Generation and Rearrangement of 4a*H*-Carbazoles

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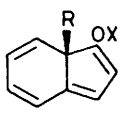
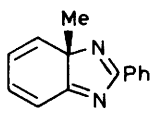
The benzotriazoles (**12a—c**) bearing *ortho*-blocked 1-aryl substituents have been decomposed thermally by flash vacuum pyrolysis, and photochemically by irradiation in acetonitrile at 254 nm. The pyrolyses are complex giving mainly mono- and di-methylcarbazoles from (**12a**), di- and trimethylcarbazoles from (**12b**), and a tetra- and a penta-methylcarbazole from (**12c**). All of these products could be formed by generation of 4a*H*-carbazole intermediates (**24**) with subsequent thermally-allowed sigmatropic rearrangements (Scheme 6). The photolyses give a different set of products consisting mainly of the cyclopentaquinolines (**27a—c**) from (**12a—c**), respectively. These products could be formed from the same 4a*H*-carbazoles (**24**) which now undergo photochemical, aza-di-π-methane, rearrangements to give intermediates (**29**) and hence products (**27**) (Scheme 7). The 4a-methyl intermediate (**29c**) is intercepted as the adduct (**30**) in an extended cycloaddition reaction with acrylonitrile. Key reaction products were synthesized by independent methods.

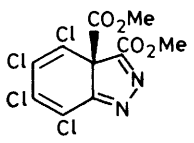
We have recently described the preparation and properties of the isolable 3a*H*-indene derivatives (**1**; X = Me or $SiMe_3$).[1–3] These bicyclic compounds in which the peripheral conjugation is interrupted by a tetrahedral carbon atom at the ring junction are the least stable of all the isomers of indene, as evidenced by MNDO molecular orbital calculations.[4] Heterocyclic analogues of 3a*H*-indene, in which the unsaturated periphery contains one or more nitrogen atoms, are also of interest and we have previously proposed derivatives of the 3a*H*-benzimidazoles (**2**) as reaction intermediates.[5] The highly substituted 3a*H*-indazole (**3**) is an isolable compound,[6] and related bicyclic compounds have been proposed as reaction intermediates.[7]



(**1**)

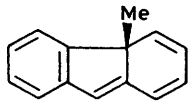


(**2**)

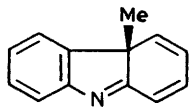


(**3**)

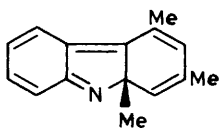
The fact that electron-withdrawing substituents stabilise these unsaturated systems prompted us to investigate whether stabilisation could also be achieved by extending the conjugation into an additional aromatic ring. Therefore the 4a*H*-fluorene (**4**)[8] and 4a*H*-carbazole (**5**) ring systems were chosen as examples where the effect of benzannelation could be studied. The closely related 8a*H*-carbazole (**6**) is presumably an intermediate in the formation of 2,4,9-trimethylcarbazole in the thermolysis of 2-azido-2′,4′,6′-trimethylbiphenyl.[9] We now report the full details of our work on 4a*H*-carbazoles.[10]



(**4**)



(**5**)

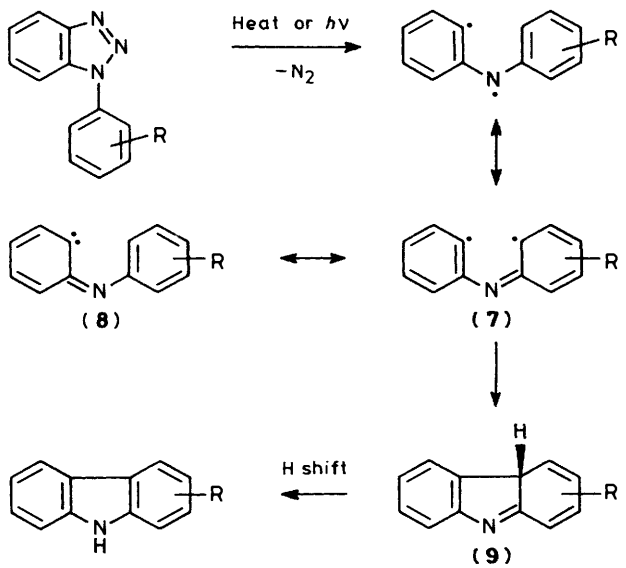


(**6**)

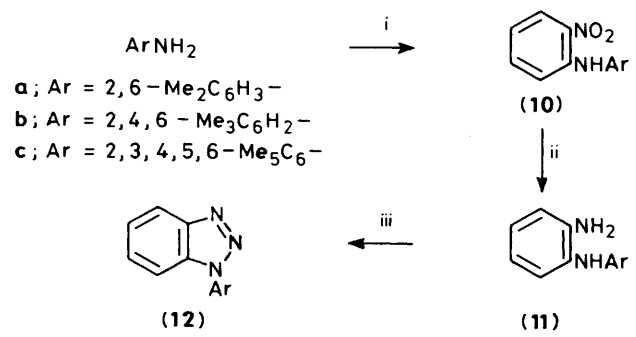
Results and Discussion

The well-known Graebe-Ullmann synthesis of carbazoles by thermal[11] or photochemical[12] extrusion of nitrogen from 1-arylbenzotriazoles is believed to involve cyclisation of the diradical (**7**), or the iminocarbene (**8**), to the 4a*H*-carbazole (**9**) followed by an aromatising hydrogen shift (Scheme 1). By replacing the ring junction hydrogen atom in the 4a*H*-carbazole (**9**) by a methyl group, it was hoped that the final isomerisation to the aromatic carbazole would be suppressed, thereby allowing isolation of the 4a*H*-isomer. Therefore a series of benzotriazoles in which both *ortho*-hydrogens of the 1-aryl group were replaced by methyl groups were prepared, and their decomposition studied under thermal and photochemical conditions.

Preparation of Benzotriazoles.—The route to the required benzotriazoles *via* 2-nitro-and 2-amino-diphenylamines was based on standard literature procedures (Scheme 2). The 2-nitrodiphenylamines (**10**) were prepared from the appropriate aniline by reaction with 2-fluoronitrobenzene in the presence of potassium fluoride.[13] Potassium fluoride is a particularly



Scheme 1.



Scheme 2. *Reagents:* i, 2-Fluoronitrobenzene, KF, heat; ii, H_2, Pd/C, EtOH; iii, HCl, $NaNO_2$, 0 °C, then room temp.

effective base for reactions in which hydrogen fluoride is generated, owing to the formation of the very stable hydrofluoride ion. Typically the reaction was performed in the absence of solvent using a slight excess of anhydrous potassium fluoride and 2 equiv. of the aniline at *ca.* 180 °C. Catalytic hydrogenation of the 2-nitrodiphenylamines gave the corresponding amines (**11**) in good yield. However, the free amines deteriorated rapidly on exposure to air and light, and so were immediately converted into their stable hydrochlorides. These could be handled conveniently, and gave high yields of the 1-arylbenzotriazoles (**12**) on diazotisation in aqueous media.

