Cyclisations of *ortho*-Substituted *N*-Arylbenzimidoyl Nitrenes. Part 1. Cyclisations with *ortho*-Alkyl Substituents: Skeletal Rearrangements and [1,9]Alkyl Migrations [1]

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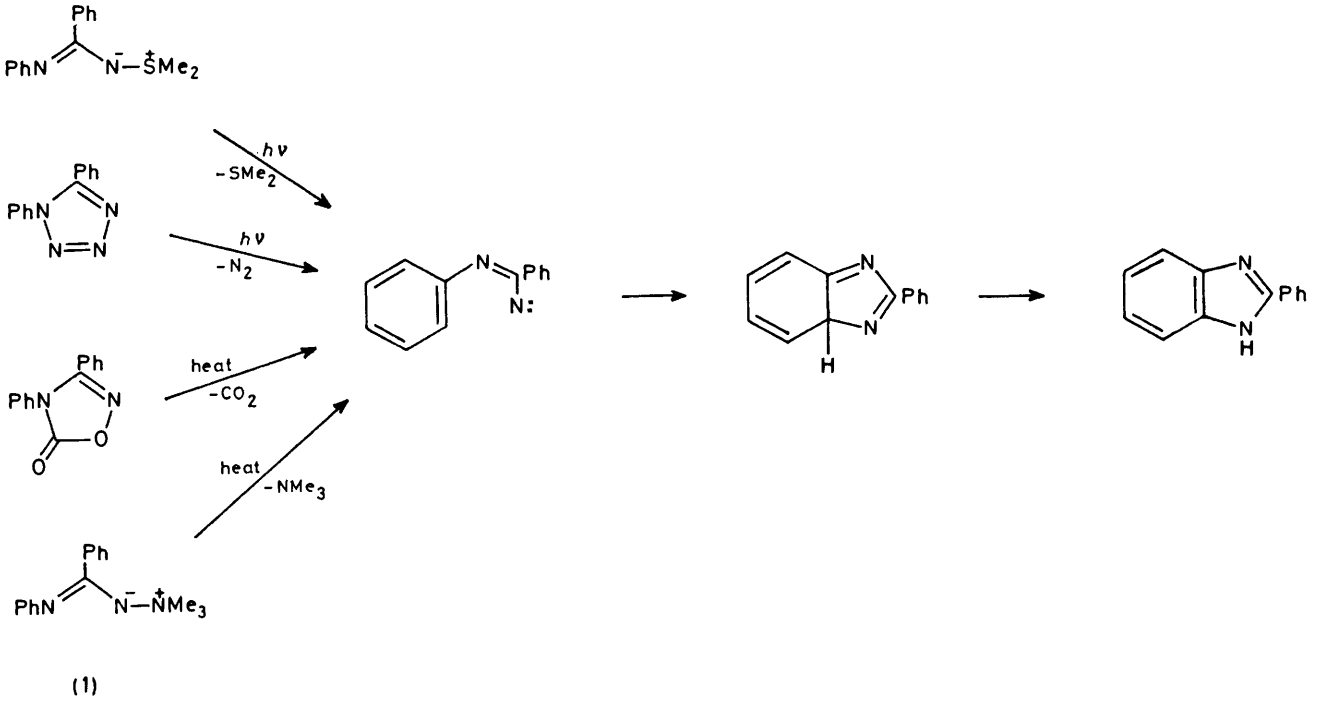
Photolysis of the *N*-(*N*-arylbenzimidoyl)sulphimides (2a)—(2c) and (2e), in which the *ortho*-positions of the *N*-aryl group carry alkyl substituents, gives the cyclopenta[*d*]pyrimidines (8), together with the carbodi-imides (6). Photolysis of the corresponding tetrazoles (3) gives the same products. The cyclopenta[*d*]pyrimidines and carbodi-imides are also produced when the tetrazoles (3), and the oxadiazolone (5), are subjected to flash vacuum pyrolysis. It is proposed that the cyclopenta[*d*]pyrimidines are formed by cyclisation of *N*-arylbenzimidoyl nitrene intermediates to give 3a*H*-benzimidazoles, which then undergo skeletal rearrangement by successive [1,5]-vinyl and -imidoyl shifts. 1-(2-Methyl-1-naphthyl)-5-phenyltetrazole (4) undergoes an analogous reaction when photolysed, giving the pyrimidine (13).

In the flash pyrolysis of the tetrazoles (3) and the oxadiazolone (5), benzimidazoles are also isolated in low yields. These products can also be accounted for by postulating the intermediacy of 3a*H*-benzimidazoles, which subsequently undergo [1,9]methyl shifts, or, with tetrazole (3c), elimination of formaldehyde.

We have previously described a method of synthesising 2-phenylbenzimidazoles by the photolysis of *N*-(*N*-arylimidoyl)sulphimides.[2] A possible mechanism for the reaction involves the generation of an imidoyl nitrene, which cyclises to a 3a*H*-benzimidazole and thence to a 1*H*-benzimidazole (Scheme 1). A number of other thermal and photochemical reactions, which also give 2-phenylbenzimidazoles as products,[3] can be rationalised in the same way; these include the photolysis of 1,5-diphenyltetrazole,[4] the thermolysis of 3,4-diphenyl-1,2,4-oxadiazol-5-one,[5] and the thermolysis of the aminimide (1).[6]



Scheme 1

The purpose of the present study was to discover more about the mechanism of these reactions, and, in particular, to attempt to get some evidence for the intermediacy of 3a*H*-benzimidazoles. Our approach was to prepare a group of compounds in which both *ortho*-positions of the *N*-aryl group were substituted. We had previously found that with only one *ortho*-methyl or -chloro-group present, the cyclisation went exclusively to the other, unoccupied *ortho*-position, to give benzimidazoles in the usual way.[2] With both positions occupied, however, if cyclisation of the nitrene still took place, the resulting 3a*H*-benzimidazole seemed less likely to aromatise.

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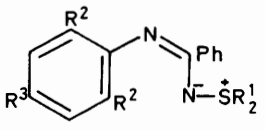
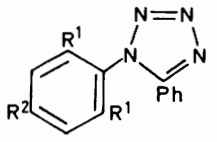
RESULTS

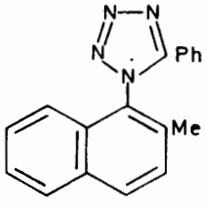
The imidoylsulphimides (2a)—(2d) were prepared from the corresponding *N*-arylbenzamidines by standard routes;[2,7] the sulphimide (2e) was prepared from *SS*-diphenylsulphimide and *N*-(2,6-dimethylphenyl)benz-



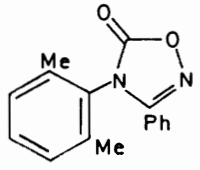
(2) a; $R^1 = R^2 = Me$, $R^3 = H$
b; $R^1 = R^2 = R^3 = Me$
c; $R^1 = Me$, $R^2 = Et$, $R^3 = H$
d; $R^1 = Me$, $R^2 = Cl$, $R^3 = H$
e; $R^1 = Ph$, $R^2 = Me$, $R^3 = H$



(3) a; $R^1 = Me$, $R^2 = H$
b; $R^1 = R^2 = Me$
c; $R^1 = OMe$, $R^2 = H$



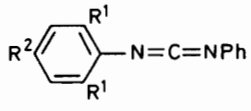
(4)



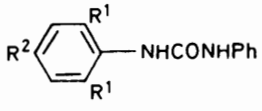
(5)

imidoyl chloride.[2,7] The tetrazoles (3a)—(3c) and (4), and the oxadiazolone (5), were prepared from the corresponding amines, also by standard routes.

