

Rearrangement of *ortho*-Blocked *N*-Arylbenzimidoyl Nitrenes. A Proposed [1,9] Methyl Migration

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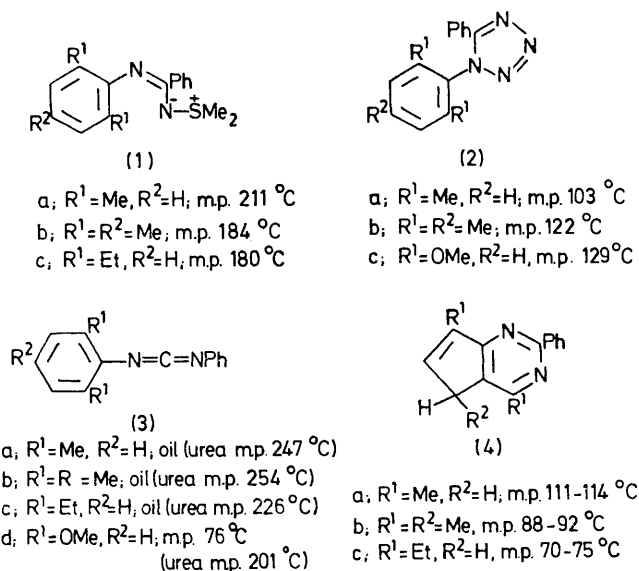
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Summary The pyrimidines (4) are isolated from the products of photolysis of the sulphimides (1) and of the tetrazoles (2); pyrolysis of the tetrazoles gives benzimidazoles (5) in addition to the pyrimidines, the formation of these products being rationalised by mechanisms involving successive [1,5] or [1,9] shifts in 3a*H*-benzimidazole intermediates.

PHOTOLYSIS of 1,5-diphenyltetrazole results in the formation of 2-phenylbenzimidazole¹ and we have recently shown that 2-phenylbenzimidazoles are also formed in the photolysis of

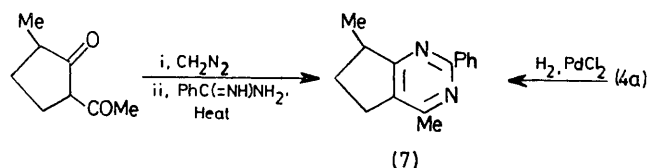
which was identical with the pyrimidine (7) prepared (48%) from 2-acetyl-5-methylcyclopentanone³ and benzamidide (Scheme 1). Photolysis of the tetrazole (2a) gave the same two products. From the vapour phase pyrolysis (600 °C and 0.04 mmHg) of the tetrazole (2a) the carbodi-imide (3a) and the pyrimidine (4a) were again isolated; in addition, a 1:1 mixture of the benzimidazoles (5a) and (5b) was obtained, the components being identified by comparison with authentic specimens.⁴

Related experiments on the decomposition of other *ortho* blocked sulphimides (1) and tetrazoles (2) gave very similar results; these are summarised in the Table. Pyrimidines (4) were isolated from both photochemical and thermal decomposition of the tetrazole (2b) as well as from photolysis of the sulphimides (1b) and (1c), indicating an underlying similarity of mechanism in this unusual transformation.

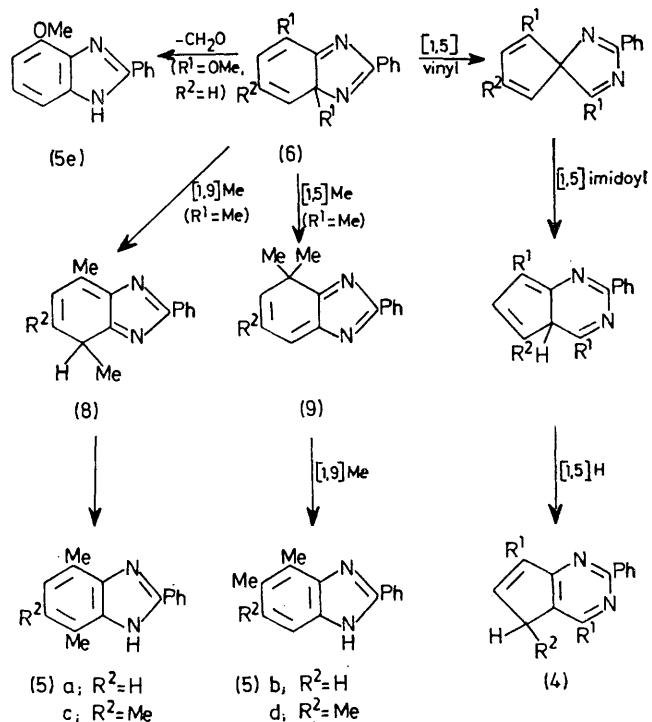


imidoyl sulphimides (1) (R¹ = H).² We have now prepared a series of sulphimides (1) and tetrazoles (2) with *ortho*-blocking groups, and have investigated their photochemical and thermal decomposition, in order to determine whether the benzimidazoles are formed by electrocyclic ring-closure of imidoyl nitrenes to 3a*H*-benzimidazoles (6). In *ortho*-substituted systems (6), aromatisation must involve the migration of a group other than hydrogen.