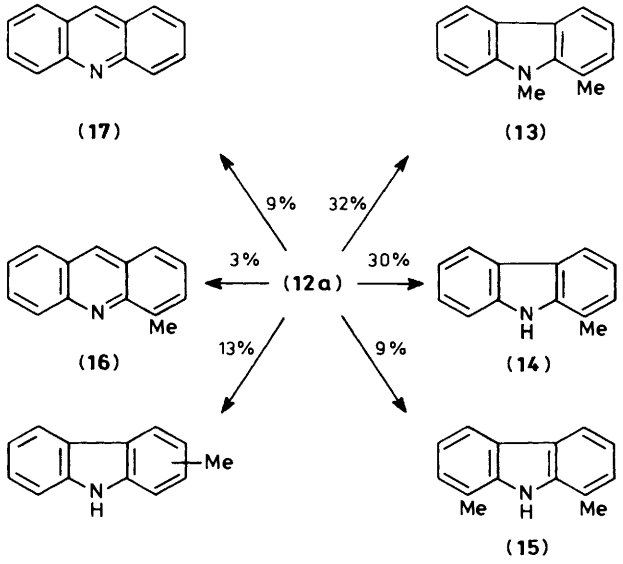
Thermolysis of the Benzotriazoles.—Flash vacuum pyrolysis (FVP) of 1-(2,6-dimethylphenyl)benzotriazole (**12a**) at 640 °C and 0.03 mmHg gave 1,9-dimethyl- (**13**) (32%) and 1-methylcarbazole (**14**) (30%) as the major products together with several minor products. Careful chromatography separated a third product, identified as 1,8-dimethylcarbazole (**15**) (9%) by comparison with independently synthesized material (see below). The independent synthesis was undertaken because of the large variation in melting point quoted for this compound in the literature.* The remaining mixture was analysed by h.p.l.c., and by using the stopped-flow technique the presence of a fourth, unidentified carbazole was detected by u.v. spectroscopy.

Further analysis of the crude pyrolysate revealed the presence of two more minor products, together with some unchanged benzotriazole (**12a**). The two products, which were clearly closely related, were both aromatic but were not carbazoles. On the basis of their spectral properties and considering literature precedent, these products were thought to be acridines or phenanthridines. Acridine itself is reportedly formed in addition to the expected carbazole on pyrolysis of 1-(*o*-tolyl)benzotriazole-5-carboxylic acid,[17] and phenanthridine has been isolated from the pyrolysis of *N*-methylcarbazole at 700 °C.[18] Although the minor products could not be obtained completely pure, nuclear Overhauser effect (n.O.e.) difference experiments clearly indicated that one of them was 1-methylacridine (**16**) (3%), since pre-irradiation of the methyl signal caused enhancement of only a single aromatic proton doublet. The other minor product is acridine itself (**17**) (9%). The results obtained on FVP of the benzotriazole (**12a**) are summarised in Scheme 3.

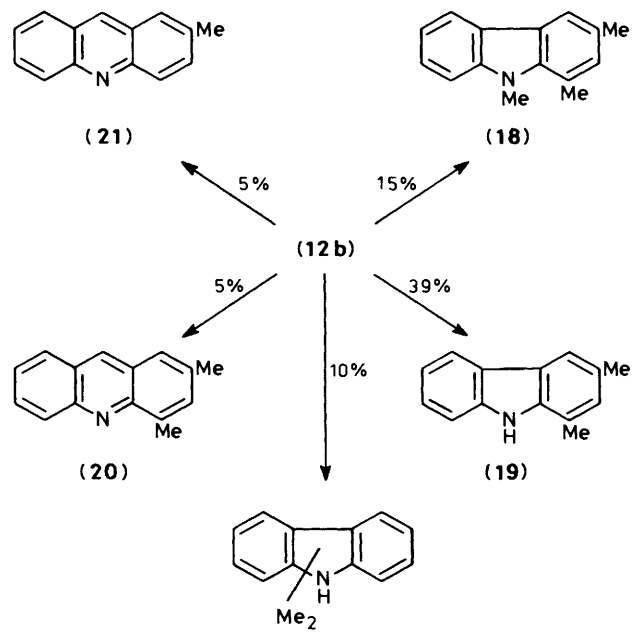
The pyrolysis of 1-(2,4,6-trimethylphenyl)benzotriazole (**12b**) under identical conditions produced similar results, and is summarised in Scheme 4. The identities of 1,3-dimethyl- (**19**), and 1,3,9-trimethyl-carbazole (**18**) were confirmed by comparison with authentic specimens (see below), and h.p.l.c. analysis confirmed the presence of three unidentified *N*-unsubstituted carbazoles (10% total). Two further minor products are tenatively assigned as 1,3-dimethylacridine (**20**) and 3-methylacridine (**21**), by analogy with the previously described acridines (**16**) and (**17**) which they closely resemble.

Pyrolysis of the pentamethylcarbazole (**12c**) gave a more complex mixture from which only the two carbazoles (**22**) and (**23**) (Scheme 5) could be identified, the structure of both products being confirmed by comparison with authentic specimens (see below). The *N*-unsubstituted carbazole (**23**) was accompanied by four other unidentified carbazoles (10% total) as indicated by h.p.l.c., although no acridines could be detected.

The formation of all the identified products from these pyrolyses, with the exception of acridines which arise by

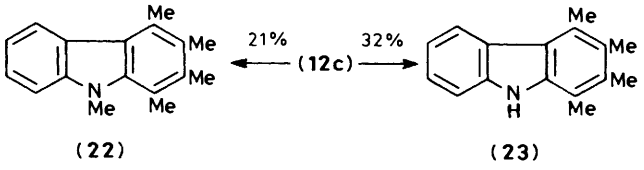


Scheme 3.

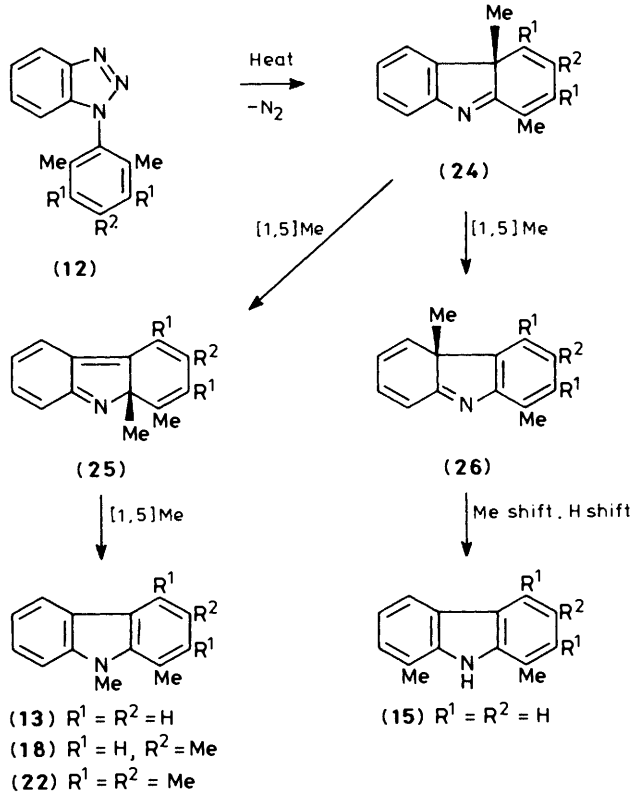


Scheme 4.

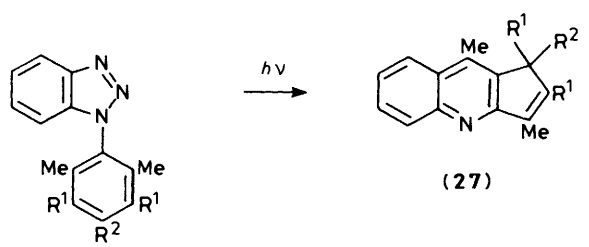
* 1,8-Dimethylcarbazole has been reported to melt at 48—50 °C,[14] and at 176—177 °C,[15] as well as being described as an oily solid.[16] We find m.p. 177.5—178.5 °C.

