683. *A Synthesis of Ellipticine.**

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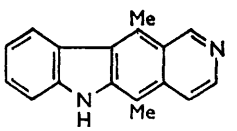
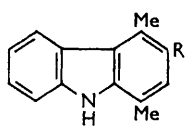
A five-stage synthesis of ellipticine from indole is described.

THE genus *Aspidosperma* elaborates numerous alkaloids, among which are three oxygen-free bases, ellipticine (I), olivacine, and uleine, of close biogenetical origin. Ellipticine occurs in the Peruvian plant "Quillo-bordon," which is reputed to be *Aspidosperma subincanum* Mart.,[1] and also in *Ochrosia elliptica* Labill. and *O. sandwicensis* A.DC.[2] Several close derivatives of ellipticine also occur naturally.[3-5] The initial isolation [2] of ellipticine was closely followed by its synthesis,[1] which established its constitution. In this communication we report an independent synthesis.



(I)



(II)

1,4-Dimethylcarbazole (II; R = H),[6] for which an improved preparation is reported, was formylated with *N*-methylformanilide and phosphorus oxychloride. The major

* A preliminary account of part of this work has been reported in *Chem. and Ind.*, 1962, 45.

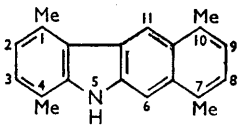
[1] Woodward, Iacobucci, and Hochstein, *J. Amer. Chem. Soc.*, 1959, **81**, 4434.
[2] Goodwin, Smith, and Horning, *J. Amer. Chem. Soc.*, 1959, **81**, 1903.
[3] Büchi, Mayo, and Hochstein, *Tetrahedron*, 1961, **15**, 167.
[4] Schmutz and Hunziker, *Helv. Chim. Acta*, 1958, **41**, 288.
[5] Lehner and Schmutz, *Helv. Chim. Acta*, 1961, **44**, 444.
[6] Robinson and Saxton, *J.*, 1952, 976.

product was shown to be 3-formyl-1,4-dimethylcarbazole (II; R = CHO), by Wolff–Kishner reduction to 1,3,4-trimethylcarbazole (II; R = Me); the constitution of the latter was confirmed by conventional preparation from 2,4,5-trimethylphenylhydrazine. The 6-position in 1,4-dimethylcarbazole is also reactive towards electrophilic reagents; 3,6-diformyl-1,4-dimethylcarbazole was isolated in small yield from the formylation, and could be obtained as the major product when large excesses of *N*-methylformanilide and phosphorus oxychloride were used. The constitution of 3,6-diformyl-1,4-dimethylcarbazole was established by Wolff–Kishner reduction to 1,3,4,6-tetramethylcarbazole; this was also prepared by synthesis of 1,4,6-trimethylcarbazole from *p*-xylidine, followed by formylation at the 3-position, and Wolff–Kishner reduction of the 3-formyl-1,4,6-trimethylcarbazole so obtained.

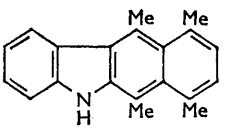
Condensation of 3-formyl-1,4-dimethylcarbazole with 2,2-diethoxyethylamine gave 3-(2,2-diethoxyethyliminomethyl)-1,4-dimethylcarbazole [II; R = $CH{:}N{\cdot}CH_2{\cdot}CH(OEt)_2$]; attempts to convert this directly into ellipticine by the Pomeranz–Fritsch synthesis were unsuccessful. Hydrogenation gave the corresponding saturated acetal [II; R = $CH_2{\cdot}NH{\cdot}CH_2{\cdot}CH(OEt)_2$], which also resisted cyclisation in the presence of a wide variety of acidic reagents. Cyclisation was eventually achieved by means of dry hydrogen chloride; the basic portion of the crude product was dehydrogenated, and the product was identified as ellipticine by comparison of the free base (mixed melting point, infrared and ultraviolet spectra, R_F value on paper chromatograms) and its methiodide (mixed melting point and infrared spectrum) with authentic samples.