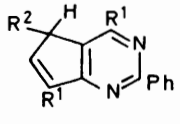
Photolysis of the sulphimide (2a) in dry acetonitrile gave two products, together with a large amount of dark coloured, polar material. One of the products was identified as the carbodi-imide (6a) (12%) by its characteristic absorption in the i.r. spectrum at 2 150 cm^{-1}, and by its hydrolysis to the crystalline urea (7a). The other product was assigned the



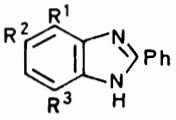
(6) a; $R^1 = Me$, $R^2 = H$
b; $R^1 = R^2 = Me$
c; $R^1 = Et$, $R^2 = H$
d; $R^1 = Cl$, $R^2 = H$
e; $R^1 = OMe$, $R^2 = H$



(7) a; $R^1 = Me$ $R^2 = H$
b; $R^1 = R^2 = Me$
c; $R^1 = Et$, $R^2 = H$
d; $R^1 = OMe$, $R^2 = H$



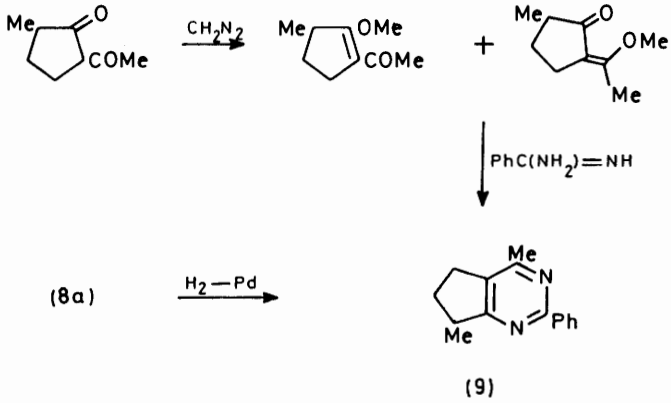
(8) a; $R^1 = Me$, $R^2 = H$
b; $R^1 = R^2 = Me$
c; $R^1 = Et$, $R^2 = H$



(10) $R^1 = R^2 = Me$, $R^3 = H$
(11) $R^1 = R^3 = Me$, $R^2 = H$
(12) $R^1 = OMe$, $R^2 = R^3 = H$

structure 4,7-dimethyl-2-phenyl-5*H*-cyclopenta[*d*]pyrimidine (8a) (18%). The ^1H n.m.r. spectrum of this compound shows several similar features to that of 1-methylindene;[8] in particular, the methyl group at C-7 appears as a quartet (*J* 2.5 Hz) with additional splitting due to long-range coupling with the methylene group at C-5. The structure of the compound was established by its catalytic hydrogenation to the crystalline dihydro-derivative (9), which was synthesised by an independent route. 2-Acetyl-5-methylcyclopentanone [9] was converted into a mixture of *O*-methyl ethers by reaction with diazomethane; the ethers then reacted with benzamidine to give the pyrimidine (9) (Scheme 2). Attempts to form compound (9) directly from 2-acetyl-5-methylcyclopentanone and benzamidine were unsuccessful because the former was sufficiently acidic to form a stable, insoluble benzamidinium salt.

Other sulphimides gave very similar products on photolysis. The *SS*-diphenylsulphimide (2e) gave the same two products as were isolated from the analogous *SS*-dimethylsulphimide (2a), but in higher yield, namely the carbodiimide (6a) (26%) and the cyclopentapyrimidine (8a) (25%). The corresponding products, the carbodi-imide (6b) (6%) and the cyclopentapyrimidine (8b) (20%) were obtained from sulphimide (2b). With *ortho*-ethyl substituents, the analogous products were again formed, the carbodi-imide (6c) (18%) and the cyclopentapyrimidine (8c) (7%) being isolated from the photolysis of the sulphimide (2c). With

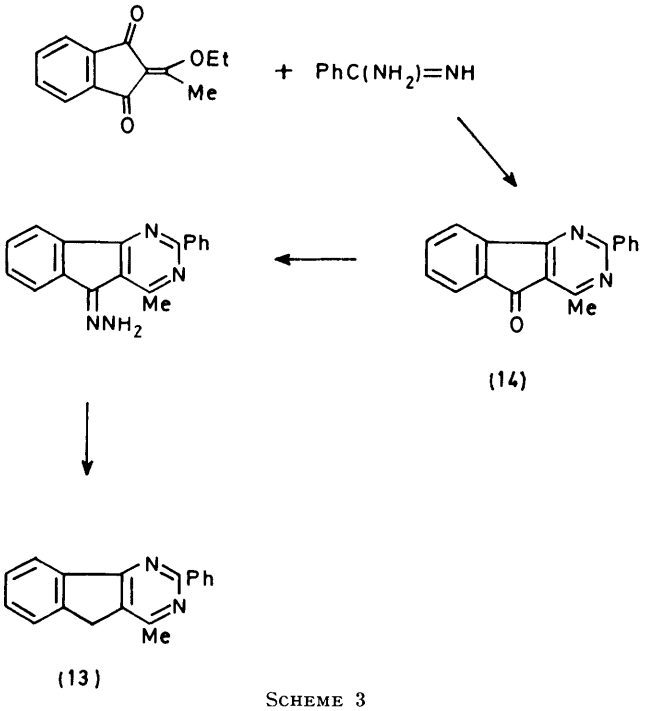


SCHEME 2

the sulphimide (2d) bearing *ortho*-chloro-substituents, however, no cyclisation product could be detected, the only compound isolated being the carbodi-imide (6d). The products obtained from these photolyses are summarised in the Table.

The tetrazoles (3a) and (3b) were then investigated as alternative sources of the imidoyl nitrenes. Photolysis of the tetrazoles (3a) and (3b) indeed followed a very similar course to that of the corresponding sulphimides, and gave the cyclopentapyrimidines (8a) (17%) and (8b) (20%) (Table). A small amount of the carbodi-imide (6a) was also detected in the photolysis of the tetrazole (3a). The thermal decomposition of the tetrazoles (3) was also investigated: flash vacuum pyrolysis at 600 °C proved to be a convenient way of carrying out the decomposition cleanly on a small scale. Under these conditions, Curtius rearrangement to the carbodi-imides was expected to be the major reaction, by analogy with earlier studies of the thermolysis of 1,5-diaryltetrazoles.[10] This indeed proved to be the case: the

carbodi-imides were isolated as the major products (39—46%) from the pyrolysis of the tetrazoles (3a)—(3c). In each case, other minor products were also isolated, however. The tetrazole (3a) gave the cyclopentapyrimidine (8a) (3%) and a 1 : 1 mixture of 4,5- and 4,7-dimethyl-2-phenylbenzimidazoles (10) and (11) (10%). The mixture could not be separated, but the components were identified by comparing the mixture with that obtained by mixing authentic



SCHEME 3

specimens [11] of the two benzimidazoles. Similarly, pyrolysis of the tetrazole (3b) gave the cyclopentapyrimidine (8b) (8%) and a mixture of 4,5,6- and 4,5,7-trimethyl-2-phenylbenzimidazoles (10%). A minor component from the pyrolysis of the tetrazole (3c) was identified as the known [12] 4-methoxy-2-phenylbenzimidazole (12).