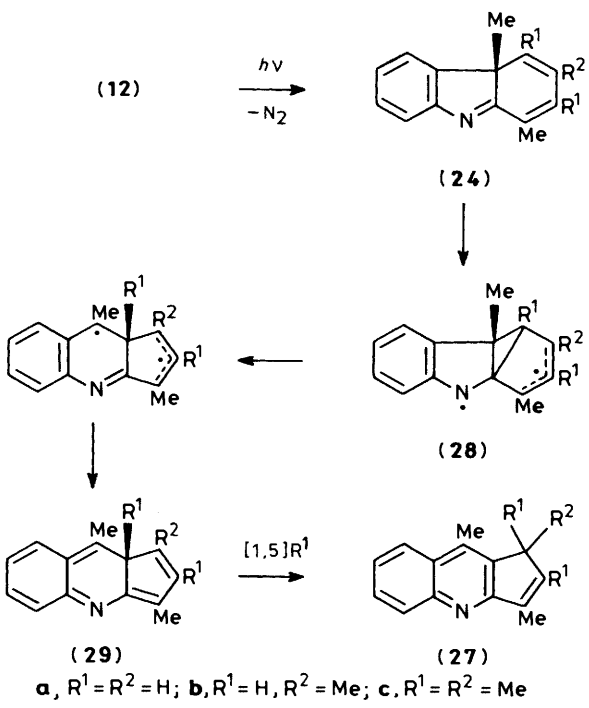


Scheme 5.



Scheme 6.





Scheme 7.

insertion of the diradical or iminocarbene intermediates (see Scheme 1) into the *ortho*-methyl group followed by aerial oxidation, is consistent with the intermediacy of 4a*H*-carbazoles (**24**) which then undergo rearrangement as shown in Scheme 6. Loss of nitrogen from the benzotriazole (**12**) is followed by cyclisation to the 4a*H*-carbazole (**24**) (see Scheme 1). Competing [1,5]-shifts of the ring junction methyl group can lead to the 8a*H*-carbazole (**25**), and hence to the *N*-methylcarbazoles (**13**), (**18**), and (**22**), or to the isomeric 4a*H*-carbazole (**26**). Further [1,5] or higher order migrations of the ring junction methyl group in (**26**), with subsequent hydrogen shifts, gives the carbazole (**15**) [from (**12a**)]. Presumably one of the unidentified carbazoles in each of the pyrolyses of triazoles (**12b**) and (**12c**) is analogous to this product. Loss of the ring junction methyl group to give the demethylated carbazoles (**14**), (**19**), and (**23**) may occur during the migrations or from any of the intermediates. The possibility that the demethylated carbazoles are formed from the corresponding *N*-methyl derivatives seems unlikely. In a control experiment, 1,3,9-trimethylcarbazole (**18**) was unchanged after FVP at 650 °C, although some demethylation was observed at temperatures above 800 °C. Likewise, the origin of the demethylated acridines (**17**) and (**21**) remains obscure.

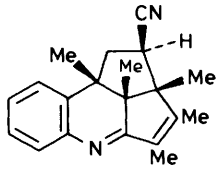
Photolysis of Benzotriazoles.—In contrast with its thermolysis, photolysis of 1-(2,6-dimethylphenyl)benzotriazole (**12a**) in acetonitrile at 254 nm gave only one product (46%), which was not a carbazole. Spectral data suggested it to be the cyclopentaquinoline (**27a**), the position of the five-membered ring methyl group being determined with the aid of the lanthanide shift reagent [Eu(fod)$_3$] in its ^{1}H n.m.r. spectrum (see Experimental section). The structure was finally confirmed by independent synthesis (see below).

The analogous cyclopentaquinoline (**27b**) was obtained (64%) on photolysis of the benzotriazole (**12b**). However, in this case a small amount of the demethylated carbazole (**19**) (6%) was also isolated. The pentamethyl derivative (**12c**) gave a much more complex mixture on photolysis, although the cyclopentaquinoline (**27c**) (20%) and the demethylated carbazole (**23**) (18%) could be isolated.

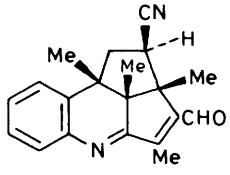
These cyclopentaquinolines are analogous to the cyclopentapyrimidines formed on thermolysis of 1-(2,6-dimethylphenyl)-tetrazoles.[5] In the latter case the products were rationalised in terms of thermal rearrangement of the 3a*H*-benzimidazole intermediate (**2**). However, in the present work, the absence of the cyclopentaquinolines (**27**) in the thermal decomposition of the benzotriazoles (**12**) suggests that such a mechanism is not operating. An alternative mechanism based on an aza-di-π-methane rearrangement[19] of the intermediate 4a*H*-carbazole (**24**) is proposed (Scheme 7), the initial diradical (**28**) rearranging to (**29**) and hence to (**27**).

The other photolysis products, the demethylated carbazoles (**19**) and (**23**) could also arise from the 4a*H*-carbazoles (**24**; R^1 = H, R^2 = Me) and (**24**; R^1 = R^2 = Me) in their highly energetic state initially formed on collapse of the diradical when nitrogen is extruded from the starting benzotriazole. Severe steric crowding in the pentamethyl case is thought to account for the increased yield of demethylated carbazole relative to cyclopentaquinoline.

The intermediate (**29**) is related to the 3a*H*-indene (**1**), and additional evidence was sought for it. Although intermediates (**29a**) and (**29b**) can aromatise rapidly by a [1,5]-hydrogen shift, the corresponding [1,5]-methyl shift in (**29c**) will be less favourable. In anticipation of this, the photolysis of the pentamethyl benzotriazole (**12c**) was repeated in the presence of acrylonitrile, since by analogy with 3a*H*-indenes, the intermediate (**29c**) was expected to undergo cycloaddition reactions with 2π-components. In the presence of acrylonitrile, neither the cyclopentaquinoline (**27c**) nor the carbazole (**23**) were formed; the major product (45%) was found to be the 1:1 adduct (**30**), formed regio- and stereo-selectivity. The structure of this adduct was elucidated by *X*-ray crystallography.* Interestingly, with time, in solution, compound (**30**) underwent aerial oxidation of the methyl group activated by the imine bond to give aldehyde (**31**).



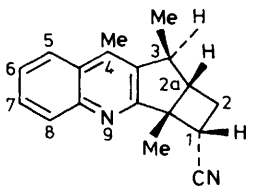
(**30**)



(**31**)

The high degree of regio- and stereo-selectivity observed in the formation of adduct (**30**) suggests that it does indeed arise by a concerted addition of acrylonitrile to the intermediate (**29c**) rather than to some diradical intermediate. The regioselectivity of this [8 + 2] cycloaddition can be rationalised on the basis of frontier orbital coefficients.[20] MNDO calculations[21] suggest that the regiochemistry may be determined by interaction of the HOMO of acrylonitrile, for which the largest coefficient is at C-2,[20] with the LUMO of intermediate (**29**). However, the observed *exo*-stereospecificity is somewhat surprising in view of the more usually preferred *endo* mode of addition.

In contrast, and in agreement with our earlier reasoning, photolysis of the benzotriazole (**12b**) in the presence of acrylonitrile gave none of the corresponding [8 + 2] adduct, the aromatisation of intermediate (**29b**) by hydrogen shift being too fast for interception to occur. The only products isolated from this photolysis experiment were three isomeric [2 + 2] adducts of the cyclopentaquinoline (**27b**) with acrylonitrile. The structure of the major adduct (**32**), accounting for 60% of the total, was established from its ^{1}H n.m.r. spectrum by decoupling and n.O.e. difference experiments. In particular, pre-irradiation

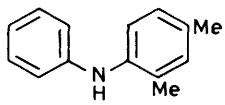


(**32**)

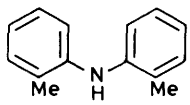
* We thank Dr. D. J. Williams of this Department for this result.

of the methyl singlets at δ 2.69 (4-Me) and δ 1.77 (9b-Me) caused enhancement of the signals due to 5-H, 3-H and 3-Me, and 1-H, 2a-H and 3-Me, respectively. Pre-irradiation of the doublet at δ 1.25 (3-Me) caused the expected enhancements of 9b-Me, 4-Me, 2a-H and 3-H. The same three [2 + 2] adducts were obtained on irradiation of a mixture of the cyclopentaquinoline (**27b**) and acrylonitrile. Attempts to intercept the intermediate (**29b**) with more reactive 2π-components, such as chloroacrylonitrile or diethyl azodicarboxylate, led only to complex mixtures containing much polymeric material, from which no adducts could be isolated.

