (0.750 g, 2.83 mmol) in acetonitrile (100 cm^3) was irradiated for 9 h and gave (i) 2-*phenylbenzimidazole*-4-*carboxyamide* (2g) (450 mg, 66%), m.p. 250—251 °C (from ethanol) (Found: C, 70.5; H, 4.8; N, 17.9. $C_{14}H_{11}N_3O$ requires C, 70.9; H, 4.6; N, 17.7%); $\nu_{max.}$ 3 320, 3 150 (NH), and 1 640 (C=O) cm^{-1}; δ[$(CD_3)_2SO$] 7.35—7.40 (1 H, m), 7.58—7.62 (3 H, m), 7.75—7.80 (2 H, m), 7.90—7.95 (1 H, m), and 8.25—8.30 (2 H, m); *m/e* 237 (M^+, base); and (ii) 2-(5-methyltetrazol-1-yl)benzamide (3c) (30 mg, 4%), which was identical with independently synthesised material.

(e) 1-[2-(5-*Phenyltetrazol*-1-*yl*)*benzoyl*]*pyrrolidine* (1g). The tetrazole (0.600 g, 2.06 mmol) in acetonitrile (120 cm^3) was irradiated for 8 h and gave (i) 1-[2-(2-*phenylbenzimidazol*-4-*yl*)*benzoyl*]*pyrrolidine* (2h) (316 mg, 53%), m.p. 138—140 °C (from aqueous ethanol) (Found: C, 69.9; H, 6.3; N, 13.8. $C_{18}H_{17}N_3O{\cdot}H_2O$ requires C, 69.9; H, 6.1; N, 13.6%); $\nu_{max.}$ (KBr) 3 200—3 400 cm^{-1} (OH, NH); δ[$(CD_3)_2SO$] 1.68—1.95 (4 H, m), 3.30—3.60 (4 H, m), 7.25 (2 H, m), 7.50—7.55 (4 H, m), and 8.24 (2 H, m); *m/e* 291 (M^+) and 83 (base); (ii) 2-phenylbenzimidazole (2d) (6 mg, 1.5%); and (iii) 1-[2-(5-methyltetrazol-l-yl)benzoyl]pyrrolidine (3d) (35 mg, 6%), which was identical with independently synthesised material.

(f) 2-(5-*Phenyltetrazol*-1-*yl*)*benzonitrile* (1h). The tetrazole (0.530 g, 2.15 mmol) in acetonitrile (125 cm^3) was irradiated for 7 h and gave (i) 2-phenylbenzimidazole-4-carbonitrile (2j) (278 mg, 62%), m.p. 255 °C (from aqueous ethanol) (Found: C, 73.4; H, 4.5; N, 18.5. $C_{14}H_9N_3{\cdot}0.5H_2O$ requires C, 73.7; H, 4.4; N, 18.4%); $\nu_{max.}$ (KBr) 3 200—3 400 (OH, NH) and 2 210 (C≡N) cm^{-1}; δ[$(CD_3)_2CO$] 7.35—7.42 (1 H, m), 7.58—7.70 (4 H, m), 7.90 (1 H, m), and 8.33—8.36 (2 H, m); *m/e* 219 (M^+, base); and (ii) 2-(5-methyltetrazol-1-yl)benzonitrile (3e) (27 mg, 7%), which was identical with independently synthesised material.

Independent Syntheses of Reaction Products.—(a) *Methyl* 4-*methyl*-2-*phenylbenzimidazole*-1-*carboxylate* (2a). 4-Methyl-2-phenylbenzimidazole (100 mg, 0.48 mmol) was dissolved in dichloromethane (3 cm^3) and water (0.25 cm^3) and the solution was stirred. Magnesium oxide (50 mg, 1.25 mmol) was added, followed by methyl chloroformate (0.2 cm^3, 164 mg, 1.73 mmol). The reaction mixture was stirred vigorously for 0.5 h, and it was then diluted with dichloromethane (20 cm^3) and filtered. The filtrate was dried and evaporated to leave a yellow oil. Layer chromatography gave the *benzimidazole* (2a) (25 mg, 20%), m.p. 128—129 °C (from dichloromethane–hexane) (Found: C, 72.0; H, 5.2; N, 10.7. $C_{16}H_{14}N_2O_2$ requires C, 72.2; H, 5.3; N, 10.5%); $\nu_{max.}$ (Nujol) 1 743 cm^{-1} (C=O); δ 2.70 (3 H), 3.90 (3 H), 7.2—7.3 (2 H, m), 7.45—7.50 (3 H, m), 7.6—7.7 (2 H, m), and 7.80—7.85 (1 H, m); *m/e* 266 (M^+, base).

(b) *Methyl* 2-*phenylbenzimidazole*-1-*carboxylate* (2c). By the method described in (a), 2-phenylbenzimidazole (250 mg, 0.29 mmol) gave the title compound (2c) (72 mg, 22%), m.p. 77—79 °C (from diethyl ether) (Found: C, 71.3; H, 4.95; N, 11.0. $C_{15}H_{12}N_2O_2$ requires C, 71.4; H, 4.8; N, 11.1%); $\nu_{max.}$ (KBr) 1 745 cm^{-1} (C=O); δ 3.92 (3 H), 7.4—7.5 (5 H, m), 7.65—7.70 (2 H, m), 7.80 (1 H, m), and 8.00—8.05 (1 H, m); *m/e* 252 (M^+) and 207 (base).