Vacuum pyrolysis of the oxadiazolone (5) gave the same products as were obtained from the tetrazole (3a), though in a slightly different ratio (Table), indicating that the reactions probably involve a common intermediate.

Photolysis of the tetrazole (4) was investigated in order to determine the effect of annelation on the course of the reaction. Cyclisation of the imidoyl nitrene derived from this tetrazole could involve attack either at an unsubstituted, but unconjugated, position (the 8-position of the naphthalene system) or at a substituted, but conjugated, position (the 2-position). The major product (40%) was the pyrimidine (13), together with a smaller amount (7%) of the corresponding ketone (14), which is presumably formed by adventitious oxidation during the photolysis and work-up. This demonstrates that cyclisation occurs at the conjugated 2-position rather than at the unconjugated 8-position. The structures of the pyrimidines (13) and (14) were confirmed by an independent synthesis (Scheme 3). The ketone (14) was prepared by a route similar to a published procedure,[13] from 2-(1-ethoxyethylidene)indane-1,3-dione [14] and benzamidine. Standard Wolff–Kishner conditions were unsuccessful for the reduction of the ketone; a modification [15] was therefore used which involved isolation of the hydrazone and its subsequent reaction with potassium t-butoxide in toluene.

A variety of other methods exists for the conversion of *N*-arylbenzamidines and their derivatives into benzimidazoles: these include the oxidation of the amidines with lead tetra-acetate,[16] the reaction of the *N*-chloroamidines with a base,[17] and the reaction of the amidoximes with benzenesulphonyl chloride.[18] Each of these methods was applied to the corresponding *N*-(2,6-dimethylphenyl)benzamidine derivative, but in no case was there any evidence for the formation of the cyclopentapyrimidine (8a), or of any other cyclisation product.

DISCUSSION

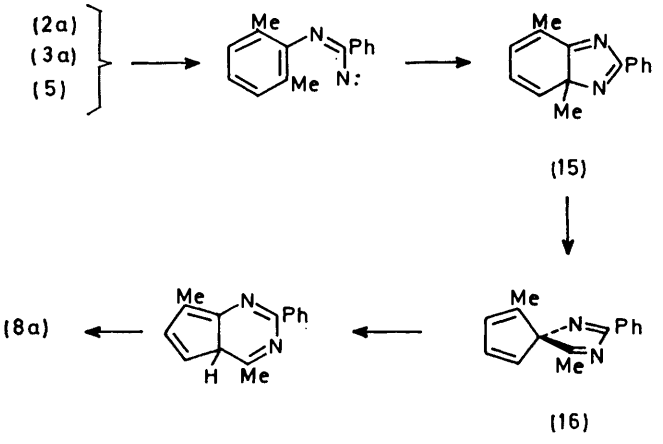
The products isolated in these reactions can be considered in three groups. The first, the carbodi-imides, occur in the decomposition of similar nitrene precursors even in the absence of *ortho*-blocking groups, so it is not surprising that they are major products in many of these reactions. They may be formed either by concerted decomposition and rearrangement of the nitrene precursors, or by rearrangement of the singlet imidoyl nitrenes. It is interesting that carbodi-imides are not the sole products even in the thermal decomposition of *ortho*-blocked tetrazoles, where cyclisation is presumably more difficult than in the unblocked systems. This tends to indicate that carbodi-imides and cyclisation products are formed by independent routes in the thermal decomposition: possibly the Curtius rearrangement is concerted with loss of nitrogen from the tetrazoles, whereas the cyclisation products are formed from nitrene intermediates.

Products of decomposition of sulphimides (2), tetrazoles (3) and (4), and the oxadiazolone (5)

Precursor	Method	Carbodi-imides [%]	Pyrimidines [%]	Benzimidazoles [%]
(2a)	*hν*	(6a) [12]	(8a) [13]	
(2b)	*hν*	(6b) [6]	(8b) [20]	
(2c)	*hν*	(6c) [18]	(8c) [7]	
(2d)	*hν*	(6d) [34]		
(2e)	*hν*	(6a) [26]	(8a) [25]	
(3a)	*hν*	(6a) [1.5]	(8a) [17]	
(3a)	Heat	(6a) [46]	(8a) [3]	(10) + (11) [10]
(3b)	*hν*		(8b) [20]	
(3b)	Heat	(6b) [39]	(8b) [8]	[10] [a]
(3c)	Heat	(6e) [44]		[6] [b]
(4)	*hν*		(13) [40] (14) [10]	
(5)	Heat	(6a) [24]	(8a) [9]	(10) + (11) [4]

[a] Mixture of 4,5,7- and 4,5,8-trimethyl-2-phenylbenzimidazoles. [b] 4-Methoxy-2-phenylbenzimidazole.

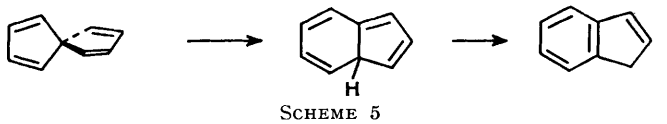
The second group of products, which are isolated from both photochemical and thermal reactions, are the cyclopenta[*d*]pyrimidines (8) and (13). We consider that the most economical explanation for the formation of these compounds, and the one with the best literature precedents, is that illustrated in Scheme 4 for the formation of compound (8a). Cyclisation of the imidoyl nitrene leads to the formation of the 3a*H*-benzimidazole (15). Although this could aromatise by a [1,5]methyl shift, there is an alternative pathway (a [1,5]vinyl shift) which leads to the spiro-compound (16), and which appears to be of lower energy. The observed product (8a) can then be derived from the spiro-intermediate by successive [1,5]imidoyl and hydrogen shifts. Because the same product is isolated from both thermal and photochemical reactions, it seems reasonable that the steps which follow the generation of the initial reactive intermediate are low-energy thermal processes.