Independent Synthesis of Reaction Products.—The di- and trimethylcarbazoles were prepared by photocyclisation[22] of diphenylamines. This route, although low yielding, was considered to be the most direct. Thus irradiation in air of the diphenylamine (**33**), obtained (58%) by decomposition of phenyl azide in *m*-xylene and trifluoroacetic acid,[23] gave 1,3-dimethylcarbazole (**19**). Methylation of (**19**) using sodium hydride–iodomethane in dimethylformamide (DMF) gave the trimethyl derivative (**18**).

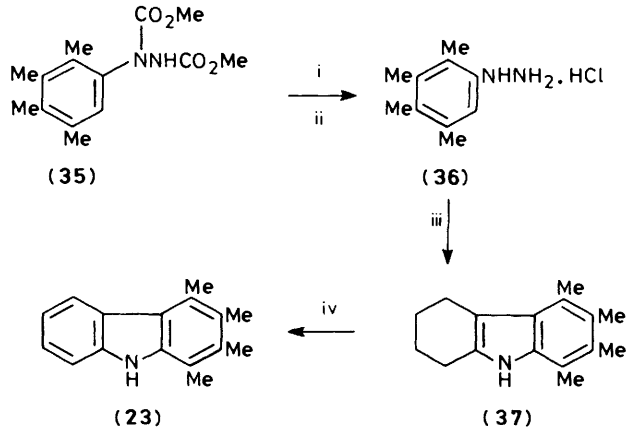


(**33**)



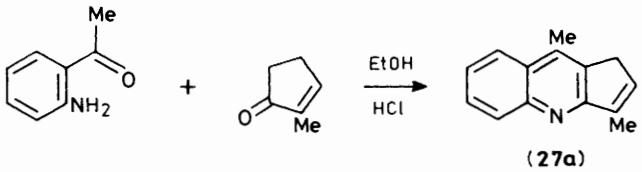
(**34**)

An analogous photocyclisation was used to prepare 1,8-dimethylcarbazole (**15**). The required diphenylamine (**34**) was prepared by condensation of 2-methylacetanilide with 2-bromotoluene in the presence of copper(I) iodide and potassium carbonate,[24] followed by alkaline hydrolysis of the *N*-acetyl group. An attempt to prepare 1,2,3,4-tetramethylcarbazole (**23**) by photocyclisation of the appropriate diphenylamine was unsuccessful, and therefore an approach based on the Fischer indole synthesis was adopted (Scheme 8). Reaction of 1,2,3,4-tetramethylbenzene with dimethyl azodicarboxylate in the presence of boron trifluoride[25] gave the protected arylhydrazine (**35**). Cleavage of the urethanes by alkaline hydrolysis was followed by conversion into the stable hydrochloride (**36**). The arylhydrazine (**36**) was used directly in the Fischer reaction with cyclohexanone and gave the unstable tetrahydrocarbazole (**37**), which was immediately dehydrogenated to the desired carbazole (**23**). Methylation of (**23**) gave the pentamethylcarbazole (**22**).



(**35**) (**36**) (**23**) (**37**)

Scheme 8. *Reagents:* i, KOH, EtOH, ii, HCl; iii, cyclohexanone, CH_3CO_2H, heat; iv, Pd/C, 220 °C.



(27a)

Scheme 9.

The cyclopentaquinoline (**27a**) was prepared by the Friedlander quinoline synthesis, in which 2-aminoacetophenone was condensed with 2-methylcyclopentenone under acidic conditions (Scheme 9).

Conclusions.—Although the 4a*H*-carbazoles (**24**) have not yet been isolated, the present results are consistent with their intermediacy in both the thermal and photochemical decomposition of benzotriazoles bearing *ortho*-blocked 1-aryl substituents. The observed products arise from further thermal (sigmatropic), or photochemical (aza-di-π-methane) rearrangement of the intermediate 4a*H*-carbazoles. The effect of benzannelation in stabilising 4a*H*-carbazoles, and allowing their isolation, thereby substantiating these mechanistic proposals, is described in the following paper.[26]

Experimental

Light petroleum refers to that fraction with b.p. 60—80 °C, and ether refers to diethyl ether. All solvents were dried by standard procedures before use. Brine refers to saturated sodium chloride solution. Chromatography was carried out on Merck silica gel 60 H at a pressure of 5—10 lb in^{-2}. Preparative layer chromatography (p.l.c.) was carried out on 20 × 20 cm glass plates coated to a thickness of 2 mm with Merck silica gel type 60 GF_{254}. I.r. spectra were recorded in the range 4 000—600 cm^{-1} on a Perkin-Elmer 257 spectrophotometer, and were calibrated against polystyrene. U.v. spectra were recorded on a Pye-Unicam SP800 recording spectrophotometer, and were calibrated against holmium glass. ^1H N.m.r. spectra were recorded at 60, 90, and 250 MHz using Varian T60, Perkin-Elmer R32, and Bruker WM250 instruments, respectively. ^{13}C N.m.r. spectra were recorded on the Bruker instrument at 62.9 MHz. Mass spectra were recorded on a VG Micromass 7070B spectrometer operating at 70 eV using a direct insertion probe. Photochemical reactions were performed in a Rayonet photochemical reactor using lamps of 254 or 300 nm wavelength. Solutions were irradiated in quartz vessels under a stream of dry nitrogen. Melting points were determined on a Kofler hot stage apparatus.

Preparation of 2-Nitrodiphenylamines (**10**): *General Procedure.*—A mixture of the amine (2 equiv.), 2-fluoronitrobenzene (1 equiv.), and freshly fused potassium fluoride (1.2 equiv.) was heated and stirred at *ca.* 180 °C. On cooling, the mixture was partitioned between chloroform (150 ml) and water (150 ml). The organic layer was separated, washed with water (100 ml), dried ($MgSO_4$), and evaporated to leave a black gum. Chromatography, eluting with light petroleum, gave the 2-nitrodiphenylamine. The following compounds were prepared in this way:

2,6-*Dimethyl-2′-nitrodiphenylamine* (**10a**). This was prepared (65%) from 2,6-dimethylaniline by heating at 190 °C for 46 h, m.p. 108.5—109.5 °C (from ethanol) (lit.,[27] 106—107 °C).

2,4,6-*Trimethyl-2′-nitrodiphenylamine* (**10b**). This was prepared (62%) from 2,4,6-trimethylaniline by heating at 180 °C for 48 h, m.p. 142—142.5 °C (from ethanol) (lit.,[28] 138.5—139.5 °C).