Photolysis of the sulphimide (1a) gave the carbodi-imide (3a) and a second product (13%) which was assigned the 5*H*-cyclopenta[*d*]pyrimidine structure (4a): δ(100 MHz, CDCl₃) 2.25 (3H, q, *J* 2.5 Hz), 2.54 (3H), 3.25 (2H, m), 6.6 (1H, m), 7.3-7.6 (3H, m), and 8.4-8.6 (2H, m). Reduction (H₂, PdCl₂) gave a dihydro derivative, m.p. 72-74 °C,



SCHEME 1.



SCHEME 2.

Formation of the carbodi-imides (3) is in accord with the results of other investigations of the decomposition of 1,5-diaryltetrazoles.^{1,5} Formation of the pyrimidines (4) and benzimidazoles (5) can be explained by assuming that *N*-arylbenzimidoyl nitrenes are generated and then undergo ring closure to 3a*H*-benzimidazoles (6). Compound (6) (R¹ = OMe, R² = H) with a bridgehead methoxy group might be expected, by analogy with a related intermediate,⁶ to aromatised by elimination of formaldehyde; the benzimid-

TABLE. Products of photolysis of sulphimides (1), and of photolysis and pyrolysis of tetrazoles (2).

Precursor	Method ^a	Carbodi-imides (3) (%)	Pyrimidines (4) (%)	Benzimidazoles (5) (%)
(1a)	<i>hν</i>	(3a) (12)	(4a) (13)	—
(2a)	<i>hν</i>	(3a) (1.5)	(4a) (17)	—
(2a)	Heat	(3a) (46)	(4a) (3)	(5a) + (5b) (10)
(1b)	<i>hν</i>	(3b) (6)	(4b) (20)	—
(2b)	<i>hν</i>	—	(4b) (20)	—
(2b)	Heat	(3b) (39)	(4b) (8)	(5c) + (5d) (9) ^b
(1c)	<i>hν</i>	(3c) (18)	(4c) (7)	—
(2c)	Heat	(3d) (44)	—	(5e) (7)

^a Photolysis in MeCN solutions; Rayonet reactor and Hg medium pressure lamps (λ_{\max} 253.7 nm). Pyrolysis in the vapour phase at 600 °C and 0.04 mmHg. ^b Structures (5c) and (5d) were assigned on the basis of the i.r. and n.m.r. spectra of the mixture.

azole (5e) was indeed formed, to the exclusion of the corresponding pyrimidine, in the pyrolysis of tetrazole (2c). The pyrimidines (4) are considered to arise from a sequence of [1,5] sigmatropic shifts (Scheme 2). Spiro intermediates similar to those of Scheme 2 have been isolated from cycloaddition reactions of diazocyclopentadienes with acetylenes, and have been shown to rearrange by [1,5] shifts.⁷ It is interesting to note that we do not observe the products of a [1,5]alkyl shift to nitrogen in (6) which would have given an aromatic product (a 1-alkylbenzimidazole) directly; [1,5] vinyl shift to give the spiro intermediate supervenes, in accord with the known mobility of vinyl groups in sigmatropic rearrangements. Sharp and his co-workers have recently reported similar preferential vinyl migrations in the rearrangement of 3-methyl-3-vinyl-

pyrazoles.⁸ At higher temperatures, as in the pyrolysis of the tetrazoles (2a) and (2b), the bridgehead methyl group does migrate, in competition with the vinyl group, but again to carbon rather than to nitrogen. An allowed [1,9] shift, involving the whole conjugated system, would give (8), from which the benzimidazole (5a) could be derived by further sigmatropic hydrogen shifts. The proposed [1,9] methyl shift in the rearrangement of (6) to (8) is stereochemically very favourable. The benzimidazole (5b) could be derived from the intermediate (6) by a [1,5] shift, to give (9), followed by a [1,9] methyl migration and subsequent hydrogen shifts.

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