SCHEME 4

Circumstantial evidence which favours the mechanism shown in Scheme 4 includes the following. (*a*) [1,5]-Vinyl shifts have been shown to occur in preference to [1,5]methyl shifts, both in five-membered carbocyclic [19] and heterocyclic systems.[20] (*b*) A [1,5]imidoyl shift has also been shown to occur with great facility, and in preference to a [1,5]methyl shift.[21] (*c*) [1,5]Rearrangement of spiro[4,4]nonatetraene to 3a*H*-indene (Scheme 5) takes place with an unusually low activation energy;[22] heterocyclic analogues of this rearrangement also occur with great facility.[23]

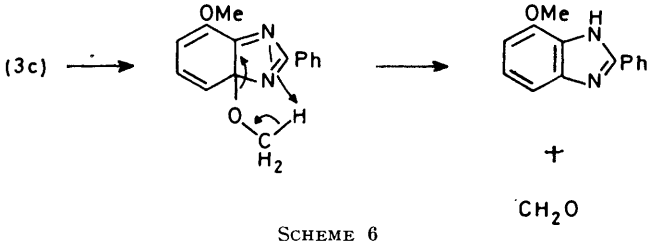
On the basis of these analogies, it is reasonable to assume that all the steps in the rearrangement of the 3a*H*-benzimidazole (15) to the pyrimidine (8a) could be low-energy thermal processes. Attempts to detect the proposed intermediate (15) or to intercept it as a Diels–Alder adduct with dimethyl acetylenedicarboxylate or with cyclohexene were unsuccessful, so more direct evidence for the proposed mechanism must await an independent synthesis of the 3a*H*-benzimidazole system, or of some related heterocycle.



SCHEME 5

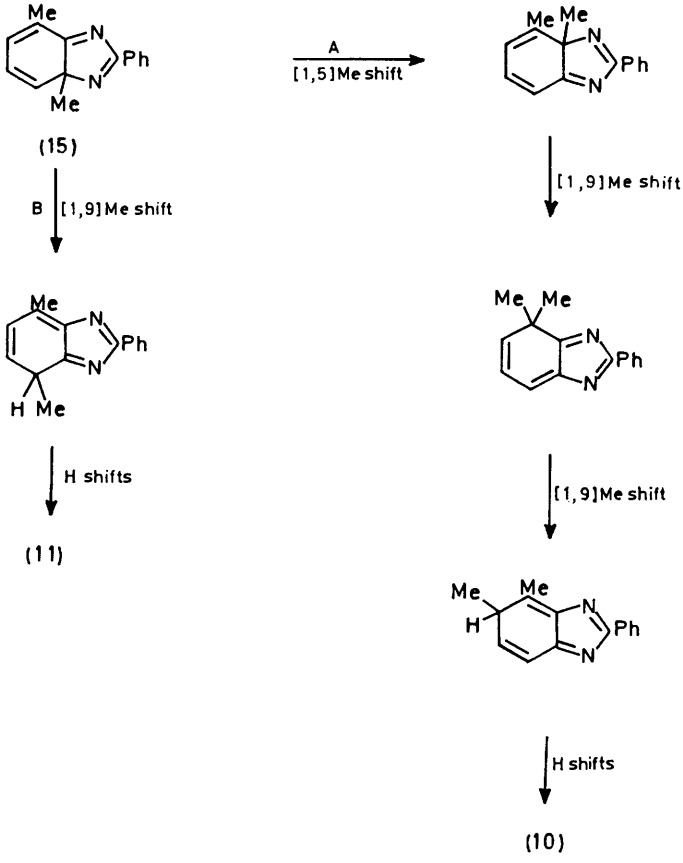
The mechanism of Scheme 4 serves to explain the formation of the other cyclopentapyrimidines; the formation of the indenopyrimidine (13) from the tetrazole (4) can be accounted for by an analogous sequence. The formation of the pyrimidine (13) in fair yield, and the absence of any product of attack at the 8-position of the naphthalene system, is a significant result. It indicates that the cyclisation involves an electrocyclic reaction which is not primarily directed by the electrophilicity of the nitrene. If the nitrene intermediate were to act simply as an electrophile, some attack at the 8-position would be expected.

The third group of products, which were detected only in the flash vacuum pyrolysis of the tetrazoles (3) and of the oxadiazolone (5), are benzimidazoles. Again, these can all be accounted for by assuming that the primary reaction products are 3a*H*-benzimidazoles. Pyrolysis of the 2,6-dimethoxyphenyltetrazole (3c) gave 4-methoxy-2-phenylbenzimidazole in low yield, this being identified by comparison with an authentic specimen.[12] The other methoxy group is probably lost as formaldehyde in a retro-ene process (Scheme 6); a similar loss of a methoxy substituent in a nitrene cyclisation has been reported previously.[24]



SCHEME 6

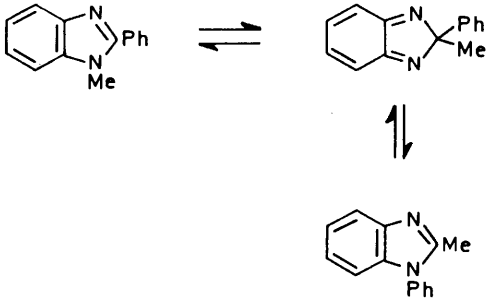
The dimethylbenzimidazoles (10) and (11) which were isolated from the pyrolysis of the tetrazole (3a) and the oxadiazolone (5) can be accounted for by postulating methyl migration in the 3a*H*-benzimidazole intermediate (15) (Scheme 7). It is notable that the second methyl group is found only at the 5-position [in compound (10)] or at the 7-position [in compound (11)]. It is possible to account logically for these observations by considering the symmetry-allowed sigmatropic shifts which could take place in the intermediate (15). The most favourable of these involve migration to an adjacent atom, thus allowing a favourable overlap in the transition state. Migration to the two adjacent carbon atoms is shown as paths A and B in Scheme 7. Path A is a [1,5]shift involving the bonds of the five-membered ring; path B is a [1.9]shift involving the whole of the peripheral π-electron system. Subsequent [1.9]shifts to adjacent atoms lead exclusively to the observed products, as shown. Apparently the intermediate (15) does not rearrange by methyl migration to the adjacent nitrogen. The possibility was considered that such a reaction might



SCHEME 7

take place reversibly, and to test this, 1-methyl-2-phenylbenzimidazole was subjected to flash pyrolysis. It did rearrange at 800 °C, but it gave exclusively 2-methyl-1-phenylbenzimidazole, probably by the mechanism shown in Scheme 8. Thus it seems that a methyl group at position 1 migrates to C-2 rather than to the bridgehead (3a) position.

[1,9]Sigmatropic alkyl shifts, though thermally allowed, had not been reported when this work was carried out,[1] though a [1,9]inter-oxygen alkyl migration has recently been proposed in the thermal rearrangement of tropolone ethers.[25] The 3a*H*-benzimidazoles and related systems described here provide a favourable bond arrangement for such shifts to take place, especially at the high temperatures of the flash pyrolysis experiments

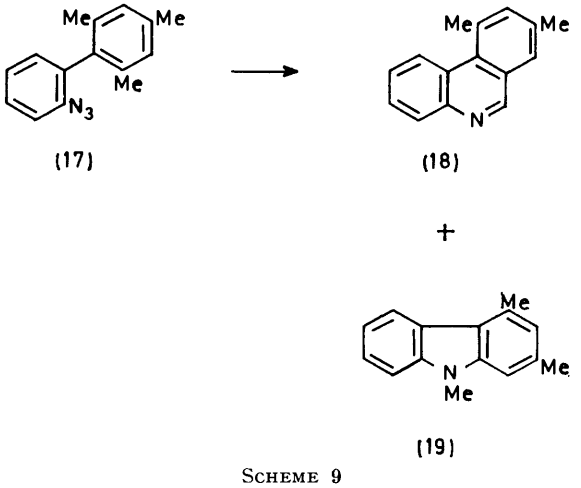


SCHEME 8

where the activation energy differences between the alkyl and vinyl shifts become less significant.