2,3,4,5,6-*Pentamethyl-2′-nitrodiphenylamine* (**10c**). This was prepared (51%) from 2,3,4,5,6-pentamethylaniline[29] by heating at 185 °C for 45 h, m.p. 153 °C (from ethanol) (Found: C, 71.6; H, 7.1; N, 9.8. $C_{17}H_{20}N_2O_2$ requires C, 71.8; H, 7.1; N, 9.85%); $\nu_{max.}$ (CCl_4) 3 350, 1 605, and 1 560 cm^{-1}; δ (90 MHz; CCl_4) 2.11 (6 H, s), 2.23 (9H, s), 6.30 (1 H, dd, *J* 9, 1 Hz), 6.65 (1 H, m), 7.22 (1 H, m), 8.16 (1 H, dd, *J* 8, 2 Hz), and 9.12 (1 H, br); *m/z* 285, 284 (M^+, base), 237, 236, 235, 222, and 221.

Reduction of 2-Nitrodiphenylamines: General Procedure.—A suspension of the nitro compound (**10**) in degassed ethanol containing 10% palladium–charcoal (10% w/w nitro compound) was shaken under an atmosphere of hydrogen until uptake of gas ceased. The mixture was filtered through Celite, and the filtrate concentrated to *ca.* 10 ml. A slight excess of concentrated hydrochloric acid was added, and the resulting amine hydrochloride salt was recrystallised from ethanol containing a little hydrochloric acid.

2-*Amino-2′,6′-dimethyldiphenylamine Hydrochloride* (**11a**·HCl). This formed grey *needles* (88%), m.p. 185 °C (decomp.) (Found: C, 67.6; H, 7.0; N, 11.3. $C_{14}H_{17}ClN_2$ requires C, 67.3; H, 7.3; N, 11.2%); $\nu_{max.}$ (Nujol) 3 320, 2 960—2 840, 2 585, 1 625, 1 510, 1 300, 770, and 745 cm^{-1}; δ [60 MHz; $(CD_3)_2SO$] 2.17 (6 H, s), 6.15 (1 H, dd, *J* 7 Hz), 6.65—7.65 (9 H, m), and 8.05 (1 H, br).

2-*Amino-2′,4′,6′-trimethyldiphenylamine Hydrochloride* (**11b**·HCl). This was an amorphous pink *solid* (93%). m.p. 172—175 °C (decomp.) (Found: C, 68.5; H, 7.35; N, 10.6. $C_{15}H_{19}ClN_2$ requires C, 68.6; H, 7.3; N, 10.7%); $\nu_{max.}$ (Nujol) 3 410, 3 350, 1 640, 1 505, 1 380, and 1 325 cm^{-1}; δ [60 MHz; $(CD_3)_2SO$] 2.00 (6 H, s), 2.18 (3 H, s), 6.05 (1 H, dd, *J* 7, 1 Hz), and 6.50—7.50 (6 H, m).

2-*Amino-2′,3′,4′,5′,6′-pentamethyldiphenylamine Hydrochloride* (**11c**·HCl). This formed colourless *needles* (92%). m.p. 175—176 °C (decomp.) (Found: C, 70.45; H, 8.0; N, 9.6. $C_{17}H_{23}ClN_2$ requires C, 70.2; H, 8.0; N, 9.6%); $\nu_{max.}$ (Nujol) 3 310, 2 550, 1 620, 1 505, and 740 cm^{-1}; δ [60 MHz; $(CD_3)_2SO$] 2.05 (6 H, s), 2.19 (9 H, s), 2.85—3.90 (3 H, br), 6.00 (1 H, d, *J* 8 Hz), and 6.40—7.45 (4 H, m).

1-(2,6-*Dimethylphenyl*)*benzotriazole* (**12a**).—The amine hydrochloride (**11a**) (3.72 g, 15 mmol) was dissolved in a hot mixture of hydrochloric acid (1M; 180 ml) and ethanol (45 ml). The solution was rapidly cooled to 0 °C with vigorous stirring, and the resulting suspension was treated dropwise with a solution of sodium nitrite (1.36 g, 20 mmol) in water (10 ml) whilst the temperature was maintained between 0 and 5 °C. After the addition, the mixture was stirred for 4 h at room temperature, and then diluted with brine (200 ml). The brown solid was filtered off, washed well with water, and purified by sublimation at 70 °C/0.02 mmHg followed by recrystallisation from light petroleum to give the *title compound* (**12a**) as large square plates (2.61 g, 78%), m.p. 68—70 °C (Found: C, 75.55; H, 6.0; N, 19.0. $C_{14}H_{13}N_3$ requires C, 75.3; H, 5.9; N, 18.8%); $\nu_{max.}$ (CCl_4) 3 060, 2 970, 2 910, 1 610, 1 490, 1 470, 1 270, 1 180, 1 060, and 1 030 cm^{-1}; $\lambda_{max.}$ (EtOH) 210 (log ε 4.26), 256 (3.94), 261sh (3.92), 272sh (3.72), and 283 nm (3.69); δ (60 MHz; CCl_4) 1.79 (6 H, s), 6.96—7.37 (6 H, m), and 8.03 (1 H, m); *m/z* 223 (M^+), 195, 194 (base), and 180.

Similarly prepared were the following. 1-(2,4,6-*Trimethylphenyl*)*benzotriazole* (**12b**). This formed colourless *prisms* (96%), m.p. 120—121 °C (Found: C, 76.0; H, 6.4, N, 17.8. $C_{15}H_{15}N_3$ requires C, 75.9; H, 6.4; N, 17.7%); $\nu_{max.}$ (CCl_4) 2 930, 1 615, 1 500, 1 455, 1 385, 1 280, and 1 070 cm^{-1}; $\lambda_{max.}$ (EtOH) 208, (log ε 4.26), 254 (3.82), and 279sh nm (3.57); δ (60 MHz; CCl_4) 1.85 (6 H, s), 2.40 (3 H, s), and 6.90—8.30 (6 H, m); *m/z* 237 (M^+), 209, 208, and 194 (base).

1-(2,3,4,5,6-*Pentamethylphenyl*)*benzotriazole* (**12c**). This formed amber *prisms* (86%), m.p. 211—213 °C (Found: C, 76.7;

H, 7.2; N, 15.8. $C_{17}H_{19}N_3$ requires C, 76.95; H, 7.2; N, 15.8%); $\nu_{max.}$ (CCl_4) 3 010, 2 940, 1 615, 1 450, 1 275, and 1 065 cm^{-1}; $\lambda_{max.}$ (EtOH) 208 (log ε 4.56), 222sh (4.17), 256 (3.95), and 276sh nm (3.80); δ (90 MHz; CCl_4) 1.72 (6 H, s), 2.31 (6 H, s), 2.37 (3 H, s), 7.05—7.65 (3 H, m), and 8.15 (1 H, m); *m/z* 265 (M^+), 237, 236, 222 (base), and 207.

FVP of 1-(2,6-*Dimethylphenyl*)*benzotriazole* (**12a**).—The benzotriazole (**12a**) (237 mg) was distilled at 110—115 °C and 0.03 mmHg through a quartz tube maintained at 640 °C to give a brown gum (207 mg). P.l.c. of this, eluting with light petroleum–dichloromethane–ether (13:6:1), gave the following fractions: (i) 1,9-dimethylcarbazole (**13**) as a buff solid (63 mg, 32%), R_F 0.67, m.p. 113—116 °C (from light petroleum) (lit.,[30] 117 °C); (ii) a brown gum (111 mg), R_F 0.52, further chromatography of which afforded 1,8-dimethylcarbazole (**15**) (9.6 mg, 5%), m.p. 176—178 °C (lit.,[15] 176—177 °C) identical with an authentic specimen (see below) and a mixture of carbazoles as a brown semi-solid (87 mg). H.p.l.c. analysis of this mixture indicated that it consisted of 1-methylcarbazole (**14**) (54 mg, 30%), more 1,8-dimethylcarbazole (8 mg, 4%), and a third unidentified carbazole (25 mg, 13%); (iii) a yellow oil (14 mg), R_F 0.36, purified by further p.l.c. to give 1-methylacridine (**16**), as a yellow oil (6.2 mg, 3%); δ (250 MHz; $CDCl_3$) 2.95 (3 H, s), 7.42 (1 H, dd, *J* 8, 6.5 Hz), 7.52 (1 H m), 7.62 (1 H, dd, *J* 6, 2.5 Hz), 7.76 (1 H, ddd, *J* 9, 7, 2 Hz), 7.85 (1 H, d, *J* 8 Hz), 7.98 (1 H, d, *J* 8.5 Hz), 8.28 (1 H, d, *J* 9 Hz), and 8.72 (1 H, s); *m/z* 193 (M^+, base); (iv) unchanged benzotriazole (**12a**) R_F 0.24 (10 mg, 4% recovery); (v) acridine (**17**) as a brown gum (17.4 mg, 9%), R_F 0.09; δ (250 MHz; $CDCl_3$) 7.48 (2 H, ddd), 7.73 (2 H, ddd), 7.92 (2 H, dd), 8.25 (2 H, dd), and 8.67 (1 H, s); *m/z* 179 (M^+), 86, 84 (base), and 71.

