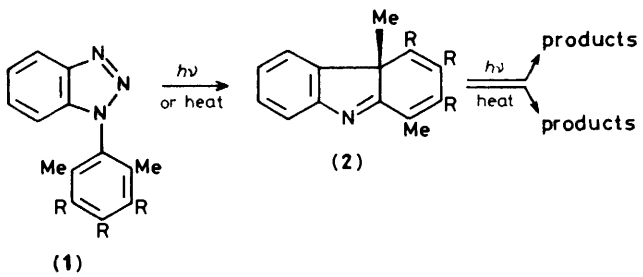
Preparation and Rearrangement of 6a-Methyl-6a*H*-benzo[*a*]carbazole and 11b-Methyl-11b*H*-benzo[*c*]carbazole

Janusz J. Kulagowski, Christopher J. Moody, and Charles W. Rees
Department of Chemistry, Imperial College of Science and Technology, London SW7 2AY

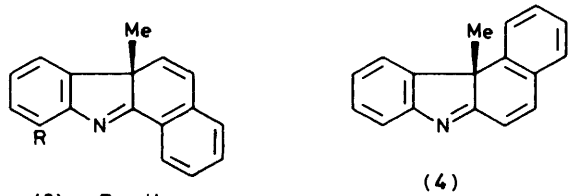
The benzo derivatives (**3**) and (**4**) of 4a-methyl-4a*H*-carbazole are isolable compounds. The 6a-methyl-6a*H*-benzo[*a*]carbazoles (**3a** and **b**) are formed by photolysis of the benzotriazoles (**7a** and **b**) (Scheme 3), but are transformed on further irradiation into the linear indenoquinolines (**10a** and **b**) by an aza-di-π-methane rearrangement. Compound (**3a**) was also prepared by bromination–dehydrobromination of its dihydro derivative (**13**) (Scheme 4); 11b-methyl-11b*H*-benzo[*c*]carbazole (**4**) was prepared by oxidation of its dihydro derivative (**18**) with benzeneseleninic anhydride (Scheme 5). Whilst compound (**3a**) is readily isomerised to the indenoquinoline (**10a**) on irradiation, compound (**4**) is unchanged; this is in keeping with the diradical structures proposed as intermediates in the aza-di-π-methane rearrangement. Flash vacuum pyrolysis of the benzo[*a*]carbazole (**3a**) gives benzo[*a*]carbazoles (**21a**) and (**21b**), together with the angular indenoquinoline (**22**). Flash vacuum pyrolysis of the benzo[*c*]carbazole (**4**) similarly gives benzo[*c*]carbazoles (**23a**) and (**23b**), and the same indenoquinoline (**22**) (Scheme 7). The spiro compound (**25**) is proposed as a common intermediate in the conversion of both compounds (**3a**) and (**4**) into the quinoline (**22**).

In the preceding paper we have described the generation of 4a*H*-carbazoles (**2**; R = H or Me) by thermal or photochemical decomposition of the 1-arylbenzotriazoles (**1**).[1] However, under the conditions of their generation, the 4a*H*-carbazoles (**2**)



(**1**) (**2**)

readily rearrange, the rearrangement being so fast as to preclude their isolation. With the aim of increasing the life-time of 4a*H*-carbazoles, we have investigated the effect of the fusion of an additional benzene ring, and find that the 6a*H*-benzo[*a*]-carbazoles (**3**) and the isomeric 11b*H*-benzo[*c*]carbazole (**4**) are isolable compounds.[2] We now report in full our study of the preparation and rearrangement of these unusual heterocyclic systems.

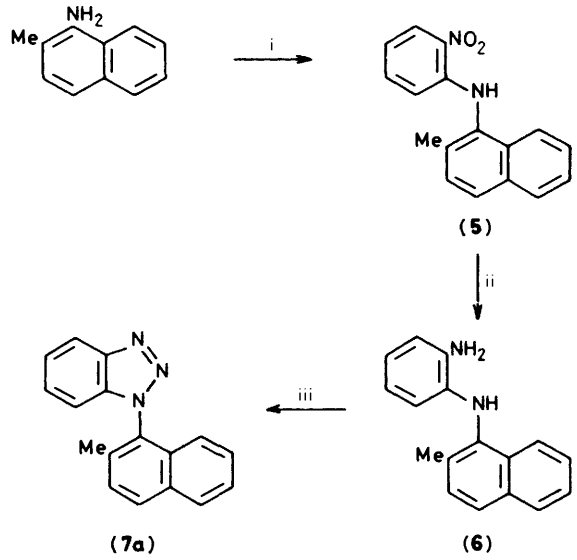


(**3**) **a**; R = H
b; R = Me

(**4**)

Results and Discussion

Preparation of 6a-*Methyl*-6aH-*benzo*[a]*carbazoles* (**3**).—Our initial approach to the 6a*H*-benzo[*a*]carbazole ring system was similar to that used for the generation of the analogous 4a*H*-carbazoles, and involved the decomposition of 1-naphthylbenzotriazoles. The starting benzotriazole (**7a**) was prepared in a conventional way from 2-methyl-1-naphthylamine (Scheme 1), although under protic diazotisation of the diarylamine (**6**)

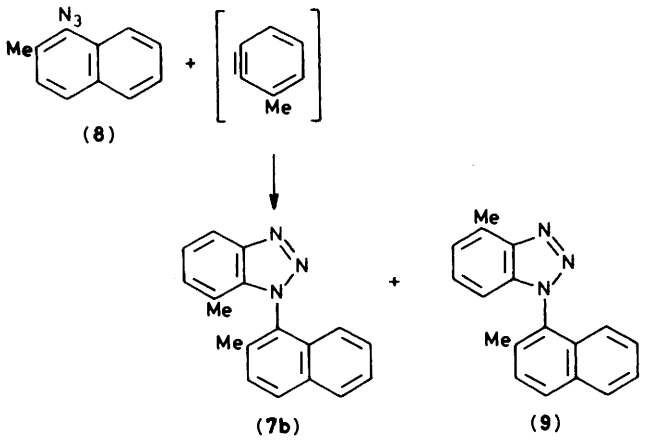


(**7a**) (**6**) (**5**)

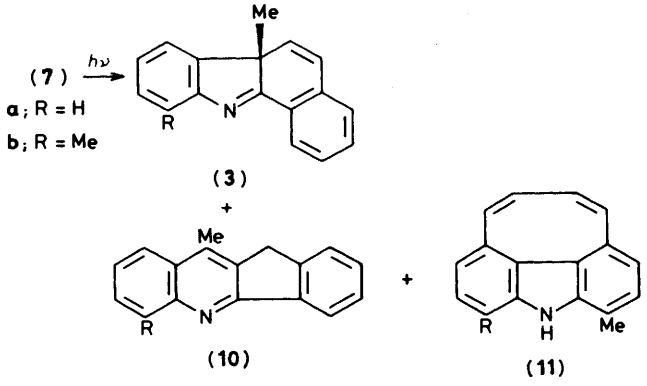
Scheme 1. *Reagents*: i, 2-fluoronitrobenzene, KF, 180 °C, 63 h; ii, H_2, Pd–C, EtOH; iii, i-$C_5H_{11}ONO$, benzene

the yields of the benzotriazole (**7a**) were somewhat irreproducible. This problem was overcome by diazotisation of the freshly prepared amine (**6**) under aprotic conditions with isopentyl nitrite in refluxing benzene. The 7-methylbenzotriazole (**7b**) was prepared by cycloaddition of 1-azido-2-methylnaphthalene (**8**) to 3-methylbenzyne, generated from 3-methylanthranilic acid, followed by separation from the regioisomer (**9**) (Scheme 2).