(c) *Methyl* 3-*methyl*-2-(5-*methyltetrazol*-1-*yl*)*benzoate* (3a). 2,8-Dimethyl-3,1-benzoxazin-4-one [11] (2.10 g, 12.0 mmol) and sodium azide (0.90 g, 13.8 mmol) in dimethylformamide

(40 cm³), gave, after 20 h at 100 °C, *3-methyl-2-(5-methyltetrazol-1-yl)benzoic acid* (1.70 g, 65%), m.p. 172—173 °C (from aqueous ethanol) (Found: C, 54.75; H, 4.7; N, 26.0. $C_{10}H_{10}N_4O_2$ requires C, 55.05; H, 4.6; N, 25.7%). The acid with an excess of diazomethane gave the *ester* (3a) (91%), m.p. 117—119 °C (Found: C, 56.7; H, 5.1; N, 23.9. $C_{11}H_{12}N_4O_2$ requires C, 56.9; H, 5.2; N, 24.1%); $\nu_{max.}$ (KBr) 1 710 cm^{-1} (C=O); δ 2.05 (3 H), 2.42 (3 H), 3.70 (3 H), 7.6—7.7 (2 H, m), and 8.0—8.1 (1 H, m); *m/e* 232 (M^+), 204, and 145 (base).

(d) *Methyl 2-(5-methyltetrazol-1-yl)benzoate* (3b). 2-Methyl-3,1-benzoxazin-4-one [12] (5.0 g, 31 mmol) and sodium azide (2.5 g, 38 mmol) in dimethylformamide (80 cm³) gave, after 48 h at 110 °C, *2-(5-methyltetrazol-1-yl)-benzoic acid* (3.5 g 55%) m.p. 170—171 °C (from ethanol) (Found: C, 52.9; H, 4.0; N, 27.7. $C_9H_8N_4O_2$ requires C, 52.9; H, 3.9; N, 27.45%). The acid with an excess of diazomethane gave the *ester* (3b) (95%), m.p. 62—63 °C (from dichloromethane–hexane) (Found: C, 54.9; H, 4.75; N, 25.9. $C_{10}H_{10}N_4O_2$ requires C, 55.05; H, 4.6; N, 25.7%); $\nu_{max.}$ (KBr) 1 720 cm^{-1} (C=O); δ 2.39 (3 H), 3.66 (3 H), 7.36—7.41 (1 H, m), 7.66—7.80 (2 H, m), and 8.12—8.16 (1 H, m); *m/e* 218 (M^+), 190, and 159 (base).

(e) *2-(5-Methyltetrazol-1-yl)benzamide* (3c). 2-(5-Methyltetrazol-1-yl)benzoic acid (1.0 g, 5.7 mmol) was converted into the acid chloride and then into the *amide* (3c) (0.900 g, 90%), m.p. 193—194 °C (Found: C, 53.3; H, 4.6; N, 34.3. $C_9H_9N_5O$ requires C, 53.2; H, 4.4; N, 34.5%); $\nu_{max.}$ (KBr) 3 300, 3 100 (NH), 1 690, and 1 645 (C=O) cm^{-1}; *m/e* 204 (M^+) and 146 (base).

(f) *1-[2-(5-Methyltetrazol-1-yl)benzoyl]pyrrolidine* (3d). 2-(5-Methyltetrazol-1-yl)benzoic acid (750 mg, 4.3 mmol) was converted into the acid chloride, which with pyrrolidine, gave the *title compound* (3d) (700 mg, 74%), m.p. 101—102 °C (from dichloromethane–ether) (Found: C, 60.7; H, 5.9; N, 27.3. $C_{13}H_{15}N_5O$ requires C, 60.7; H, 5.8; N, 27.3%); $\nu_{max.}$ (KBr) 1 620 cm^{-1} (C=O); δ 1.85 (4 H, m), 2.53 (3 H), 3.38—3.48 (4 H, m), 7.35—7.40 (1 H, m), and 8.02—8.20 (3 H, m); *m/e* 257 (M^+) and 119 (base).

(g) *2-(5-Methyltetrazol-1-yl)benzonitrile* (3e). The amide (3c) (1.2 g, 5.9 mmol) and phosphorus pentaoxide (1.0 g, 7.0 mmol) gave the *nitrile* (0.900 g, 82%), m.p. 84—85 °C (from dichloromethane–diethyl ether) (Found: C, 58.25; H, 3.9; N, 38.1. $C_9H_7N_5$ requires C, 58.4; H, 3.8; N, 37.8%); $\nu_{max.}$ (KBr) 2 212 cm^{-1} (C≡N); δ 2.61 (3 H), 7.60—7.65 (1 H, m), and 7.8—8.0 (3 H, m); *m/e* 185 (M^+), 157, and 129 (base).

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