

Generation and Rearrangement of 4aH-Carbazoles

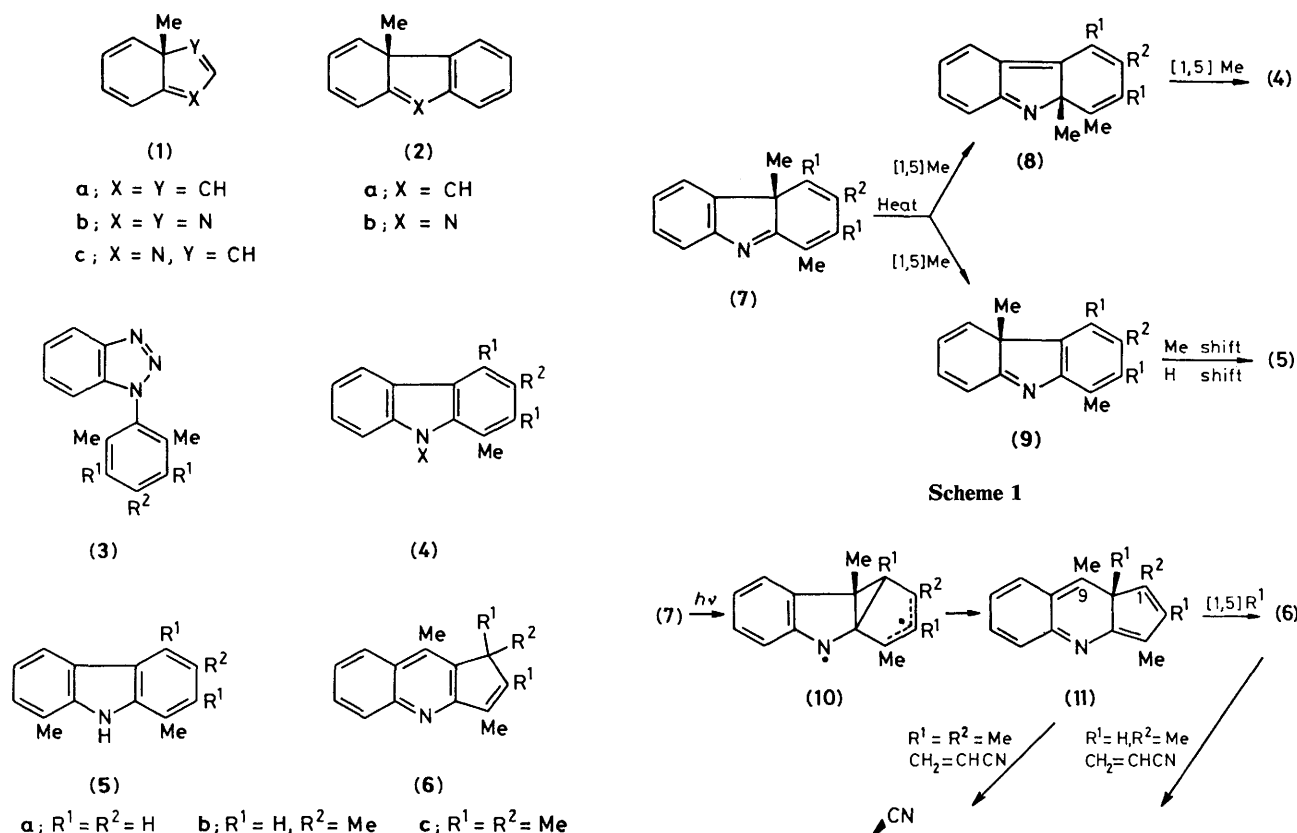
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Thermal and photochemical decomposition of benzotriazoles (**3**) gives carbazoles (**4**) and (**5**), and cyclopentaquinolines (**6**), the formation of these products being rationalised by rearrangements in 4aH-carbazole intermediates (**7**); one proposed intermediate (**11c**) has been intercepted in an extended cycloaddition reaction with acrylonitrile.