FVP of 1-(2,4,6-*Trimethylphenyl*)*benzotriazole* (**12b**).—The benzotriazole (**12b**) (155 mg) was sublimed at 100 °C and 0.075 mmHg into a quartz tube maintained at 700 °C. The resulting pyrolysate (136 mg) was chromatographed to give (i) 1,3,9-*trimethylcarbazole* (**18**) (20.4 mg, 15%), m.p. 99.5—100.5 °C, undepressed when mixed with an authentic specimen (see below); (ii) a yellow solid (63 mg), which h.p.l.c. analysis indicated was mainly 1,3-dimethylcarbazole (**19**) (50 mg, 39%) together with three unidentified carbazoles (10% total); (iii) 1,3-dimethylacridine (**20**) (7.2 mg, 5%); δ (250 MHz; CCl_4) 2.83 (6 H, s), 6.8—8.1 (6 H, m), and 8.35 (1 H, s); (iv) unchanged benzotriazole (**12b**) (2.2 mg, 2% recovery); and (v) 3-methylacridine (**21**) (7.4 mg, 5%); δ (250 MHz; CCl_4) 2.56 (3 H, s), 7.2—8.2 (7 H, m), and 8.50 (1 H, s).

FVP of 1-(2,3,4,5,6-*Pentamethylphenyl*)*benzotriazole* (**12c**).—The benzotriazole (**12c**) (228 mg) was sublimed at 120—150 °C and 0.04 mmHg through a quartz tube maintained at 640 °C to give a brown gum (196 mg). Chromatography gave (i) 1,2,3,4,9-*pentamethylcarbazole* (**22**) (43 mg, 21%), m.p. 149—152 °C undepressed when mixed with an authentic specimen (see below); (ii) a pale brown solid (83 mg) which h.p.l.c. indicated to consist of 1,2,3,4-tetramethylcarbazole (**23**) (62 mg, 32%), and four other unidentified carbazoles; and (iii) unchanged benzotriazole (**12c**) (18 mg, 8% recovery).

Photolysis of 1-(2,6-*Dimethylphenyl*)*benzotriazole* (**12a**).—A solution of the benzotriazole (**12a**) (225 mg) in acetonitrile (150 ml) was irradiated at 254 nm for 6.25 h. The solvent was evaporated, and the residue chromatographed to give (i) unchanged starting material (**12a**) (91 mg, 40% recovery), and (ii) 1,4-*dimethyl*-3H-*cyclopenta*[b]*quinoline* (**27a**) (53 mg, 46% based on starting material consumed), m.p. 106—108 °C, identical with an authentic specimen (see below).

Photolysis of 1-(2,4,6-*Trimethylphenyl*)*benzotriazole* (**12b**).—A solution of the benzotriazole (**12b**) (310 mg) in acetonitrile (180 ml) was irradiated at 254 nm for 22 h. Evaporation of the solvent and chromatography of the residue gave (i) 1,3-dimethylcarbazole (**19**) (43.6 mg, 14%), (ii) unchanged starting benzotriazole (**12b**) (28.2 mg, 9% recovery), and (iii) 1,3,4-*trimethyl*-3H-*cyclopenta*[b]*quinoline* (**27b**) (142 mg, 64%), b.p. 85—90 °C (Kugelrohr) at 0.35 mmHg; $\nu_{max.}$ (CCl_4) 1 625 cm^{-1}; $\lambda_{max.}$ (EtOH) 211 (log ε 4.42), 225 (4.52), 249 (4.64), 289 (3.98), 293 (3.99), 297sh (3.97), 306 (3.96), 313sh (3.81), 320 (4.00), 328 (3.71), and 335 nm (4.08); δ (250 MHz; $CDCl_3$) 1.34 (3 H, d, *J* 7 Hz), 2.29 (3 H, t, *J* 2 Hz), 2.69 (3 H, s), 3.61 (1 H, m), 6.62 (1 H, m), 7.48 (1 H, ddd), 7.63 (1 H, ddd), 7.98 (1 H, dd), and 8.13 (1 H, dd); *m/z* 209 (M^+), 194 (base), 180, 167, 152, 139, 115, 89, and 77; *picrate*, m.p. 184—185 °C (decomp. from ethanol) (Found: C, 57.55; H, 4.1; N, 12.7. $C_{21}H_{18}N_4O_7$ requires C, 57.5; H, 4.1; N, 12.8%).

Photolysis of 1-(2,3,4,5,6-*Pentamethylphenyl*)*benzotriazole* (**12c**).—A solution of the benzotriazole (**12c**) (122 mg) in acetonitrile (100 ml) was irradiated at 254 nm for 14.5 h. Evaporation of the solvent, and chromatography of the residue gave (i) 1,2,3,4-tetramethylcarbazole (**23**) (16.5 mg, 18%), and (ii) a yellow gum which consisted of unchanged starting material (**12c**) and 1,2,3,3,4-*pentamethyl*-3H-*cyclopenta*[b]-*quinoline* (**27c**) in the ratio 1:2. The quinoline was separated by acid extraction, and was an oil, b.p. 120 °C (Kugelrohr) at 0.02 mmHg; $\nu_{max.}$ (CCl_4) 1 610 cm^{-1}; $\lambda_{max.}$ (EtOH) 226 (log ε 4.10), 258 (4.30), 283sh (3.81), 312 (3.71), 320sh (3.61), 326 (3.84), 335 (3.63), and 342 nm (3.92); δ (250 MHz; $CDCl_3$) 1.38 (6 H, s), 2.00 (3 H, s), 2.19 (3 H, s), 2.76 (3 H, s), 7.44 (1 H, m), 7.61 (1 H, m), 7.99 (1 H, m), and 8.08 (1 H, d); *m/z* 237 (M^+), 222 (base), 167, 123, 114, and 87; *picrate* m.p. 212—215 °C (decomp. from ethanol) (Found: C, 59.1; H, 4.7; N, 11.9. $C_{23}H_{22}N_4O_7$ requires C, 59.2; H, 4.75; N, 12.0%).