In none of the pyrolyses was any product obtained which could have resulted from nitrene cyclisation into an *ortho*-methyl group. This may seem surprising in view of the work of Smolinsky,[26] who found that pyrolysis of the biphenylyl azide (17) in solution at 230 °C gave the insertion product phenanthridine (18) in 48% yield, with the carbazole (19) as a minor product (Scheme 9). The imidoyl nitrenes show a clear preference for cyclisation and rearrangement over insertion; possibly the greater rigidity of the aryl nitrene derived from the azide (17) makes the insertion reaction easier in this system.

In view of the molecular rearrangements undergone by these proposed 3a*H*-benzimidazole intermediates it seemed interesting to vary the *ortho*-blocking substituents. Groups which migrate more readily than vinyl should favour the formation of benzimidazoles at the expense of cyclopentapyrimidines; the presence of different *ortho*-substituents in the same molecule should lead, competitively, to two 3a*H*-benzimidazoles, and hopefully should thereby provide a mechanistic probe. Experiments along these lines are currently in progress.



SCHEME 9

EXPERIMENTAL

^{1}H N.m.r. spectra were obtained on a Varian HA 100 instrument operating at 100 MHz, with $CDCl_3$ as solvent, except where indicated otherwise. Mass spectra were recorded at 70 eV, using a direct-insertion probe. Preparative layer chromatography was carried out using silica gel PF_{254} (Merck) as the stationary phase. Photochemical reactions were carried out in a Rayonet reactor with lamps of 253.7 nm wavelength, with dry acetonitrile as solvent, the concentration of the solution being 0.02 mol dm^{-3}. Vapour phase pyrolysis was carried out in an apparatus described earlier.[27]

N-*Arylbenzamidines*.—Equimolar amounts of the aniline, benzonitrile, and powdered aluminium chloride were heated together at 180—200 °C for 0.5 h and the products were isolated according to the general method described by Oxley *et al.*[28] The following amidines have not previously

been reported. N-2,6-*Dichlorophenylbenzamidine*, m.p. 134—135 °C (from light petroleum) (Found: C, 59.05; H, 3.7; N, 10.4. $C_{13}H_{10}Cl_2N_2$ requires C, 58.9; H, 3.8; N, 10.6%); $\nu_{max.}$ 3 450, 3 300, 3 160 (NH), 1 627, and 1 568 cm^{-1}. N-2,6-*Diethylphenylbenzamidine*, m.p. 108—109 °C (from hexane) (Found: C, 80.8; H, 8.1; N, 11.3. $C_{17}H_{20}N_2$ requires C, 80.95; H, 7.9; N, 11.1%); $\nu_{max.}$ 3 450, 3 320, 3 150, 1 640, and 1 568 cm^{-1}; δ 1.16 (6 H, t), 2.48 (4 H, q), 4.54 (2 H), 6.8—7.5 (6 H, m), and 7.7—7.9 (2 H, m). N-2,4,6-*Trimethylphenylbenzamidine*, m.p. 111—112 °C (from hexane) (Found: C, 80.8; H, 7.4; N, 11.8. $C_{16}H_{18}N_2$ requires C, 80.7; H, 7.6; N, 11.8%); $\nu_{max.}$ 3 450, 3 300, 3 130, 1 640, and 1 575 cm^{-1}; δ 2.10 (6 H), 2.25 (3 H), 4.58 (2 H), 6.84 (2 H), 7.2—7.5 (3 H, m), and 7.7—8.0 (2 H, m). *N*-2,6-Dimethylphenylbenzamidine has been reported previously; it had m.p. 102—105 °C (lit.,[29] m.p. 112 °C).

N-(N-*Arylbenzimidoyl*)*sulphimides*.—(*a*) *From amidines*. The general method described earlier (method B in ref. 2) was used. The following sulphimides were prepared. N-[N-(2,6-*Dimethylphenyl*)*benzimidoyl*]-SS-*dimethylsulphimide* (2a) (41%), m.p. 211—213 °C; δ 2.00 (6 H), 2.70 (6 H), and 6.5—7.4 (8 H, m); *m/e* 284 (M^+, base); the *picrate* had m.p. 231—233 °C (from ethanol) (Found: C, 53.65; H, 4.7; N, 13.6. $C_{23}H_{23}N_5O_7S$ requires C, 53.8; H, 4.5; N, 13.65%). SS-*Dimethyl*-N-[N-(1,4,6-*trimethylphenyl*)*benzimidoyl*]*sulphimide* (2b) (38%), m.p. 184—186 °C (Found: C, 72.2; H, 7.1; N, 9.1. $C_{18}H_{22}N_2S$ requires C, 72.5; H, 7.4; N, 9.4%); δ 2.00 (6 H), 2.14 (3 H), 2.78 (6 H), 6.64 (2 H), and 7.8—8.4 (5 H, m); *m/e* 298 (M^+) and 238 (base). N-[N-(2,6-*Diethylphenyl*)*benzimidoyl*]-SS-*dimethylsulphimide* (2c) (41%), m.p. 175—180 °C; δ 1.10 (6 H, t), 2.40 (4 H, dq), 2.74 (6 H), and 6.7—7.5 (8 H, m); *m/e* 312 (M^+) and 235 (base); the *picrate* had m.p. 203—205 °C (from ethanol) (Found: C, 54.9; H, 5.1; N, 12.7. $C_{25}H_{27}N_5O_7S$ requires C, 55.45; H, 5.0; N, 12.9%). N-[N-(2,6-*Dichlorophenyl*)*benzimidoyl*]-SS-*dimethylsulphimide* (2d) (71%), m.p. 204—206 °C (from ethanol) (Found: C, 55.1; H, 4.5; N, 8.6. $C_{15}H_{14}Cl_2N_2S$ requires C, 55.4; H, 4.3; N, 8.6%); δ 2.84 (6 H), 6.60 (1 H, m), and 6.9—7.5 (7 H, m); *m/e* 326 and 324 (M^+).

(*b*) *From the imidoyl chloride;* N-[N-(2,6-*dimethylphenyl*)-*benzimidoyl*]-SS-*diphenylsulphimide* (2e). 2′,6′-Dimethylbenzanilide was converted into the corresponding imidoyl chloride by heating with thionyl chloride. This was then used to prepare the sulphimide by a method previously described (method 3 in ref. 2). The *sulphimide* (62%) had m.p. 127—129 °C (Found: C, 79.3; H, 5.9; N, 6.9. $C_{27}H_{24}N_2S$ requires C, 79.4; H, 5.9; N, 6.9%); δ 1.94 (6 H) and 6.6—8.0 (18 H, m); *m/e* 408 (M^+) and 186 (base).