We have recently described the synthesis of a derivative of the 3aH-indene (**1a**),¹ and have previously proposed the 3aH-benzimidazoles (**1b**) as reaction intermediates.² These hitherto unexplored bicyclic compounds in which the peripheral

conjugation is interrupted by a tetrahedral carbon atom at the ring junction undergo a variety of rearrangement and cycloaddition reactions.^{1,2} By extending the conjugation into an additional aromatic ring, we hoped that 4aH-fluorene (**2a**) and



Scheme 1

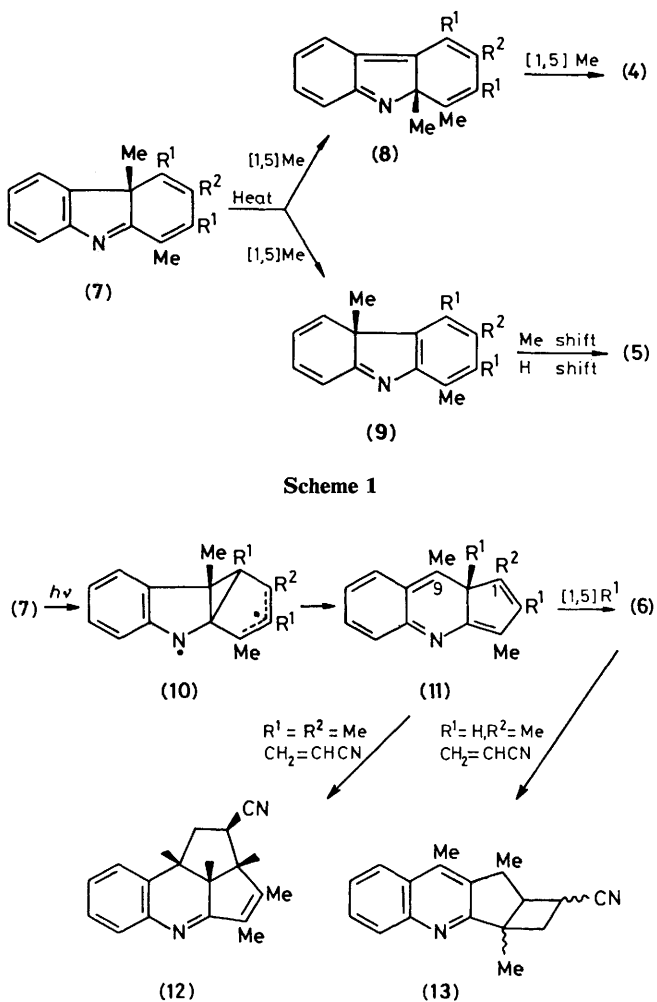
Scheme 2

4*aH*-carbazole (2b), the benzo derivative of 3*aH*-indole (1c), would be stable enough for them to be isolated. We now report the generation of some 4*aH*-carbazoles (7),[†] and find that under the reaction conditions they cannot be isolated but undergo a series of rearrangements.

Decomposition of 1-phenylbenzo-1,2,3-triazole gives carbazole in good yield *via* cyclisation of the diradical intermediate on to the benzene ring.⁴ We have prepared the benzotriazoles (3) in which both *ortho*-positions are blocked by methyl groups so that similar cyclisation of the diradical would lead directly to the 4*aH*-carbazole system. The benzotriazoles (3) were prepared from the appropriate aniline by reaction with 2-fluoronitrobenzene in the presence of potassium fluoride,⁵ followed by reduction of the nitrodiphenylamine and diazotisation of the resulting aminodiphenylamine.

The 1-arylbenzotriazoles (3) were decomposed thermally and photochemically. Flash vacuum pyrolysis (F.V.P.) of (3a), m.p. 68 °C, at 640 °C and 3×10^{-2} mmHg gave the *N*-methylcarbazole (4a, X = Me) (30%), the demethylated carbazole (4a, X = H) (35%), and a third unexpected product (10%) which was identified as 1,8-dimethylcarbazole (5a). The benzotriazoles (3b), m.p. 120–121 °C, and (3c), m.p. 211–213 °C, gave similar results on F.V.P. The major products were carbazoles resulting from the loss of a methyl group and from the migration of a methyl group on to nitrogen; minor amounts of other carbazoles with all the methyl groups retained on carbon were also formed. Since phenanthridine was reported to be the major product in the melt pyrolysis of *N*-methylcarbazole,⁶ phenanthridines were sought in our pyrolyses but were not found.

