

Preparation and Rearrangement of 6a-Methyl-6a*H*-benzo[*a*]carbazole and 11b-Methyl-11b*H*-benzo[*c*]carbazole

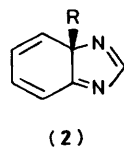
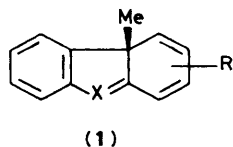
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The non-aromatic benzocarbazoles (**4**) and (**10**) are isolable stable compounds; (**4**) are produced by photolysis of the benzotriazoles (**3**), and on further irradiation undergo aza-di- π -methane rearrangement to give the indenoquinolines (**5**), whilst as expected (**10**) is photostable.

We have recently reported the generation of some 4a*H*-carbazoles (**1**, X = N) in which the peripheral conjugation is interrupted by a tetrahedral carbon atom at a ring junction.¹ In common with the related 4a*H*-fluorenes (**1**, X = CH)² and 3a*H*-benzimidazoles (**2**),³ these unusual compounds readily rearrange under thermal or photochemical conditions, the rearrangement being so fast as to preclude their isolation. With the aim of increasing the life-time of 4a*H*-carbazoles, we have now investigated the 6a*H*-benzo[*a*]carbazoles (**4**) and the 11b*H*-benzo[*c*]carbazole (**10**), and find that fusion of the additional benzene ring allows the isolation and study of these ring systems, confirming our earlier mechanistic proposals.¹

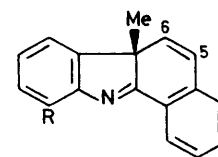
Although thermal decomposition of the benzotriazole (**3a**), m.p. 135–137 °C, resulted in a complex mixture, irradiation



(3)

a; R = H

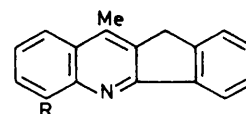
b; R = Me



(4)

a; R = H

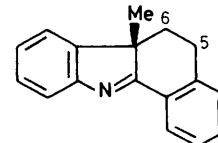
b; R = Me



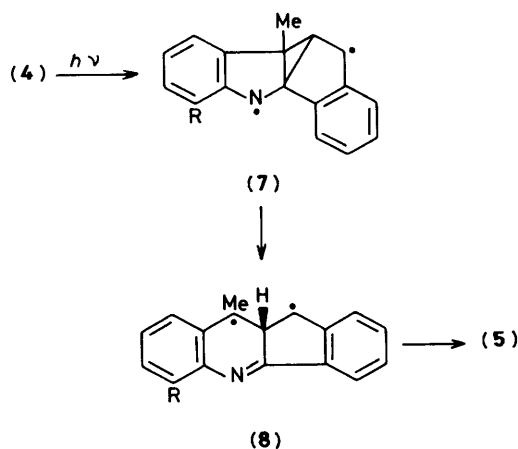
(5)

a; R = H

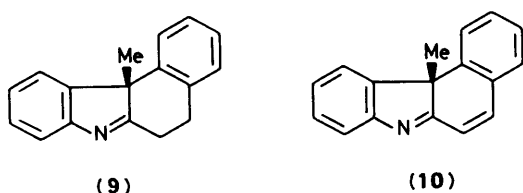
b; R = Me



(6)



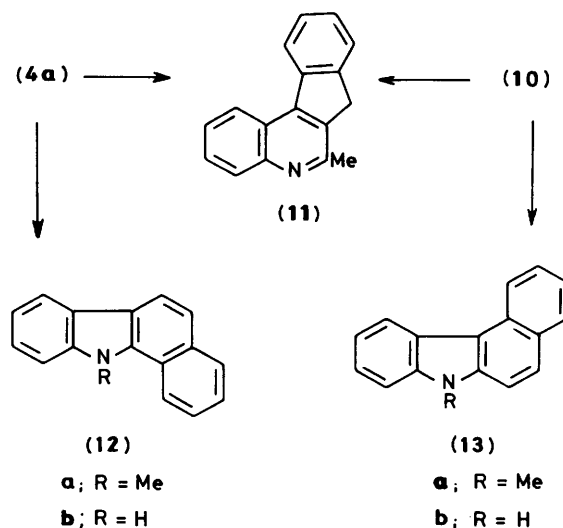
Scheme 1



of an acetonitrile solution at 300 nm led to three products. That the first product was the required 6aH-benzo[a]carbazole (4a) (38%) was apparent from its n.m.r. spectrum which showed *inter alia* a methyl singlet at δ 1.45 and doublets (J 8.6 Hz) for H-5 and H-6 at 6.43 and 6.52. The second product, m.p. 118–120 °C, which in a subsequent experiment was shown to arise by photochemical rearrangement of (4a), was assigned the indenoquinoline structure (5a) (21%), and this was confirmed by independent synthesis by Friedlander condensation of 2-aminoacetophenone with indan-1-one. The structure and chemistry of the third product, a red compound, which results from a novel molecular rearrangement is discussed separately.⁴ Irradiation of (3b), m.p. 150.5–152 °C, similarly but at 254 nm, gave the 6aH-benzo[a]carbazole (4b) (25%), more of its rearrangement product (5b) (42%), m.p. 110–112 °C, and an analogous red product (20%).⁴

The key 6aH-benzo[a]carbazole (4a) was also prepared by a non-photochemical route from the known dihydro-compound (6),⁵ by radical bromination using *N*-bromosuccinimide followed by dehydrobromination with 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) as base. The product from this reaction sequence was identical with that isolated from the photolysis of the benzotriazole (3a). The photochemical rearrangement of the 6aH-benzo[a]carbazoles (4) to the quinolines (5) is analogous to the rearrangement of 4aH-carbazoles,¹ and probably proceeds by a similar mechanism involving an aza-di- π -methane rearrangement⁶ via the di-radical intermediates (7) and (8) (Scheme 1).

Since the related dihydro-11bH-benzo[c]carbazole (9) is also readily available,⁵ its conversion into the corresponding 11bH-benzo[c]carbazole (10) was undertaken. This was achieved (64%) simply by dehydrogenation with benzene-seleninic anhydride and iodoxybenzene⁷ in refluxing benzene. The 11bH-benzo[c]carbazole (10) is a stable crystalline solid,



Scheme 2

m.p. 90–92 °C, which, in contrast with its isomer (4a) and in agreement with the mechanism of Scheme 1, is unchanged on irradiation.

Both the benzo derivatives (4a) and (10) of 4aH-carbazole, in common with their non-benzo fused analogues,¹ rearrange on flash vacuum pyrolysis at 640 °C and 3×10^{-2} mmHg. The 6aH-benzo[a]carbazole (4a) gave the benzo[a]carbazoles (12a) (24%) and (12b) (32%), together with the 'angular' indenoquinoline (11) (23%). Under identical conditions the isomeric benzannelated 4aH-carbazole (10) gave the benzo[c]carbazoles (13a) (12%) and (13b) (19%) and the same indenoquinoline (11) (47%) (Scheme 2). The isolation of (11) from both benzo fused derivatives suggests that a common, spiro, intermediate is involved in its formation, and it is possible to rationalise the formation of (11) and the benzo-carbazoles (12a) and (13a) in terms of thermally allowed [1,5]-sigmatropic rearrangements. Loss of the methyl group to give the demethylated compounds (12b) and (13b) must occur from one of the intermediates in the rearrangement, since pyrolysis of the substituted carbazole (13a) at 640 °C afforded no demethylated product.

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