Although flash vacuum pyrolysis (FVP) of the benzotriazole (**7a**) at 640 °C gave a complex mixture, irradiation of an acetonitrile solution at 254 nm led to three products (Scheme 3), which could be separated by careful chromatography. The first product was identified as the required 6a*H*-benzo[*a*]carbazole



Scheme 2.



Scheme 3.

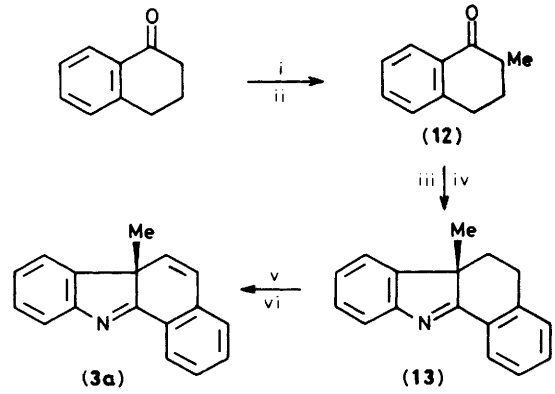
(**3a**) (24%) from its ^{1}H n.m.r. spectrum which showed a methyl signal at δ 1.45 and doublets for 5-H and 6-H at δ 6.52 and 6.43, in addition to aromatic signals, and by comparison with an independently prepared specimen (see below).

The second and major (31%) component, which in a subsequent experiment was shown to arise by photochemical rearrangement of compound (**3a**) (see below), was identified as the indenoquinoline (**10a**) on the basis of its spectral properties, and this was confirmed by independent synthesis by a Friedlander quinoline synthesis involving condensation of 2-aminoacetophenone with indan-1-one. The third product, a red compound, was identified as the cyclo-octa[*def*]carbazole (**11a**) (30% based on consumed starting material). The chemistry of this compound has been discussed elsewhere.[3]

When the benzotriazole (**7a**) was irradiated at 300 nm, the relative yield of the 6a*H*-benzo[*a*]carbazole (**3a**) (30%) was increased with respect to its rearrangement product the indenoquinoline (**10a**) (21%).

Irradiation of the 7-methylbenzotriazole (**7b**) at 254 nm gave analogous results, the 6a*H*-benzo[*a*]carbazole (**3b**), the indenoquinoline (**10b**), and the cyclo-octa[*def*]carbazole (**11b**) being formed in 25, 42, and 20% yield respectively based on consumed starting material.

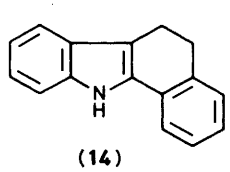
The 6a*H*-benzo[*a*]carbazole (**3a**) was prepared independently by a non-photochemical route from the known dihydro compound (**13**)[4] (Scheme 4). 2-Methyl-1-tetralone (**12**) was prepared by direct methylation of the lithium enolate of 1-tetralone with iodomethane in the presence of hexamethylphosphoramide (HMPA), although the product was always contaminated with unchanged 1-tetralone. This mixture of



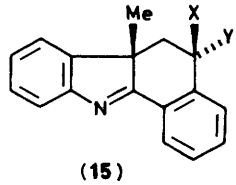
Scheme 4. *Reagents:* i, LDA, THF, −78 °C; ii, MeI, HMPA; iii, $PhNHNH_2$, 105 °C; iv, AcOH, $BF_3 \cdot Et_2O$, reflux; v, NBS, AIBN, CCl_4, reflux; vi, DBU, benzene, reflux

ketones was converted into the corresponding mixture of phenylhydrazones which, on refluxing in acetic acid containing boron trifluoride–diethyl ether, gave the required carbazolenine (**13**), which was readily separated from the indole (**14**) impurity by virtue of its greater basicity. This method of effecting the Fischer cyclisation represents a considerable improvement, both in ease of manipulation and yield of product obtained, over the literature procedure in which polyphosphoric acid is used.[4]

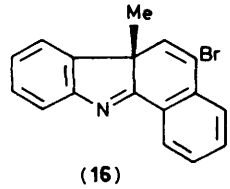
Attempts to dehydrogenate the dihydro compound (**13**) to the 6a*H*-benzo[*a*]carbazole (**3a**) directly, using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in refluxing toluene,[5] benzeneseleninic anhydride (BSA) in chlorobenzene at 100 °C,[6] or selenium dioxide in ethyl acetate,[7] led only to recovery of starting material. Use of the last reagent in acetic acid–acetic anhydride resulted in a complex mixture of polar components. However, benzylic bromination was more successful. Thus irradiation of a refluxing solution of the carbazolenine (**13**) in tetrachloromethane containing suspended *N*-bromosuccinimide (NBS) gave three products together with some unchanged starting material. One of these was isolated as a crystalline solid, and identified as the β-bromide (**15a**) on the basis of n.m.r. coupling constants. The other two products were inseparable, but their spectroscopic properties indicated them to be the α-bromide (**15b**) and the vinyl bromide (**16**). The relative yields of these products were dependent on reaction conditions, and the



(**14**)



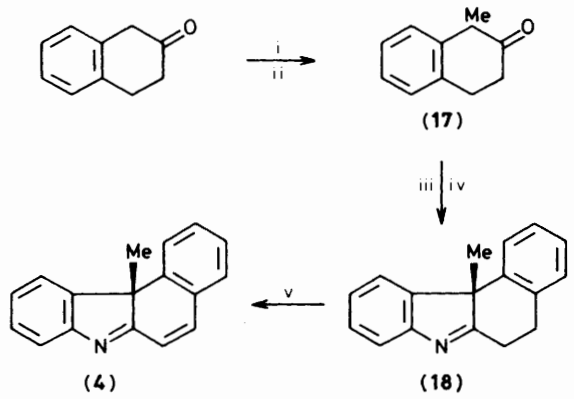
(**15**)
a; X = Br, Y = H
b; X = H, Y = Br
c; X = Y = Br



(**16**)

highest yields of monobromides (**15a**) and (**15b**) were obtained using 1.25 equiv. of NBS in refluxing tetrachloromethane with irradiation in the presence of a trace of azobisisobutyronitrile (AIBN) as radical initiator. Under these conditions, all of the starting material was consumed to give the α-bromide (**15b**) as the major product. The presence of the *gem*-dibromide (**15c**) was also detected but its instability precluded isolation; on chromatography rapid elimination occurred to give the vinyl bromide (**16**). Smooth elimination of hydrogen bromide occurred from both bromides (**15a**) and (**15b**) in treatment with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in refluxing benzene to give the 6a*H*-benzo[*a*]carbazole (**3a**) in good yield. This benzocarbazole was stable under non-photolytic conditions and was purified by short-path distillation.