Tetrazoles; General Procedure.—The appropriate imidoyl chloride (0.01 mol) prepared from the amide, was dissolved in dry dimethylformamide (10 cm^3) and the solution was stirred at room temperature while finely ground sodium azide (0.01 mol) was added. An exothermic reaction ensued. After 10 min a further portion of sodium azide (0.002 mol) was added and the mixture was stirred for 18 h. Water (200 cm^3) was added, and the precipitated tetrazole was filtered off (if no precipitate appeared the solution was saturated with sodium chloride and the product was isolated by extraction with ethyl acetate). The tetrazoles were purified by column chromatography (silica; chloroform). The following were prepared. 1-(2,6-*Dimethylphenyl*)-5-*phenyltetrazole* (3a) (64%), m.p. 103—105 °C (from ethanol) (Found: C, 71.7; H, 5.4; N, 22.6. $C_{15}H_{14}N_4$ requires C, 72.0; H, 5.6; N, 22.4%); $\lambda_{max.}$(EtOH) 241 nm (ε 12 500); δ 1.86 (6 H) and 7.0—7.7 (8 H, m); *m/e* 250 (M^+) and 222 (base). 1-(2,4,6-*Trimethylphenyl*)-5-*phenyltetrazole* (3b) (46%), m.p. 122—124 °C (from ethyl acetate) (Found: C, 72.9; H, 5.9; N, 21.3. $C_{16}H_{16}N_4$ requires C, 72.7; H, 6.1; N, 21.2%); $\lambda_{max.}$(EtOH) 242 nm (ε 11 600); δ 1.88 (6 H), 2.40 (3 H), 6.04 (2 H), and 7.2—7.7 (5 H, m); *m/e* 264 (M^+) and 236 (base). 1-(2,6-*Dimethoxyphenyl*)-5-*phenyltetrazole* (3c) (64%), m.p. 129—131 °C (from hexane–dichloromethane) (Found: C, 63.7; H, 5.0; N, 20.1. $C_{15}H_{14}N_4O_2$ requires C, 63.8; H, 5.0; N, 19.9%); $\lambda_{max.}$ (EtOH) 234 (sh) (ε 14 800) and 277 nm (4 300); δ 3.62 (6 H), 6.64 (2 H, m), and 7.1—7.7 (6 H, m); *m/e* 282 (M^+) and 254 (base). 1-(2-*Methyl*-1-*naphthyl*)-5-*phenyltetrazole* (4) (47%), m.p. 135—136 °C (from hexane–dichloromethane) (Found: C, 75.5; H, 4.9; N, 19.5. $C_{18}H_{14}N_4$ requires C, 75.5; H, 4.9; N, 19.6%); $\lambda_{max.}$(EtOH) 276 (ε 7 700) and 285 nm (7 400); δ 2.01 (3 H), 6.8—7.5 (9 H, m), and 7.6—8.0 (2 H, m); *m/e* 286 (M^+), 258, and 157 (base).

N-(2,6-*Dimethylphenyl*)*benzamide Oxime*.—To a solution of benzhydroximoyl chloride (1.555 g, 0.01 mol) in dry ether (100 cm^3) was added 2,6-dimethylaniline (12.1 g, 0.1 mol); triethylamine (1.01 g, 0.01 mol) was then added dropwise during 5 min. After 44 h the ether and the excess of dimethylaniline were removed by distillation. The residue was subjected to column chromatography [silica; chloroform–ethyl acetate (9 : 1)] and this gave the *amide oxime* (0.980 g, 41%), m.p. 199—200 °C (from ethanol) (Found: C, 75.0; H, 6.8; N, 11.9. $C_{15}H_{16}N_2O$ requires C, 75.0; H, 6.7; N, 11.7%); $\nu_{max.}$ 3 350 (NH), 3 150br (OH), and 1 640 cm^{-1}.

4-(2,6-*Dimethylphenyl*)-3-*phenyl*-1,2,4-*oxadiazol*-5-*one* (5).—The general procedure of Boyer *et al.*[30] was used. Ethyl chloroformate (109 mg, 1.0 mmol) was added dropwise with stirring to a solution of *N*-(2,6-dimethylphenyl)benzamide oxime (240 mg, 1.0 mmol) in toluene (3 cm^3) and pyridine (0.3 cm^3). The mixture was then refluxed for 0.5 h, and evaporated to dryness. The residue, after washing with dilute hydrochloric acid, gave the *oxadiazolone* (202 mg, 76%), m.p. 143.5—145.5 °C (Found: C, 72.0; H, 5.2; N, 10.8. $C_{16}H_{14}N_2O_2$ requires C, 72.2; H, 5.3; N, 10.5%); $\nu_{max.}$ 1 770 cm^{-1} (C=O); δ 2.14 (6 H) and 7.0—7.4 (8 H, m); *m/e* 266 (M^+) and 222 (base).

Photolysis of Sulphimides.—(*a*) N-[N-(2,6-*Dimethylphenyl*)*benzimidoyl*]-SS-*dimethylsulphimide*. The sulphimide (426 mg) was irradiated for 4 h. Removal of the solvent left an orange oil. P.l.c. gave [with chloroform–ethyl acetate (50 : 1)] 4,7-*dimethyl*-2-*phenyl*-5H-*cyclopenta*-[d]*pyrimidine* (8a) (44 mg, 13%), as pale yellow crystals, m.p. 111—114 °C (after sublimation); $\nu_{max.}$ 1 595, 1 580, and 1 556 cm^{-1}; $\lambda_{max.}$(EtOH) 249 nm; δ 2.25 (3 H, q, *J* 2.5 Hz), 2.54 (3 H), 3.25 (2 H, m), 6.60 (1 H, m), 7.3—7.6 (3 H, m), and 8.4—8.6 (2 H, m); *m/e* 222 (M^+, base); the *picrate* had m.p. 163—165 °C (from ethanol) (Found: C, 55.9; H, 4.1; N, 15.65. $C_{21}H_{17}N_5O_7$ requires C, 55.9; H, 3.8; N, 15.5%). A second product was *N*-(2,6-dimethylphenyl)-*N*′-phenylcarbodi-imide (6a) (39 mg, 12%), which was isolated as an oil, $\nu_{max.}$ 2 150 cm^{-1}. This was heated in ethanolic hydrochloric acid for 1 h to give N-(2,6-*dimethylphenyl*)-N′-*phenylurea* (7a), m.p. 247—248 °C (from ethanol) (Found: C, 74.85; H, 6.8; N, 11.8. $C_{15}H_{16}N_2O$ requires C, 75.0; H, 6.7; N, 11.7%); $\nu_{max.}$ 3 300 (NH) and 1 630 (C=O) cm^{-1}; δ[$(CD_3)_2SO$] 2.54 (6 H), 7.1—7.9 (8 H, m), 8.04 (1 H), and 9.06 (1 H).

The cyclopenta[*d*]pyrimidine (8a) was further characterised by reduction. Hydrogenation over $PdCl_2$ at atmos-

pheric pressure gave a mixture, from which was isolated by p.l.c. 6,7-dihydro-4,7-dimethyl-2-phenyl-5*H*-cyclopenta[*d*]-pyrimidine (9) (28%), m.p. 72—74 °C, which was identical to the independently synthesised material.