[†] Related work on 4*aH*-fluorene (2a) has also been successful.⁸



Photochemical decomposition of the benzotriazoles (3) in acetonitrile at 254 nm was also investigated. The dimethylphenyl compound (3a) gave only the cyclopentaquinoline (6a) (45%), m.p. 106–108 °C, and no carbazole. The trimethylphenyl compound (3b) gave the cyclopentaquinoline (6b) (64%) (picrate, m.p. 184–185 °C) together with a small amount of the carbazole (4b, X = H) (6%); the pentamethylphenyl compound (3c) gave approximately equal amounts of the cyclopentaquinoline (6c) (20%) (picrate, m.p. 212–215 °C) and the carbazole (4c, X = H) (18%). The structure of (6a) was confirmed by independent synthesis by condensation of 2-aminoacetophenone with 2-methylcyclopent-2-enone.

The thermal and photochemical reaction products are consistent with the formation and rearrangement of 4*aH*-carbazole intermediates (7) (Schemes 1 and 2). In the pyrolyses, the carbazoles (4, X = Me) and (5) could arise from competing [1,5]sigmatropic shifts of the ring-junction methyl group, *via* (8) and (9); formation of the demethylated carbazoles (4, X = H) results from loss of this methyl group, possibly from (7) or (8). The minor thermal products (5) could be formed from (9) by [1,5] and higher order shifts of methyl and hydrogen; as far as we are aware, this reaction provides the first example of the transfer of a substituent from one aromatic ring to another in this kind of cyclisation process.

The major photolysis products, the cyclopentaquinolines (6), which are not observed in the pyrolyses, are probably also

formed from the intermediates (**7**) in a further photochemical process which starts as an aza-di- π -methane rearrangement⁷ to give the diradical (**10**) which rearranges to (**11**). The other photolysis product, the demethylated carbazole (**4**, X = H), could again arise from (**7**) in the energetic state initially formed by collapse of the diradical produced when nitrogen is extruded from the starting benzotriazole. The intermediate (**11**) is clearly related to 3a*H*-indene (**1a**), and additional evidence was sought for it. Although (**11a**) and (**11b**) can aromatise rapidly by a [1,5] hydrogen shift, the corresponding [1,5] methyl shift in (**11c**) will be less favourable, and it was in anticipation of the likely intermediacy of (**11**) that the pentamethylphenylbenzotriazole (**3c**) was investigated. In common with 3a*H*-indenes, (**11c**) was expected to undergo cycloaddition reactions. When the benzotriazole (**3c**) was photolysed in the presence of acrylonitrile neither cyclopentaquinolines nor carbazoles were formed; the major product (45%) was the adduct (**12**), formed regio- and stereo-selectively, presumably by an 8 (or 12) + 2 concerted cycloaddition of the highly reactive (**11**) to acrylonitrile.† The intermediate (**7**) is not intercepted in this way, presumably because extended cycloaddition to it would disrupt the aromaticity of the benzo ring.

† The regioselectivity can be rationalised on the basis of the frontier orbital coefficients (*cf.* ref. 8). MNDO calculations with full geometry optimisation⁹ for unsubstituted (**11**, R = H) predict the following orbital coefficients for the π -type HOMO (*E*, -8.3 eV; C-1 -0.33, C-9 0.33) and the LUMO (*E*, -1.1 eV; C-1 0.20, C-9 0.46). Although the more favourable interaction is predicted to be between the LUMO of acrylonitrile and the HOMO of (**11**) (ΔE ca. 8.3 eV) these coefficients suggest that the cyclisation would be non-regioselective. However, interaction of the HOMO of acrylonitrile, for which the largest coefficient is on C-2,⁸ and the LUMO of (**11**) (ΔE ca. 9.5 eV) leads to the observed regioselectivity.

The structure of (**12**) was confirmed by X-ray crystallography.§ The intermediate (**11b**) aromatised too fast to be intercepted by acrylonitrile; the only product (53%) was an isomeric mixture of 2 + 2 cycloadducts (**13**) of the cyclopentaquinoline (**6b**) with acrylonitrile.

Thus, although 4a*H*-carbazoles have not yet been isolated, the present results are all consistent with their intermediacy; the products are analogous to those obtained in reactions where 3a*H*-benzimidazoles have been proposed as intermediates, indicating an underlying similarity of reactivity in these systems.

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§ Determined by Dr D. J. Williams of this department.