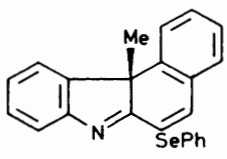
Preparation of 11b-*Methyl*-11bH-*benzo*[c]*carbazole* (**4**).—The 11b*H*-benzo[*c*]carbazole (**4**) was prepared by a similar strategy to that described for the 6a*H*-benzo[*a*]isomer (Scheme 5). 1-Methyl-2-tetralone (**17**) was prepared in excellent yield by



Scheme 5. *Reagents:* i, Pyrrolidine, H^+ cat; ii, MeI; iii, $PhNHNH_2$, benzene, reflux; iv, EtOH, HCl, 2 °C; v, BSA, PhCl, 100 °C

methylation of 2-tetralone *via* its pyrrolidine enamine,[8] and converted into its phenylhydrazone. On being refluxed in acetic acid the phenylhydrazone gave a carbazolenine (61%) which, unexpectedly, was found to be identical with the carbazolenine (**13**) derived from the isomeric ketone. In retrospect this result is not too surprising since similar 'Plancher rearrangements' have been reported,[4] and are believed to involve successive Wagner–Meerwein shifts. The required carbazolenine (**18**) could be prepared, however, by treatment of the phenylhydrazone of (**17**) with cold ethanolic hydrogen chloride.[4]

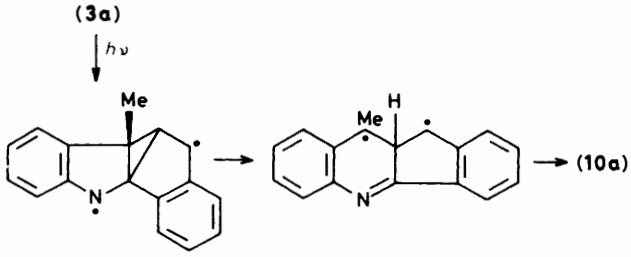
Dehydrogenation of the carbazolenine (**18**) proved to be easier than that for the benzo[*a*] isomer (**13**) presumably because of the extra activation provided by the imine group. Although DDQ in toluene gave a complex mixture, dehydrogenation occurred on treatment with BSA in chlorobenzene to give 11b-methyl-11b*H*-benzo[*c*]carbazole (**4**) in 49% yield. In addition to the required product, substantial quantities of the 6-phenylseleno derivative (**19**) were also obtained. Analogous formation of vinyl selenides has been observed in the oxidation



(**19**)

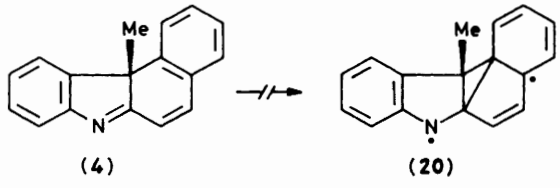
of steroidal ketones with BSA,[9] and is thought to involve low-valent selenium species as the seleniating agents. A solution to this problem makes use of a co-oxidant, and iodylbenzene has been found to be particularly effective both in suppressing side-reactions and allowing catalytic quantities of BSA to be used.[9] Application of these conditions to the dehydrogenation of the carbazolenine (**18**) resulted in an improved yield (64%) of the 11b*H*-benzo[*c*]carbazole (**4**) at the expense of the vinyl selenide (**19**). As with the 6a*H*-benzo[*a*]isomer, compound (**4**) could be purified by short-path distillation, and was obtained as a gum which later solidified.

Rearrangement.—Irradiation of an acetonitrile solution of 6a*H*-benzo[*a*]carbazole (**3a**) at 254 nm gave two products. The minor (3%) product was shown to be benzo[*a*]carbazole (**21a**), whilst the major product (40%) was the indenoquinoline (**10a**). This photochemical rearrangement of 6a*H*-benzo[*a*]carbazoles (**3**) to quinolines (**10**) is analogous to the rearrangement of 4a*H*-carbazoles,[1] and probably proceeds by a similar mechanism involving an aza-di-π-methane rearrangement[10] (Scheme 6). The benzo[*c*] derivative (**4**), in contrast with its isomer (**3a**) and in agreement with the mechanism in Scheme 6, is un-

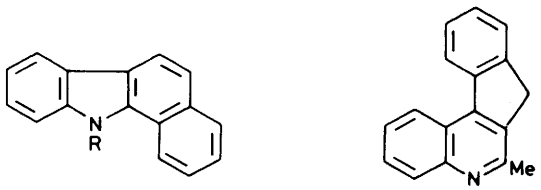


Scheme 6.

changed on irradiation. Presumably the first step of the aza-di-π-methane rearrangement is unfavourable in this case owing to the more extensive disruption of aromaticity in the formation of the analogous diradical intermediate (**20**).

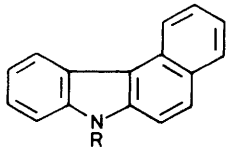


Both of the benzo derivatives (**3a**) and (**4**) of 4a*H*-carbazole, in common with their non-benzo-fused analogues,[1] rearrange on FVP at 640 °C and 0.03 mmHg. The 6a*H*-benzo[*a*]carbazole (**3a**) gave three products, the major of which was benzo[*a*]carbazole (**21a**) (32%). The second product was the corresponding *N*-methylbenzo[*a*]carbazole (**21b**) (24%), and the third product, which was very similar to the 'linear' indenoquinoline (**10a**) derived from photolysis of (**3a**), was assigned the 'angular' indenoquinoline structure (**22**) (23%). The structure (**22**) was confirmed by ^1H n.m.r. studies including nuclear Overhauser effect difference (n.O.e.d.) experiments and the use of a lanthanide shift reagent. In the n.O.e. experiment pre-irradiation of the methylene CH_2 resulted in enhancement of the signals of the methyl group and an aromatic proton. Pre-irradiation of the methyl group enhanced only the methylene signal, suggesting that the methyl group was adjacent to the



(21)
a; R = H
b; R = Me

(22)