(*b*) N-[N-(2,6-*Dimethylphenyl*)*benzimidoyl*]-SS-*diphenylsulphimide*. The sulphimide (408 mg) was irradiated for 4 h. Work-up as in (*a*) gave the pyrimidine (8a) (23 mg, 25%), the carbodi-imide (6a) (25 mg, 26%), and diphenyl sulphide (78 mg, 42%).

(*c*) SS-*Dimethyl*-N-[N-(2,4,6-*trimethylphenyl*)*benzimidoyl*]-*sulphimide*. The sulphimide (486 mg) was irradiated for 10 h. P.l.c. gave 2-*phenyl*-4,5,7-*trimethyl*-5H-*cyclopenta*[d]-*pyrimidine* (8b) (75 mg, 20%), m.p. 88—92 °C (from ether–hexane) (Found: M^+, 236.1301. $C_{16}H_{16}N_2$ requires M^+, 236.1313); $\nu_{max.}$ 1 586, 1 568, and 1 550 cm^{-1}; $\lambda_{max.}$(EtOH) 253 nm; δ 1.33 (3 H, d, *J* 7 Hz), 2.23 (3 H, q, *J* 2.5 Hz), 2.60 (3 H), 3.50 (1 H, m), 6.58 (1 H, m), 7.3—7.6 (3 H, m), and 8.4—8.6 (2 H, m); *m/e* 236 (M^+, base).

A second product was *N*-phenyl-*N'*-(2,4,6-trimethylphenyl)carbodi-imide (6b), which was obtained as an oil (22 mg, 6%), $\nu_{max.}$ 2 150 cm^{-1}. Hydrolysis gave N-*phenyl*-N'-(2,4,6-*trimethylphenyl*)*urea* (7b), m.p. 253—254 °C (from ethanol) (Found: C, 75.5; H, 7.2; N, 11.3. $C_{16}H_{18}N_2O$ requires C, 75.6; H, 7.1; N, 11.0%); $\nu_{max.}$ 3 300 (NH) and 1 630 (C=O) cm^{-1}; δ[$(CD_3)_2SO$] 2.52 (6 H), 2.60 (3 H), 7.1—8.0 (8 H, m), and 9.02 (1 H).

(*d*) N-[N-(2,6-*Diethylphenyl*)*benzimidoyl*]-SS-*dimethylsulphimide*. The sulphimide (575 mg) was irradiated for 9 h. P.l.c. gave 4,7-*diethyl*-2-*phenyl*-5H-*cyclopenta*[d]-*pyrimidine* (8c) (31 mg, 7%), m.p. 70—75 °C (from ether–hexane); $\nu_{max.}$ 1 590, 1 581, and 1 551 cm^{-1}; δ 1.2—1.4 (6 H, 2 t), 2.5—3.0 (4 H, m), 3.25 (2 H, m), 6.55 (1 H, m), 7.2—7.5 (3 H, m), and 8.4—8.6 (2 H, m); *m/e* 250 (M^+) and 235 (base); the *picrate* had m.p. 146—148 °C (from ethanol) (Found: C, 57.0; H, 4.4; N, 14.5. $C_{23}H_{21}N_5O_7$ requires C, 57.6; H. 4.4; N, 14.6%).

A second product was *N*-(2,6-diethylphenyl)-*N'*-phenylcarbodi-imide (6c) (85 mg, 18%), which was obtained as an oil, $\nu_{max.}$ 2 150 cm^{-1}. Hydrolysis gave N-(2,6-*diethylphenyl*)-N'-*phenylurea* (7c), m.p. 226—227 °C (from ethanol) (Found: C, 75.65; H, 7.6; N, 10.75. $C_{17}H_{20}N_2O$ requires C, 76.1; H, 7.5; N, 10.45%); $\nu_{max.}$ 3 300 (NH) and 1 640 (C=O) cm^{-1}; δ[$(CD_3)_2SO$] 1.50 (6 H, t), 2.96 (4 H, q), 7.0—8.1 (9 H, m), and 9.10 (1 H).

(*e*) N-[N-(2,6-*Dichlorophenyl*)*benzimidoyl*]-SS-*dimethylsulphimide*. The sulphimide (618 mg) was irradiated for 7 h. P.l.c. gave N-(2,6-*dichlorophenyl*)-N'-*phenylcarbodiimide* (6d) (172 mg, 34%), m.p. 40—42 °C after sublimation (Found: C, 59.55; H, 3.3; N, 10.5. $C_{13}H_8Cl_2N_2$ requires C, 59.3; H, 3.0; N, 10.65%); $\nu_{max.}$ 2 150 cm^{-1}; *m/e* 266, 264, and 262 (M^+, base).

Photolysis of Tetrazoles.—(*a*) 1-(2,6-*Dimethylphenyl*)-5-*phenyltetrazole*. The tetrazole (500 mg) was irradiated for 9 h, and gave the pyrimidine (8a) (75 mg, 17%) and the carbodi-imide (6a) (7 mg, 1.5%).

(*b*) 1-(2,4,6-*Trimethylphenyl*)-5-*phenyltetrazole*. The tetrazole (200 mg) was irradiated for 15 h, and gave the pyrimidine (8b) (36 mg, 20%).

(*c*) 1-(2-*Methyl*-1-*naphthyl*)-5-*phenyltetrazole*. The tetrazole (150 mg) was irradiated for 9 h. P.l.c. gave 4-methyl-2-phenyl-5*H*-indeno[1,2-*d*]pyrimidine (13) (54 mg, 40%), m.p. 116—118 °C (from dichloromethane–hexane), and the corresponding pyrimidinone (14) (10 mg, 7%), m.p. 161—163 °C (from methanol). These compounds were identified by comparison with independently synthesised specimens.

Pyrolysis of Tetrazoles.—(*a*) 1-(2,6-*Dimethylphenyl*)-5-*phenyltetrazole*. The tetrazole (150 mg) was vaporised at 140 °C and 0.04 mmHg, and the vapour was passed through a quartz tube at 600 °C. P.l.c. of the pyrolysate gave the carbodi-imide (6a) (61 mg, 46%), the pyrimidine (8a) (4 mg, 3%), and a solid (14 mg, 10%), m.p. 175—212 °C; $\nu_{max.}$ 2 850 cm^{-1} (NH); $\lambda_{max.}$ (dichloromethane) 245, 251, and 304 nm; δ 2.36, 2.48, 2.52, 6.93, 6.98, 7.06, 7.1—7.6 (m), and 7.9—8.2 (m). These properties were identical to those of a 1 : 1 mixture of 4,5- and 4,7-dimethyl-2-phenylbenzimidazoles;[11] authentic specimens of the two benzimidazoles were obtained by oxidation of the corresponding amidines with lead tetra-acetate.

Pyrolyses were also carried out at 500 and 400 °C. At 500 °C a very similar mixture of products as described above was obtained; at 400 °C some tetrazole (36%) was recovered, the products being the carbodi-imide (6a) (40%) and the mixture of benzimidazoles (10) and (11) (6%). No pyrimidine (8a) was detected in this reaction.