Photolysis of the Benzotriazole (**12c**) *in the Presence of Acrylonitrile.*—A solution of the benzotriazole (**12c**) (100 mg) in a mixture of acetonitrile (90 ml) and acrylonitrile (10 ml) was irradiated at 254 nm for 6 h. The resulting turbid suspension was filtered through Celite, evaporated, and chromatographed to give (i) unchanged starting material (**12c**) (10 mg, 10% recovery); (ii) an unidentified adduct (4 mg, 4%); (iii) the *adduct* (**30**) (44.3 mg, 45% based on starting material consumed), m.p. 169—170 °C (decomp.) (Found: C, 82.6; H, 7.7; N, 9.6. $C_{20}H_{22}N_2$ requires C, 82.7; H, 7.6; N, 9.65%); $\nu_{max.}$ (CCl_4) 2 230 and 1 620 cm^{-1}; δ (250 MHz; $CDCl_3$) 0.69 (3 H, s), 1.53 (3 H, s), 1.63 (3 H, s), 1.83 (1 H, dd, *J* 13.8, 9.6 Hz), 1.94 (6 H, s), 1.96 (1 H, dd, *J* 13.8, 1.3 Hz), 2.64 (1 H, dd, *J* 9.6, 1.3 Hz), 7.19 (1 H, dt, *J* 7.5, 1.6 Hz), 7.31 (1 H, dt, *J* 7.5, 1.6 Hz), 7.40 (1 H, dd, *J* 7.5, 1.6 Hz), and 7.43 (1 H, dd, *J* 7.5, 1.6 Hz); δ_C (62.9 MHz; $CDCl_3$) 9.3, 11.9, 12.4, 19.6, 20.2, 33.0, 41.4, 45.7, 52.5, 58.7, 121.9, 125.7, 126.3, 127.4, 127.9, 132.0, 134.7, 142.7, 158.6, and 181.3; *m/z* 290 (M^+), 275, 237, and 222 (base).

With time, in solution in contact with air, the adduct (**30**) was oxidised to the aldehyde (**31**), m.p. 260—262 °C (decomp.) (Found: C, 78.75; H, 6.6; N, 9.1. $C_{20}H_{20}N_2O$ requires C, 78.9; H, 6.6; N, 9.2%); $\nu_{max.}$ (CH_2Cl_2) 1 660 cm^{-1}; δ (250 MHz; $CDCl_3$) 0.70 (3 H, s), 1.65 (3 H, s), 1.71 (3 H, s), 1.81 (1 H, dd, *J* 14, 9.8 Hz), 1.98 (1 H, dd, *J* 14, 1 Hz), 2.39 (3 H, s), 2.88 (1 H, dd, *J* 9.8, 1 Hz), 7.28 (1 H, m), 7.36 (1 H, m), 7.43 (1 H, dd), 7.49 (1 H, dd), and 10.47 (1 H, s); *m/z* 305, 304 (M^+, base), 251, 236, 222, and 208.

Photolysis of the Benzotriazole (**12b**) *in the Presence of Acrylonitrile.*—A solution of the benzotriazole (**12b**) (212 mg) in a mixture of acetonitrile (90 ml) and acrylonitrile (10 ml) was irradiated at 254 nm for 7 h. Evaporation of the solvent to small volume, filtration through Celite, and chromatography of the

filtrate gave (i) unchanged starting material (**12b**) (53 mg, 25% recovery); (ii) the *adduct* (**32**) (56 mg, 32%), m.p. 183—185 °C (sublimed at 145 °C and 0.075 mmHg) (Found: C, 82.6; H, 7.0; N, 10.7. $C_{18}H_{18}N_2$ requires C, 82.4; H, 6.9; N, 10.7%); $\nu_{max.}$ (CCl_4) 2 225 and 1 600 cm^{-1}; δ (250 MHz; $CDCl_3$) 1.25 (3 H, d, *J* 7.5 Hz), 1.77 (3 H, s), 1.93 (1 H, m), 2.48 (1 H, ddd), 2.69 (3 H, s), 2.86 (1 H, m), 3.15 (1 H, m), 3.22 (1 H, q), 7.54 (1 H, ddd), 7.67 (1 H, ddd), 8.02 (1 H, dd), and 8.08 (1 H, dd); *m/z* 262 (M^+), 210, 209 (base), 208, 194, and 182; *picrate*, m.p. 229—230 °C (decomp. from acetonitrile) (Found: C, 58.8; H, 4.3; N, 14.2. $C_{24}H_{21}N_5O_7$ requires C, 58.65; H, 4.3; N, 14.25%); (iii) an unidentified [2 + 2]-adduct (29 mg, 17%), and (iv) another unidentified [2 + 2]-adduct (7 mg, 4%).

Photocycloaddition of the Cyclopentaquinoline (**27b**) *to Acrylonitrile*.—A solution of the cyclopentaquinoline (**27b**) (45 mg) in a mixture of acetonitrile (45 ml) and acrylonitrile (5 ml) was irradiated at 254 nm for 2 h. The solvent was evaporated and the residue dissolved in tetrahydrofuran (3 ml). Methanol (30 ml) was added to precipitate polymeric material, which was removed by filtration through Celite. Evaporation of the filtrate and separation of the residue by p.l.c. gave (i) the adduct (**32**) (22 mg, 39%), and (ii) a colourless oil (11 mg, 20%) which was a 1:1 mixture of the two unidentified [2 + 2]-adducts.

Independent Syntheses

2,4-*Dimethyldiphenylamine* (**33**)[23].—A solution of phenyl azide (6.0 g, 50 mmol) and trifluoroacetic acid (16 ml) in *m*-xylene (200 ml) was stirred at 100 °C for 26 h. On cooling, ether (200 ml) was added and the mixture was washed with saturated aqueous sodium hydrogen carbonate (250 ml) and water (250 ml), dried ($MgSO_4$), and evaporated. The residue was treated with aqueous sodium hydroxide (10%; 100 ml) and extracted with ether (3 × 250 ml). The combined ether extracts were washed with water, dried, evaporated and the residue distilled to give the title compound (**33**) (5.20 g, 53%), b.p. 110—115 °C at 0.1 mmHg (lit.,[31] m.p. 43 °C).

1,3-*Dimethylcarbazole* (**19**)[22].—A solution of the diphenylamine (**33**) (900 mg) in light petroleum (700 ml) was irradiated at 300 nm for 30 h. Evaporation of the solvent, and chromatography of the residue gave 1,3-dimethylcarbazole (**19**) (230 mg, 26%). m.p. 100 °C (lit.,[17] 95 °C); *picrate*, m.p. 192—193 °C (from benzene) (lit.,[17] 188.5 °C).

1,3,9-*Trimethylcarbazole* (**18**).—Sodium hydride (50% dispersion in oil; 60 mg, 1.25 mmol) was washed free of oil and suspended in DMF (4 ml), and the mixture cooled to 0 °C. The carbazole (**19**) (193 mg, 1 mmol) in DMF (1 ml) was added and the mixture stirred at room temperature for 1.5 h. Iodomethane (250 mg, 1.8 mmol) was added, and after 3 h, the reaction was quenched by addition of water (25 ml). The precipitated product was filtered, washed with water, dried and recrystallised from light petroleum to give the *title compound* (**18**) (146 mg, 70%), m.p. 100—101 °C (Found: C, 86.1; H, 7.2; N, 6.7. $C_{15}H_{15}N$ requires C, 86.1; H, 7.2; N, 6.7%); δ (90 MHz; CCl_4) 2.42 (3 H, s), 2.76 (3 H, s), 4.04 (3 H, s), 6.98 (1 H, d, *J* 1 Hz), 7.0—7.3 (3 H, m), 7.61 (1 H, d, *J* 1 Hz), and 7.88 (1 H, dd, *J* 7, 1 Hz); *m/z* 210, 209 (M^+, base).