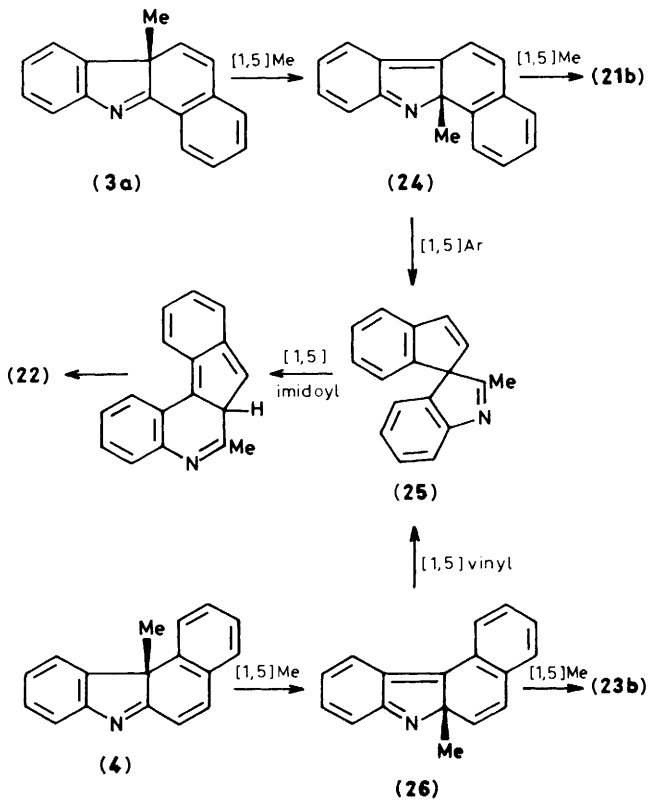
(23)
a; R = H
b; R = Me

quinoline nitrogen. This was confirmed by the addition of Eu(fod)$_3$,* which exerted a large effect on the chemical shift of the methyl group.

Under identical FVP conditions, the isomeric benzannelated 4a*H*-carbazole (**4**) gave the benzo[*a*]carbazoles (**23a**) (19%) and (**23b**) (12%), and the same indenoquinoline (**22**) (47%).

Both *N*-methylated carbazoles (**21b**) and (**23b**) are probably formed by two subsequent [1,5]methyl migrations. Loss of the methyl groups to give the demethylated compounds (**21a**) and (**23a**) must occur during the course of these migrations rather than from the nitrogen of the final product, since FVP of the *N*-methyl compound (**23b**) at 640 °C gave no demethylated product. This loss of methyl probably results from radical cleavage competing with [1,5]methyl migration, analogous to that reported in the thermolysis of 5,5-dimethylcyclohexa-1,3-diene.[11] The isolation of the indenoquinoline (**22**) from both benzo-fused derivatives suggests that a common intermediate is involved in its formation. The spiro intermediate (**25**) is the most likely candidate (Scheme 7).

The 11a*H*-benzo[*a*]carbazole intermediate (**24**), formed by a [1,5]methyl shift in (**3a**), can undergo competing [1,5]methyl or [1,5]aryl migration to give the *N*-methylated carbazole (**21b**) or the spiro intermediate (**25**) respectively. Its benzo[*c*] counterpart (**26**) can likewise undergo competing [1,5]methyl or [1,5]vinyl migrations to give the *N*-methyl compound (**23b**) or the same spiro intermediate (**25**). The greater proportion of the indenoquinoline (**22**) formed on FVP of compound (**4**) may reflect the greater migratory aptitude of vinyl over aryl groups.



Scheme 7.

* fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionate.

Experimental

For general points see ref. 1.

1-(2-*Methylnaphthyl*)*benzotriazole* (**7a**).—A mixture of 2-methyl-1-naphthylamine (2 equiv.), 2-fluoronitrobenzene (1 equiv.), and anhydrous potassium fluoride (1.2 equiv.) was heated at 180 °C and stirred for 63 h. Work-up and chromatography as before [1] gave 2-*methyl*-N-(2-*nitrophenyl*)-1-*naphthylamine* (**5**) (52%) as yellow prisms, m.p. 142—144 °C (from ethanol–benzene) (Found: C, 73.2; H, 5.05; N, 10.0. $C_{17}H_{14}N_2O_2$ requires C, 73.4; H, 5.1; N, 10.1%); $\nu_{max.}$(CCl_4) 3 360, 1 620, 1 500, and 1 275 cm^{-1}; δ (90 MHz; CCl_4) 2.42 (3 H, s), 6.2—8.3 (10 H, m), and 9.43 (1 H, br); *m/z* 278 (M^+, base).

A suspension of 2-methyl-*N*-(2-nitrophenyl)-1-naphthylamine (**5**) (2.78 g, 10 mmol) and palladium–charcoal (5%; 638 mg) in methanol (50 ml) was stirred vigorously under an atmosphere of hydrogen until uptake of gas ceased (observed uptake 745 ml; calc. 721 ml). The mixture was filtered through Celite, and the filtrate was evaporated to give the crude amine (**6**) as a green gum. This gum was dissolved in benzene (40 ml) and isopentyl nitrite (1.75 g, 15 mmol) was added and the mixture was heated under reflux for 4 h. Evaporation of the solvent and chromatography gave 1-(2-*methylnaphthyl*)-*benzotriazole* (**7a**) (1.30 g, 50%), m.p. 135—137 °C (Found: C, 78.4; H, 5.0; N, 16.15. $C_{17}H_{13}N_3$ requires C, 78.7; H, 5.05; N, 16.2%); $\lambda_{max.}$(EtOH) 225 (log ε 4.90). 259sh (4.08), 263 (4.10), 276sh (4.12), 285 (4.10), 306sh (3.64), and 321 nm (3.21); δ (90 MHz; CCl_4) 2.12 (3 H, s), 6.80—7.15 (2 H, m), 7.21—7.60 (5 H, m), 7.76—8.05 (2 H, m), and 8.18 (1 H, m); *m/z* 259 (M^+), 231, 230 (base), 217, 216, and 115.

In a separate experiment the crude amine (**6**) was treated with conc. hydrochloric acid to give 1-(2-*aminophenyl*)-2-*methyl*-1-*naphthylamine hydrochloride* (**6**)·HCl, m.p. 192—194 °C (from ethanol containing hydrochloric acid) (Found: C, 71.8; H, 6.0; N, 9.8. $C_{17}H_{17}ClN_2$ requires C, 71.8; H, 6.0; N, 9.8%).