(*b*) 1-(2,4,6-*Trimethylphenyl*)-5-*phenyltetrazole*. The tetrazole (152 mg) was pyrolysed by passage of the vapour through a quartz tube at 600 °C. P.l.c. of the pyrolysate gave the carbodi-imide (6b) (53 mg, 39%), the pyrimidine (8b) (11 mg, 8%), and a solid (14 mg, 10%). The n.m.r. spectrum of the solid showed signals at δ 2.20, 2.26, 2.34, 2.48, 2.54, 6.86, 7.2—7.5 (m), and 7.9—8.1 (m), which is consistent with that expected for a 1 : 1 mixture of 4,5,6- and 4,5,7-trimethyl-2-phenylbenzimidazoles.

(*c*) 1-(2,6-*Dimethoxyphenyl*)-5-*phenyltetrazole*. The tetrazole (78 mg) was pyrolysed by passage of the vapour through a quartz tube at 600 °C. P.l.c. of the pyrolysate gave 4-methoxy-2-phenylbenzimidazole (4 mg, 6%), m.p. 214—216 °C (lit.,[12] 214—215 °C), and *N*-(2,6-dimethoxyphenyl)-*N'*-phenylcarbodi-imide (6e) (31 mg, 44%), m.p. 75—76 °C; $\nu_{max.}$ 2 180 cm^{-1}. Hydrolysis of the carbodi-imide gave N-(2,6-*dimethoxyphenyl*)-5-*phenylurea* (7d), m.p. 201—202 °C (from ethanol) (Found: C, 66.2; H, 5.7; N, 10.55. $C_{15}H_{16}N_2O_3$ requires C, 66.2; H, 5.9; N, 10.3%); $\nu_{max.}$ 3 260 (NH) and 1 650 (C=O) cm^{-1}; δ[$(CD_3)_2SO$] 3.72 (6 H), 6.64 (2 H, d), 6.7—7.5 (7 H, m), and 8.64 (1 H).

Pyrolysis of 4-(2,6-*Dimethylphenyl*)-3-*phenyl*-1,2,4-*oxadiazol*-5-*one*.—The oxadiazolone (92 mg) was pyrolysed at 600 °C and gave the carbodi-imide (6a) (11 mg, 24%), the pyrimidine (8a) (4 mg, 9%), and a mixture of the benzimidazoles (10) and (11) (2 mg, 4%). Some of the oxadiazolone (38 mg, 41%) was recovered.

Pyrolysis of 1-*Methyl*-2-*phenylbenzimidazole*.—The benzimidazole [31] (75 mg) was pyrolysed at 800 °C and gave 2-methyl-1-phenylbenzimidazole (20 mg, 38%); δ 2.50 (3 H) and 7.0—8.2 (9 H, m); the picrate had m.p. 221—224 °C (lit.,[32] 223—224 °C). 1-Methyl-2-phenylbenzimidazole (23 mg, 31%) was recovered.

Independent Synthesis of Reaction Products.—(*a*) 6,7-*Dihydro*-4,7-*dimethyl*-2-*phenyl*-5H-*cyclopenta*[d]*pyrimidine* (9). 2-Acetyl-5-methylcyclopentanone [9] (339 mg, 2.42 mmol) was dissolved in dry ether (20 cm^3) and the solution cooled in ice. A threefold excess of diazomethane was added and the solution set aside at room temperature for 65 h. The ether was removed and the residue was distilled to yield an oil (295 mg), m.p. 150 °C at 15 mmHg. N.m.r. showed the presence of two *O*-methylated compounds: δ 3.81 and 3.91. The mixture (295 mg) and benzamidine (230 mg, 1.92 mmol) were heated in dry toluene under reflux for 5 h; p.l.c. gave the *pyrimidine* (9) (206 mg, 48%), which was purified by sublimation at 111 °C

and 0.01 mmHg, m.p. 72—74 °C (Found: C, 79.9; H, 7.1; N, 12.6. $C_{15}H_{16}N_2$ requires C, 80.3; H, 7.2; N, 12.5%); $\nu_{max.}$ 1 589 and 1 560 cm^{-1}; $\lambda_{max.}$(EtOH) 258 nm (ε 24 000); δ 1.36 (3 H, d, *J* 7 Hz), 1.4—1.9 (2 H, m), 2.1—2.9 (2 H, m), 2.44 (3 H), 3.0—3.3 (1 H, q), 7.3—7.6 (3 H, m), and 8.3—8.6 (2 H, m); *m/e* 224 (M^+, base).

(*b*) 4-*Methyl*-2-*phenyl*-5H-*indeno*[1,2-d]*pyrimidin*-5-*one* (14). A mixture of benzamidine hydrochloride dihydrate (0.96 g, 5 mmol) and sodium methoxide [from sodium (0.115 g) and methanol (10 cm^3)] in methanol (25 cm^3) was added dropwise with stirring to a solution of 2-(1-ethoxyethylidene)indan-1,3-dione [14] in methanol (50 cm^3). After 8 h the methanol was removed and water (250 cm^3) was added to the residue. Column chromatography (silica; chloroform) gave the *pyrimidinone* (14) (1.14 g, 84%), m.p. 161—163 °C (from methanol) (Found: C, 79.3; H, 4.6; N, 10.5. $C_{18}H_{12}N_2O$ requires C, 79.4; H, 4.4; N, 10.3%); $\nu_{max.}$ 1 700 cm^{-1} (C=O); $\lambda_{max.}$(EtOH) 246 (ε 28 500) and 290 nm (35 100); δ 2.77 (3 H), 7.3—8.2 (7 H, m), and 8.5—8.9 (2 H, m); *m/e* 272 (M^+, base).

(*c*) 4-*Methyl*-2-*phenyl*-5H-*indeno*[1,2-d]*pyrimidine* (13). The pyrimidinone (14) (544 mg, 2 mmol) and anhydrous hydrazine (0.4 cm^3) were heated in propanol (40 cm^3) containing acetic acid (0.1 cm^3) for 2 h. The solution was cooled and the precipitate was filtered off; crystallisation gave the *pyrimidinone hydrazone* (428 mg, 75%), as yellow needles, m.p. 218—220 °C (from ethanol) (Found: C, 75.2; H, 5.0; N, 19.85. $C_{18}H_{14}N_4$ requires C, 75.5; H, 4.9; N, 19.6%). The hydrazone (90 mg, 0.31 mmol) and potassium t-butoxide (40 mg, 0.36 mmol) were refluxed in toluene (20 cm^3) for 3 h to give, by p.l.c., the *pyrimidine* (13) (30 mg, 37%), m.p. 116—118 °C (from hexane–dichloromethane) (Found: C, 83.7; H, 5.6; N, 10.8. $C_{18}H_{14}N_2$ requires C, 83.7; H, 5.4; N, 10.85%); $\nu_{max.}$ 1 593 and 1 565 cm^{-1}; $\lambda_{max.}$(EtOH) 226 (ε 22 500), and 255 (43 600), 287 (18 300), and 301 nm (19 700); δ 3.60 (3 H), 3.76 (2 H), 7.2—8.4 (7 H, m), and 8.5—8.8 (2 H, m); *m/e* 258 (M^+) and 217 (base).

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