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

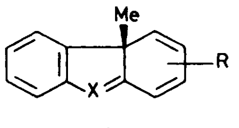
Janusz J. Kulagowski, Glynn Mitchell, Christopher J. Moody, and Charles W. Rees

Department of Chemistry, Imperial College of Science and Technology, London SW7 2AY, U.K.

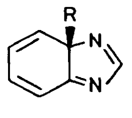
The non-aromatic benzocarbazoles (**4**) and (**10**) are isolable stable compounds; (**4**) are produced by photolysis of the benzotriazoles (**3**), and on further irradiation undergo aza-di-π-methane rearrangement to give the indenoquinolines (**5**), whilst as expected (**10**) is photostable.

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]

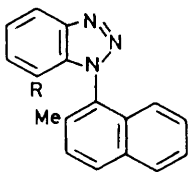
Although thermal decomposition of the benzotriazole (**3a**), m.p. 135—137 °C, resulted in a complex mixture, irradiation



(**1**)



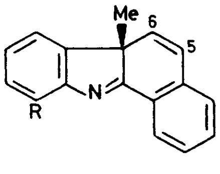
(**2**)



(**3**)

a; R = H

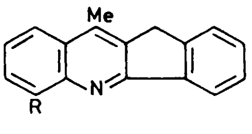
b; R = Me



(**4**)

a; R = H

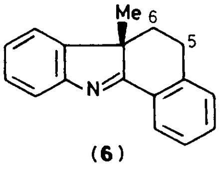
b; R = Me



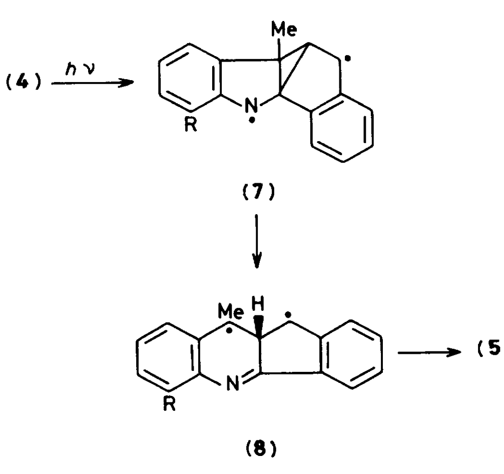
(**5**)

a; R = H

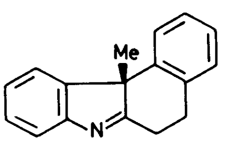
b; R = Me



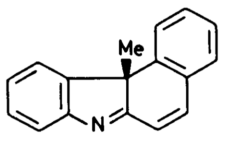
(**6**)



Scheme 1



(9)

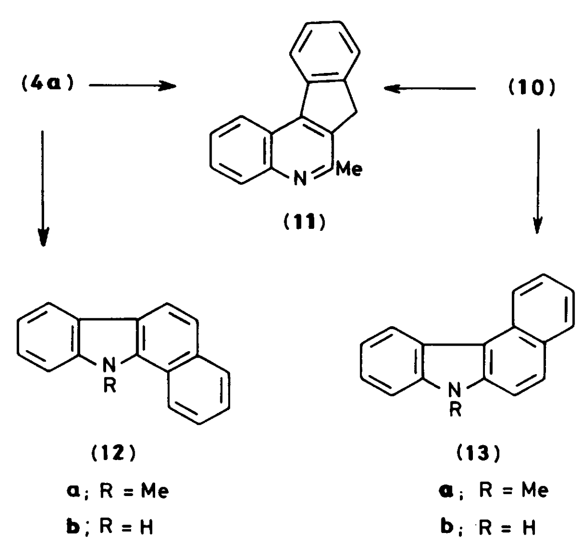


(10)

of an acetonitrile solution at 300 nm led to three products. That the first product was the required 6a*H*-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 6a*H*-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 6a*H*-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 6a*H*-benzo[*a*]carbazoles (**4**) to the quinolines (**5**) is analogous to the rearrangement of 4a*H*-carbazoles,[1] and probably proceeds by a similar mechanism involving an aza-di-π-methane rearrangement[6] *via* the di-radical intermediates (**7**) and (**8**) (Scheme 1).

Since the related dihydro-11b*H*-benzo[*c*]carbazole (**9**) is also readily available,[5] its conversion into the corresponding 11b*H*-benzo[*c*]carbazole (**10**) was undertaken. This was achieved (64%) simply by dehydrogenation with benzeneseleninic anhydride and iodoxybenzene[7] in refluxing benzene. The 11b*H*-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 4a*H*-carbazole, in common with their non-benzo fused analogues,[1] rearrange on flash vacuum pyrolysis at 640 °C and 3×10^{-2} mmHg. The 6a*H*-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 4a*H*-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 benzocarbazoles (**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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