7-*Methyl*-1-(2-*methylnaphthyl*)*benzotriazole* (**7b**).—Diazotisation of 2-methyl-1-naphthylamine and treatment with sodium azide in the usual way afforded 1-*azido*-2-*methylnaphthalene* (**8**) (54%) as a pale yellow oil (Found: C, 72.05; H, 5.0; N, 23.0. $C_{11}H_9N_3$ requires C, 72.1; H, 4.95; N, 22.9%); $\nu_{max.}$(neat) 2 100 cm^{-1}; δ (90 MHz; $CDCl_3$) 2.43 (3 H, s), 7.07 (1 H, d, *J* 8.0 Hz), 7.18—7.70 (4 H, m), and 8.03 (1 H, m); *m/z* 183 (M^+), 155, 154 (base), and 140.

A solution of 1-azido-2-methylnaphthalene (**8**) (1.65 g, 9

mmol) and isopentyl nitrite (1.90 ml, 14 mmol) in dichloromethane (80 ml) was heated to reflux, and a solution of 3-methylanthranilic acid (2.00 g, 13 mmol) in acetone (20 ml) was added during 1.5 h. The mixture was heated for a further 2 h; the dark solution was then cooled and evaporated. The residue was partitioned between ether (70 ml) and aqueous sodium hydroxide (2M; 50 ml). The ether layer was separated, washed successively with aqueous sodium hydroxide (2M; 50 ml) and water (2 × 50 ml), and dried ($MgSO_4$). Evaporation of the solvent and chromatography of the residue gave (i) a mixture of isomers [predominantly 4-methyl-1-(2-methylnaphthyl)benzotriazole (**9**)] (740 mg), and (ii) *7-methylnaphthyl)benzotriazole* (**7b**) (520 mg, 21%), m.p. 150.5—152 °C from aqueous ethanol (Found: C, 79.05; H, 5.5; N, 15.1. $C_{18}H_{15}N_3$ requires C, 79.1; H, 5.5; N, 15.35%; δ (250 MHz; $CDCl_3$) 1.79 (3 H, s), 2.11 (3 H, s), 6.84 (1 H, d, *J* 8.5 Hz), 7.13—7.54 (5 H, m), 7.92 (1 H, d, *J* 8.5 Hz), 8.00 (1 H, d, *J* 8.6 Hz), and 8.07 (1 H, d, *J* 8.4 Hz); *m/z* 273 (M^+), 245, 244, 230 (base), and 115.

Photolysis of the Benzotriazole (**7a**).—A solution of the benzotriazole (**7a**) (253 mg) in acetonitrile (200 ml) was irradiated at 254 nm for 10 h. Evaporation of the solvent and chromatography of the residue gave (i) 1-*methylcyclo-octa*[def]-*carbazole* (**11a**) (52 mg, 24%; 30% based on consumed starting material) as a red gum, data discussed elsewhere,[3] (ii) a green gum (157 mg) which n.m.r. spectroscopy indicated to consist of starting benzotriazole (**7a**) (61 mg, 24%), the 6a*H*-benzo[*a*]carbazole (**3a**) [42 mg, 19% (24% based on starting material consumed)], and the indenoquinoline (**10a**) [53 mg, 23% (31% based on starting material consumed)]. The latter two products were identified by comparison with independently prepared materials (see below).

Independent Synthesis of 10-*Methyl*-11H-*indeno*[1,2-b]*quinoline* (**10a**).—A mixture of indan-1-one (0.33 g, 2.5 mmol) and 2-aminoacetophenone (0.34 g, 2.5 mmol) in aqueous ethanol (50%; 4 ml) and conc. hydrochloric acid (1.5 ml) was heated under reflux for 5.5 h. After having cooled, the solution was basified with aqueous ammonia and extracted with ether. The extracts were washed with water, dried over Na_2SO_4, evaporated, and the residue was triturated with light petroleum and recrystallised from ether–light petroleum to give the *title compound* (**10a**) (133 mg, 23%), m.p. 188—120 °C (Found: C, 88.4; H, 5.7; N, 6.1. $C_{17}H_{13}N$ requires C, 88.3; H, 5.7; N, 6.1%); $\lambda_{max.}$(EtOH) 212 (log ε 4.52), 224 (4.43), 256sh (4.53), 262 (4.66), 288 (3.74), 296sh (3.80), 304sh (3.90), 309sh (3.98), 314 (4.09), 321 (4.08), 328 (4.31), 337 (4.13), and 344 nm (4.48); δ (250 MHz; CCl_4) 2.60 (3 H, s), 3.80 (2 H, s), and 7.30—8.30 (8 H, m); *m/z* 231 (M^+, base).

Photolysis of the Benzotriazole (**7b**).—A solution of the benzotriazole (**7b**) (100 mg) in acetonitrile (100 ml) was irradiated at 254 nm for 20 h. Evaporation of the solvent and chromatography of the residue gave (i) 6,10-*dimethyl*-11H-*indeno*[1,2-b]*quinoline* (**10b**) (34 mg, 37%; 42% based on consumed material), m.p. 111—112 °C (from Et_2O-pentane) (Found: C, 87.9; H, 6.2; N, 5.65. $C_{18}H_{15}N$ requires C, 88.1; H, 6.2; N, 5.7%); $\nu_{max.}$(Nujol) 1 620, 1 608, 1 580, and 1 576 cm^{-1}; δ (250 MHz; $CDCl_3$) 2.73 (3 H, s), 2.94 (3 H, s), 3.98 (2 H, s), 7.38—7.64 (5 H, m), 7.88 (1 H, dd, *J* 8.0 and 0.5 Hz), and 8.29 (1 H, m); (ii), 1,10-dimethylcyclo-octa[*def*]carbazole (**11b**) (16 mg, 18%; 25% based on consumed starting material) as a red solid;[3] (iii) 6a,10-*dimethyl*-6aH-*benzo*[a]*carbazole* (**3b**) (20 mg, 22%; 25% based on consumed starting material) as a pale cream solid, m.p. 71.5—73 °C (Found: C, 87.9; H, 6.3; N, 5.6. $C_{18}H_{15}N$ requires C, 88.1; N, 6.2; N, 5.7%); $\nu_{max.}$ 1 561, 1 553, 1 480, 1 471, 1 460, and 1 441 cm^{-1}; δ (250 MHz; $CDCl_3$) 1.43 (3 H, s), 2.66 (3 H, s), 6.43 (1 H, d, *J* 9.0 Hz), 6.52 (1 H, d, *J* 9.0 Hz), 7.10—7.28 (4 H, m), 7.32—7.47 (2 H, m), and 8.03 (1 H, dd, *J* 7 and 2 Hz); *m/z* 245 (M^+, base) and 230; and (iv) starting benzotriazole (**7b**) (11 mg, 11% recovery).