2,2′-*Dimethyldiphenylamine* (**34**)[24].—2-Methylacetanilide (7.45 g, 50 mmol) was refluxed in 2-bromotoluene (8.55 g, 50 mmol) in the presence of copper(I) iodide (0.9 g) and anhydrous potassium carbonate (5 g) for 19 h. On cooling, the mixture was partitioned between ether (150 ml) and water (150 ml). The ether layer was dried ($MgSO_4$), evaporated, and the residue purified by chromatography and recrystallisation to give *N*-acetyl-2,2′-dimethyldiphenylamine (4.33 g, 36%), m.p. 89—90 °C (lit.,[32] 82—83 °C). A mixture of the *N*-acetyl compound (2.4 g, 10 mmol) and potassium hydroxide (3.3 g, 60 mmol) in ethylene glycol (40 ml) was heated under reflux for 24 h. The cooled mixture was poured into water (100 ml) and extracted with ether (3 × 50 ml). The combined ether extracts were washed with water (3 × 50 ml), dried (Na_2SO_4) and evaporated. The residue was distilled at 140 °C (Kugelrohr) and 3 mmHg to give the diphenylamine (**34**) (1.73 g, 88%) as a yellow oil which crystallised with time, m.p. 46—49 °C (lit.,[33] 48.5—49.5 °C).

1,8-*Dimethylcarbazole* (**15**).—An aerated solution of the diphenylamine (**34**) (985 mg) in light petroleum (1 000 ml) was irradiated with a medium-pressure immersion lamp for 24 h. The solvent was evaporated, and the residue chromatographed to give (i) unchanged starting material (346 mg, 35% recovery), and (ii) the title carbazole (**15**) (125 mg, 20%), m.p. 177.5—178.5 °C (lit.,[15] 176—177 °C)

Dimethyl 1-(2,3,4,5-*tetramethylphenyl*)*hydrazine*(1,2-*dicarboxylate* (**35**)[25].—Dimethyl azodicarboxylate (2.92 g, 20 mmol) was added to a vigorously stirred, cooled solution of 1,2,3,4-tetramethylbenzene (3.35 g, 25 mmol) in boron trifluoride etherate (4 ml). After 1 h, ether (5 ml) was added and the precipitated solid collected, washed with cold ether, and recrystallised from methanol to give the *title compound* (**35**) (4.23 g, 76%), m.p. 173—174 °C (Found: C, 60.0; H, 7.2; N, 9.95. $C_{14}H_{20}N_2O_4$ requires C, 60.0; H, 7.2; N, 10.0%); $\nu_{max.}$ (Nujol) 3 290, 1 755, and 1 695 cm^{-1}; δ (90 MHz; $CDCl_3$) 2.18 (6 H, s), 2.20 (3 H, s), 2.25 (3 H, s), 3.73 (6 H, s), 7.09 (1 H, s), and 7.22 (1 H, br).

2,3,4,5-*Tetramethylphenylhydrazine Hydrochloride* (**36**).—A mixture of the urethane (**35**) (2.00 g, 7.1 mmol), potassium hydroxide (2 g), and ethanol (10 ml) was heated under reflux for 24 h. On cooling, water (20 ml) was added, and the mixture was extracted with ether (2 × 20 ml). The combined ether extracts were washed with brine (20 ml), dried (K_2CO_3), and evaporated. The resulting brown gum was redissolved in ether (10 ml) and treated with a saturated ethereal solution of hydrogen chloride. The precipitated *title compound* (**36**) was collected as a beige powder (0.86 g, 60%), m.p. 195.5—196.5 °C (decomp.) (Found: C, 60.2; H, 8.6; N, 13.6. $C_{10}H_{17}ClN_2$ requires C, 59.8; H, 8.5; N, 14.0%).

1,2,3,4-*Tetramethylcarbazole* (**23**).—2,3,4,5-Tetramethylphenylhydrazine hydrochloride (**36**) (400 mg, 2 mmol) was refluxed with cyclohexanone (290 mg, 3 mmol) in acetic acid (3 ml) for 0.5 h. The cooled reaction mixture was filtered, and the filtrate evaporated. The residue was dissolved in ether (5 ml) and the solution washed with water (10 ml) and saturated aqueous sodium hydrogen carbonate (10 ml), dried ($MgSO_4$), and evaporated to give crude 1,2,3,4-tetrahydro-5,6,7,8-tetramethylcarbazole (**37**) (360 mg) as a brown solid. This solid was intimately mixed with palladium–charcoal (10%, 125 mg) and heated to 220 °C for 0.5 h. The product was extracted into chloroform and purified by chromatography to give the title compound (**23**) (178 mg, 39%), m.p. 135—137 °C (lit.,[34] 144 °C); *picrate*, m.p. 208—210 °C (decomp. from ethanol) (Found: C, 58.8; H, 4.5; N, 12.1. $C_{22}H_{20}N_4O_7$ requires C, 58.4; H, 4.5; N, 12.4%).

1,2,3,4,9-*Pentamethylcarbazole* (**22**).—Sodium hydride (50% in oil; 30 mg, 0.63 mmol) was de-oiled and suspended in dry DMF (0.5 ml). A solution of the carbazole (**23**) (90 mg, 0.4 mmol) in DMF (1 ml) was added. After being stirred at room

temperature for 0.75 h, the mixture was cooled to 0 °C and treated with iodomethane (0.25 ml) in DMF (0.25 ml). After being stirred for 0.5 h, the mixture was diluted with water (10 ml) and extracted with chloroform (3 × 10 ml). The combined chloroform extracts were washed with water (3 × 10 ml), dried ($MgSO_4$), evaporated, and the residue chromatographed to give the *title compound* (**22**) (53 mg, 56%), m.p. 155—157 °C (Found: C, 85.9; H, 8.3; N, 6.1. $C_{17}H_{19}N$ requires C, 86.0; H, 8.1; N, 5.9%); δ (90 MHz; CCl_4) 2.30 (6 H, s), 2.60 (3 H, s), 2.74 (3 H, s), 3.90 (3 H, s), 6.98—7.42 (3 H, m), and 8.08 (1 H, m); *m/z* 237 (M^+, base); *picrate*, m.p. 178 °C (from ethanol) (Found: C, 59.4; H, 4.7; N, 11.8. $C_{23}H_{21}N_4O_7$ requires C, 59.2; H, 4.75; N, 12.0%).

1,4-*Dimethyl*-3H-*cyclopenta*[b]*quinoline* (**27a**).—2-Methylcyclopent-2-enone (240 mg, 2.5 mmol) and 2-aminoacetophenone hydrochloride (430 mg, 2.5 mmol) were heated together in aqueous ethanol (50%, 1.5 ml) and concentrated hydrochloric acid (0.5 ml) under reflux for 19 h. On cooling, the solution was basified by the addition of ammonia solution (35%, 5 ml) and extracted with dichloromethane (3 × 10 ml). The combined organic extracts were washed with water (10 ml), dried (Na_2SO_4), evaporated and the residue chromatographed to give the *title compound* (**27a**) (105 mg, 21%), m.p. 105—107 °C (Found: C, 85.7; H, 6.7; N, 7.1. $C_{14}H_{13}N$ requires C, 86.1; H, 6.7; N, 7.2%); δ (250 MHz; $CDCl_3$) 2.35 (3 H, q, *J* 1.5 Hz), 2.69 (3 H, s), 3.39 (2 H, t, *J* 1.5 Hz), 6.76 (1 H, m), 7.52 (1 H, ddd), 7.67 (1 H, ddd), 8.02 (1 H, m), and 8.16 (1 H, m); on addition of [Eu(fod)$_3$] the signals at δ 2.35 and 8.16 were markedly shifted; *m/z* 196, 195 (M^+, base), 194, 180, and 152; *picrate*, m.p. 222—224 °C (decomp. from ethanol) (Found: C, 56.7; H, 3.8; N, 13.2. $C_{20}H_{16}N_4O_7$ requires C, 56.6; H, 3.8; N, 13.2%).

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