2-*Methyl*-1-*tetralone* (**12**).—n-Butyl-lithium in hexane (1.5M, 75 ml, 0.11 mol) was added to a solution of di-isopropylamine (10.12 g, 0.10 mol) in tetrahydrofuran (THF) (100 ml) at 0 °C. After being stirred for 15 min, the solution was cooled to − 78 °C, and a solution of 1-tetralone (14.6 g, 0.10 mol) in THF (100 ml) was added, followed after 30 min by a mixture of iodomethane (15.7 g, 0.11 mol) and HMPA (21.5 g, 0.12 mol). After 3 h at − 78 °C the mixture was allowed to warm to room temperature, and worked up in the standard way to give a dark coloured oil. Distillation at 122—130 °C and 10 mmHg gave a mixture (14.83 g) of 2-methyl-1-tetralone (**12**) and 1-tetralone [7:3 by g.l.c. analysis (10% OV-17 on 80—100 mesh Chromosorb WAW DMCS; $\frac{1}{8}''$ × 2 m; 100 °C)].

6,6a-*Dihydro*-6a-*methyl*-5H-*benzo*[a]*carbazole* (**13**).—A mixture of 2-methyl-1-tetralone (**12**) and 1-tetralone (*ca.* 7:3, 6.2 g) was heated with phenylhydrazine (4.32 g, 40 mmol) at 105 °C under reduced pressure for 1.25 h. The resulting crude phenylhydrazone was dissolved in a mixture of acetic acid (25 ml) and boron trifluoride–diethyl ether (5.7 g, 40 mmol), and the solution was heated under reflux for 3 h. After the mixture had cooled, aqueous ammonia (15%; 50 ml) was added and the mixture was extracted with ether (1 × 50 ml; 2 × 25 ml). The combined extracts were washed with hydrochloric acid (2M; 4 × 25 ml), dried, and evaporated to leave an orange solid. Recrystallisation from methanol gave 5,6-dihydro-11*H*-benzo[*a*]carbazole (**14**) (1.30 g, 45% based on 1-tetralone consumed), m.p. 163—164 °C (lit.,[12] 163—164 °C). The acid washings from above were re-basified with ammonia and extracted with dichloromethane (4 × 25 ml). The CH_2Cl_2 extracts were dried and evaporated to give a brown oil which was distilled at 122 °C (Kugelrohr) and 0.02 mmHg, to give 6,6a-dihydro-6a-methyl-5*H*-benzo[*a*]carbazole (**13**) (3.60 g, 60% based on 2-methyl-1-tetralone consumed) as an oil which solidified with time, m.p. 95—98 °C (lit.,[4] 98—98.5 °C).

Bromination of the Carbazolenine (**13**).—A mixture of the carbazolenine (**13**) (1.186 g, 5.1 mmol), NBS (1.13 g, 6.35 mmol), and AIBN (20 mg) in tetrachloromethane (25 ml) was irradiated (100 W tungsten lamp) under reflux for 0.5 h, during which all of the suspended solid was observed to float near the surface. The hot suspension was filtered and the filtrate was evaporated to leave an orange syrup, which n.m.r. spectroscopy indicated to consist of the α- and β-bromide (**15b**) and (**15a**), and the *gem*-dibromide (**15c**), with no trace of the vinyl bromide (**16**). Chromatography of the syrup gave (i) a brown gum (55 mg) consisting of the *gem*-dibromide (**15c**) (40%; 1% overall yield), δ (90 MHz; CCl_4) 1.51 (3 H, s, Me), 3.04 (1 H, d, *J* 15 Hz, 6-H), 3.87 (1 H, d, *J* 15 Hz, 6-H), and 7.10—8.30 (8 H, m, ArH), and the vinyl bromide (**16**) (60%); δ (90 MHz; CCl_4) 1.40 (3 H, s, Me), 6.94 (1 H, s, 6-H), and 7.10—8.30 (8 H, m, ArH); *m/z* 311 and 309 (*M*), 296, 294, and 230 (base); (ii) a pale yellow gum (738 mg) consisting of the vinyl bromide (**16**) (30%; 16% overall yield) and 5α-bromo-6,6a-dihydro-6a-methyl-5*H*-benzo[*a*]-carbazole (**15b**) (70%; 32% overall yield), δ (90 MHz; CCl_4) 1.18 (3 H, s, Me), 2.18 (1 H, dd, *J* 13 and 11 Hz, 6-H), 3.02 (1 H, dd, *J* 13 and 7 Hz, 6-H), 5.72 (1 H, dd, *J* 11 and 7 Hz, 5-H), and 7.05—8.20 (8 H, m, ArH); *m/z* 313 and 311 (M^+), 233, 232 (base), 231, 230, 217, and 216; (iii) a sticky brown solid (532 mg) which on trituration with hot light petroleum afforded 5β-*bromo*-6,6a-*dihydro*-6a-*methyl*-5H-*benzo*[a]*carbazole* (**15a**) as a buff solid (413 mg, 26%), m.p. 140—141 °C (from light petroleum–dichloromethane) (Found: C, 65.4; H, 4.4; N, 4.6. $C_{17}H_{14}BrN$ requires C, 65.4; H, 4.5; N, 4.5%); δ (90 MHz; CCl_4–$CDCl_3$) 1.62 (3 H, s, Me), 2.25 (1 H, dd, *J* 15 and 6 Hz, 6-H_β), 2.96 (1 H, d,

J 15 Hz, 6-H_α), 5.76 (1 H, d, *J* 6 Hz, 5-H), 7.10—7.80 (7 H, m, ArH), and 8.08 (1 H, m, ArH); *m/z* 313 and 311 (M^+), 233, 232 (base), 231, 230, 217, and 216.

6a-*Methyl*-6aH-*benzo*[a]*carbazole* (**3a**).—A solution of the β-bromide (**15a**) (312 mg, 1 mmol) and DBU (168 mg, 1.1 mmol) in benzene (10 ml) was refluxed for 1 h, allowed to cool, and filtered, and the filtrate was evaporated. Distillation of the residue at 132 °C (Kugelrohr) and 7 × 10^{-2} mmHg gave 6a-methyl-6a*H*-benzo[*a*]carbazole (**3a**) as a pale green gum (220 mg, 95%); $\nu_{max.}$(film) 3 060, 3 040, 2 980, 2 915, 1 565, 1 555, 1 455, 1 445, 790, 775, and 755 cm^{-1}; $\lambda_{max.}$(EtOH) 209 (log ε 4.15), 243 (4.49), 249 (4.49), and 326 nm (3.88); δ_H (250 MHz; $CDCl_3$) 1.45 (3 H, s, Me), 6.43 (1 H, d, *J* 8.6 Hz, 6-H), 6.52 (1 H, d, *J* 8.6 (Hz, 5-H), 7.22 (2 H, m, ArH), 7.30—7.47 (4 H, m, ArH), 7.68 (1 H, d, *J* 7.5 Hz, 7-H), and 8.01 (1 H, dd, *J* 6.5 and 1.5 Hz, 1-H); δ_C (62.9 MHz; $CDCl_3$) (quaternary) 57.1, 129.2, 136.6, 142.0, 154.7, and 185.4, (non-quaternary) 28.1, 121.4, 121.5, 125.3, 125.6, 126.8, 127.5, 128.1, 128.4, 131.6, and 134.0; *m/z* 232, 231 (M^+, base), 230, 216, 115, and 108; *picrate*, yellow needles, m.p. 163—164 °C (decomp.) (from ethanol) (Found: C, 59.8; H, 3.45; N, 12.1. $C_{23}H_{16}N_4O_7$ requires C, 60.0; H, 3.5; N, 12.2%).

Similar results were obtained by using the α-bromide (**15b**), although in this case the product had to be separated from the vinyl bromide (**16**) by a combination of fractional distillation and careful chromatography.

1-*Methyl*-2-*tetralone* (**17**).—Prepared in 80% yield by the literature method.[8]

6,11b-*Dihydro*-11b-*methyl*-5H-*benzo*[c]*carbazole* (**18**).—A solution of 1-methyl-2-tetralone (**17**) (1.60 g, 10 mmol) and phenylhydrazine (1.19 g, 11 mmol) in benzene (10 ml) was refluxed with a Dean–Stark trap for 0.75 h, after which the solvent was replaced by ethanol (15 ml), and the solution was cooled to 0 °C and saturated with hydrogen chloride. After being kept for 3 days at 2 °C the dark mixture was poured into water (75 ml), and the resulting suspension was basified with aqueous ammonia and extracted with ether (3 × 25 ml). The combined extracts were washed with hydrochloric acid (2M; 3 × 25 ml); the washings were basified with aqueous ammonia and extracted with dichloromethane (4 × 25 ml). The gum remaining after drying ($MgSO_4$) and evaporation of the CH_2Cl_2 extracts was distilled to give the title compound as an orange gum (1.55 g, 66%), b.p. 130 °C (Kugelrohr) at 0.06 mmHg (lit.,[4] b.p., 159—163 °C at 1 mmHg).

Oxidation of the Carbazolenine (**18**) *with BSA*.—(*a*) BSA (1.80 g, 5 mmol) was added to a solution of the carbazolenine (**18**) (1.09 g, 4.7 mmol) in chlorobenzene (25 ml) at 100 °C. After 2 min, the red solution was cooled, chloroform (25 ml) was added, and the mixture was washed with aqueous potassium hydroxide (10%; 2 × 25 ml), dried ($MgSO_4$), and evaporated. The red residual gum was chromatographed to give (i) diphenyl diselenide (400 mg); (ii) 11b-methyl-6-phenylseleno-11b*H*-benzo[*c*]carbazole (**19**) as an orange gum (518 mg, 29%); $\nu_{max.}$(film) 3 060, 1 550, 1 475, 1 440, 750, 740, and 690 cm^{-1}; $\lambda_{max.}$(EtOH) 207 (log δ 4.48), 253 (4.44), 284sh (3.79), 328 (3.76), and 380 nm (3.75); δ (90 MHz; CCl_4) 1.52 (3 H, s, Me), 6.60 (1 H, s, 5-H), and 6.90—7.84 (13 H, m, ArH); *m/z* 387 (M^+, base), 385, 372, 307, 291, 230, and 145; *picrate*, scarlet prisms, m.p. 149—151 °C (from ethanol) (Found: C, 56.8; H, 3.2; N, 9.1. $C_{29}H_{18}N_4O_7Se$ requires C, 56.6; H, 3.3; N, 9.1%); (iii) 11b-*methyl*-11b*H*-*benzo*[c]*carbazole* (**4**) as an orange gum (529 mg, 49%), b.p. 130 °C (Kugelrohr) at 0.05 mmHg, which solidified with time, m.p. 90—92 °C (from light petroleum) (Found: C, 88.1; H, 5.7; N, 6.05. $C_{17}H_{13}N$ requires C, 88.3; H, 5.7; N, 6.1%); $\nu_{max.}$(CCl_4) 3 070, 2 980, 2 920, 2 860, 1 590, 1 445, 1 195, 670, and 635 cm^{-1}; $\lambda_{max.}$(EtOH) 209 (log ε 4.18), 245 (4.31), 330sh (3.76), 354 (3.86), and 391sh nm (3.40); δ_H (250 MHz; $CDCl_3$) 1.55 (3 H, s, Me), 6.79 (1 H, d, *J* 10 Hz, 6-H), 7.05 (1 H, d, *J* 10 Hz, 5-H), 7.19—7.44 (5 H, m, ArH), 7.68 (1 H, dd, *J* 6 and 1 Hz, ArH), 7.73 (1 H, m, ArH), and 7.82 (1 H, d, *J* 7.5 Hz, ArH); δ_C (62.9 MHz; $CDCl_3$) (quaternary) 58.3, 132.0, 141.1, 143.0, 155.2, and 184.9, (non-quaternary) 33.2, 121.4, 121.8, 123.5, 124.6, 127.0, 128.2, 128.5, 130.1, and 139.1; *m/z* 232, 231 (M^+, base), 230, 216, 214, 190, and 189; *picrate*, yellow prisms, m.p. 200—202 °C (decomp.) (from ethanol) (Found: C, 60.3; H, 3.5; N, 12.2. $C_{23}H_{16}N_4O_7$ requires C, 60.0; H, 3.5; N, 12.2%).

(*b*) When the carbazolenine (**18**) (176 mg, 0.75 mmol) was refluxed with a suspension of BSA (67.5 mg, 0.19 mmol) and iodylbenzene (226 mg, 1.13 mmol) in benzene (8 ml) for 1.75 h, a dark mixture was obtained which was filtered, the filtrate was evaporated, and the residue was chromatographed to give (i) diphenyl diselenide as an orange oil (26 mg); (ii) an orange gum (53.6 mg) which n.m.r. spectroscopy indicated to consist of the selenide (**19**) (44%; 8% overall yield), and an unidentified component (56%), δ (90 MHz; CCl_4) 1.18 (3 H, s, Me), 3.15 (1 H, d, *J* 17 Hz), 3.75 (1 H, d, *J* 17 Hz), and 6.80—7.95 (ArH); (iii) the benzo[*c*]carbazole (**4**) (111 mg, 64%).

Photochemical Rearrangement of 6a-*Methyl*-6aH-*benzo*[a]*carbazole* (**3a**).—A solution of compound (**3a**) (226 mg) in acetonitrile (110 ml) was irradiated at 254 nm for 7 h. The solvent was evaporated off and the residue was chromatographed to give (i) 11*H*-benzo[*a*]carbazole (**21a**) (5 mg, 3% based on conversion), m.p. 219—222 °C (lit.,[12] 227—229 °C), undepressed when mixed with an authentic specimen obtained by dehydrogenation of the dihydro compound (**14**) (see below); (ii) recovered starting material (**3a**) (70 mg, 31% recovery); (iii) the indenoquinoline (**10a**) (63 mg, 40% based on conversion).

Thermal Rearrangement of 6a-*Methyl*-6aH-*benzo*[a]*carbazole* (**3a**).—The benzo[*a*]carbazole (**3a**), was distilled at 90 °C and 0.03 mmHg through a quartz tube, maintained at 640 °C, to give a brown gum (140 mg). A portion (106 mg) of the pyrolysate was separated by preparative t.l.c. (p.l.c.) and gave (i) 11-methyl-11*H*-benzo[*a*]carbazole (**21b**) as a buff solid (24 mg, 24% based on conversion), R_F 0.75; m.p. 165—167 °C (from light petroleum–ether), undepressed on admixture with an authentic sample (see below); (ii) 11*H*-benzo[*a*]carbazole (**21a**) as a buff solid (29 mg, 32% based on conversion), R_F 0.50, identical with an authentic specimen (see below); (iii) unchanged starting material as a yellow gum (8 mg, 7% recovery), R_F 0.42; (iv) 6-*methyl*-7H-*indeno*[2,1-c]*quinoline* (**22**) as a pale yellow gummy solid (23 mg, 23% based on conversion), R_F 0.09, which resisted further purification (Found: M^+, 231.1046. $C_{17}H_{13}N$ requires *M*, 231.1048); $\lambda_{max.}$(EtOH) 214sh, 224, 228sh, 237, 245, 274sh, 282, 312sh, 316, and 330 nm; δ(250 MHz; $CDCl_3$) 2.83 (3 H, s, Me), 3.97 (2 H, s, CH_2), 7.42—7.76 (5 H, m, ArH), 8.17 (1 H, d, *J* 7 Hz, 4-H), 8.42 (1 H, d, *J* 7 Hz, 11-H), and 8.64 (1 H, d, *J* 8.5 Hz, 1-H); *m/z* 232, 231 (M^+, base), 230, 216, and 189; *picrate*, yellow microcrystalline powder, m.p. 243—245 °C (decomp.) (from acetonitrile) (Found: C, 60.3; H, 3.45; N, 12.1. $C_{23}H_{16}N_4O_7$ requires C, 60.0; H, 3.5; N, 12.2%).

Thermal Rearrangement of 11b-*Methyl*-11bH-*benzo*[c]*carbazole* (**4**).—The benzo[*c*]carbazole (**4**) (114 mg) was distilled at 100 °C and 0.03 mmHg through a quartz tube maintained at 640 °C. The pyrolysate was separated by p.l.c. to give (i) 7-methyl-7*H*-benzo[*c*]carbazole (**23b**) (11 mg, 12% based on conversion), identical with an authentic specimen (see below); (ii) 7*H*-benzo[*c*]carbazole (**23a**) (16 mg, 19% based on conversion), identical with an authentic specimen; (iii) starting material (**4**) (12 mg, 12% recovery); and (iv) the indenoquinoline (**22**) (43 mg, 47% based on conversion).

Independent Syntheses

5,6-*Dihydro*-11H-*benzo*[a]*carbazole* (**14**).—Prepared in 43% yield by the literature method,[12] m.p. 163—164.5 °C (lit.,[12] 163—164 °C).

11H-*Benzo*[a]*carbazole* (**21a**).—An intimate mixture of the dihydro compound (**14**) (1.30 g) and palladium–charcoal (10%; 237 mg) was heated at 215 °C for 0.5 h. After having cooled, the mixture was extracted with boiling chloroform, the extracts were filtered through Celite and evaporated, and the residue was recrystallised from benzene to give the title compound (**21a**) (0.83 g, 64%), m.p. 224.5—225.5 °C (lit.,[12] 227—229 °C).

11-*Methyl*-11bH-*benzo*[a]*carbazole* (**21b**).—The carbazole (**21a**) was methylated with sodium hydride and iodomethane in dimethylformamide (DMF) as described previously[1] to give the *title compound* (**21b**) (59%), m.p. 172.5—173.5 °C (from chloroform) (Found: C, 88.3; H, 5.7; N, 6.1. $C_{17}H_{13}N$ requires C, 88.3; H, 5.7; N, 6.1%); δ (90 MHz; $CDCl_3$) 4.26 (3 H, s), 7.0—7.54 (6 H, m), 7.78—8.04 (3 H, m), and 8.49 (1 H, m); *m/z* 231 (M^+, base), 230, 216, and 202.

7H-*Benzo*[c]*carbazole* (**23a**).—Prepared in 50% yield by the literature method,[12] m.p. 136—138 °C (lit.,[12] 135—136 °C).

7-*Methyl*-7H-*benzo*[c]*carbazole* (**23b**).—Prepared (72%) by *N*-methylation of the carbazole (**23a**) using sodium hydride and iodomethane in DMF, m.p. 117—118 °C (lit.,[13] 117—118 °C).

Acknowledgements

We thank the S.E.R.C. for a studentship (to J. J. K.), and Dr Glynn Mitchell for the preparation and photolysis of compound (**7b**).

References

1 J. J. Kulagowski, C. J. Moody, and C. W. Rees, *J. Chem. Soc., Perkin Trans., 1*, 1985, preceding paper.
2 Preliminary communication, J. J. Kulagowski, G. Mitchell, C. J. Moody, and C. W. Rees, *J. Chem. Soc., Chem. Commun.*, 1985, 650.
3 J. J. Kulagowski, G. Mitchell, C. J. Moody, and C. W. Rees, *J. Chem. Soc., Chem. Commun.*, 1985, 652.
4 M. Nakazaki, K. Yamamoto, and K. Yamagani, *Bull. Chem. Soc. Jpn.*, 1960, **33**, 466.
5 D. Walter and J. D. Hiebert, *Chem. Rev.*, 1967, **67**, 153.
6 D. H. R. Barton, R. A. H. F. Hui, D. J. Lester, and S. V. Ley, *Tetrahedron Lett.*, 1979, 3331.
7 N. Rabjohn, *Org. React.*, 1976, **24**, 261.
8 G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Am. Chem. Soc.*, 1963, **85**, 207.
9 D. H. R. Barton, J. W. Morzycki, W. B. Motherwell, and S. V. Ley, *J. Chem. Soc., Chem. Commun.*, 1981, 1044.
10 *cf.* D. Armesto, J. A. F. Martin, R. Pérez-Ossorio, and W. M. Horspool, *Tetrahedron Lett.*, 1982, **23**, 2149, and references therein.
11 C. W. Spangler and D. L. Boles, *J. Org. Chem.*, 1972, **37**, 1020.
12 M. Nakazaki, *Bull. Chem. Soc. Jpn.*, 1960, **33**, 461.
13 D. R. Roberts and E. H. White, *J. Am. Chem. Soc.*, 1970, **92**, 4861.

Received 31*st May* 1985; *Paper* 5/920