The possibility of preparing ellipticine by other routes was also explored, but without success. Thus 3-aminomethyl-1,4-dimethylcarbazole (II; R = $CH_2{\cdot}NH_2$) gave no basic product when its condensation product with glyoxal monoacetal was treated with sulphuric acid or sulphuric acid and hydrogen chloride, according to Schlittler's conditions.[7] Attempts to cyclise *N*-(1,4-dimethyl-3-carbazolylmethyl)glycine (II; R = $CH_2{\cdot}NH{\cdot}CH_2{\cdot}CO_2H$) or its *N*-toluene-*p*-sulphonyl derivative also failed. The latter experiment gave *N*-toluene-*p*-sulphonylglycine, which must be formed by benzylamine fission, analogous to the formation of 3,4-methylenedioxybenzyl acetate and *N*-2′-acetoxyethyl-*N*-methylacetamide from *N*-2′-hydroxyethyl-*N*-methyl-3,4-methylenedioxybenzylamine and acetic anhydride.[8]

The preparation of 1,4-dimethylcarbazole by reaction of indole with hexane-2,5-dione normally yields in addition some ketonic material, owing presumably to uncyclised intermediates.[6] From attempts to ensure complete cyclisation by using more vigorous conditions no 1,4-dimethylcarbazole was isolated. Instead, the tarry product furnished a very small yield of a substance, $C_{20}H_{19}N$, which could also be prepared by condensation of 1,4-dimethylcarbazole with hexane-2,5-dione. Its ultraviolet spectrum strongly suggested that it was a derivative of 5*H*-benzo[*b*]carbazole; [9] two formulations are possible, namely, (III) and (IV). *A priori*, the latter was the expected product, by analogy with the known behaviour of 1,4-dimethylcarbazole (*e.g.*, formylation) towards electrophilic reagents.



(III)



(IV)

However, the product did not exhibit strong absorption at 770—735 cm.$^{-1}$, characteristic of four adjacent hydrogen atoms in an aromatic ring. In contrast, the infrared spectrum of this product was consistent with its formulation as 1,4,7,10-tetramethyl-5*H*-benzo[*b*]-carbazole(III). This conclusion is supported by the fact that 1,4,6-trimethylcarbazole

[7] Schlittler and Müller, *Helv. Chim. Acta*, 1948, **31**, 914.
[8] Kaufmann and Dürst, *Ber.*, 1917, **50**, 1630,
[9] Clemo and Felton, *J.*, 1952, 1658.

did not give a derivative of 5*H*-benzo[*b*]carbazole with hexane-2,5-dione under similar reaction conditions. On the other hand, 1,3,4-trimethylcarbazole gave with hexane-2,5-dione a product whose spectrographic properties are consistent with its formulation as 1,2,4,7,10-pentamethyl-5*H*-benzo[*b*]carbazole.

The formation of benzocarbazole derivatives by this novel route demonstrates the ability of hexane-2,5-dione to react with reactive vicinal aromatic positions with the formation of a new aromatic ring in the molecule. Previous reactions of this type [6,10] have been concerned with indole or pyrrole derivatives, in which the reactivity of the five-membered ring towards carbonyl compounds in general, and towards hexane-2,5-dione in particular, has been amply demonstrated. The formation of 1,4,7,10-tetramethyl-5*H*-benzo[*b*]carbazole in preference to its 6,7,10,11-tetramethyl isomer (IV) suggests that formation of the latter may be prevented by steric factors, owing presumably to the presence in (IV) of two pairs of methyl groups substituted in the *peri*-positions in a naphthalenoid system. Finally, the formation of linear rather than angular benzocarbazoles following initial attack *para* to the nitrogen atom is consistent with the relative electron densities calculated for the relevant positions in the carbazole nucleus.[11]

Experimental

1,4-*Dimethylcarbazole*.—A rapid stream of dry hydrogen chloride was passed into a solution of indole (40 g.) and hexane-2,5-dione (80 g.) in ethanol (130 ml.) for 7 min. The solution was boiled for 45 min. and then cooled, and the crude solid was dried and extracted with boiling light petroleum (b. p. 60—80°) (charcoal). The residue obtained on evaporation was dissolved in ethanol (120 ml.), and added to a mixture of semicarbazide hydrochloride (30 g.), sodium acetate (30 g.), and aqueous ethanol (1 : 1 mixture; 100 ml.). The solution was gently heated (steam-bath) for 5 min., allowed to cool, and the precipitated semicarbazone washed with ethanol. The filtrate and washings were combined and diluted with much water; the product was recrystallised from aqueous ethanol. 1,4-Dimethylcarbazole (24 g., 36%) formed needles, m. p. 97—98°.

3-*Formyl*-1,4-*dimethylcarbazole*.—1,4-Dimethylcarbazole (11·5 g.) was added in small portions to a cooled solution of *N*-methylformanilide (10·6 g.) and phosphorus oxychloride (10·7 g.) in *o*-dichlorobenzene (30 ml.), and the mixture was heated (steam-bath) under reflux for 3½ hr. A solution of sodium acetate (25 g.) in water (100 ml.) was added and the mixture was distilled in steam until all the volatile material had been removed. When cold, the solid residue was dried and extracted with benzene (charcoal). The extracts yielded a green solid, which was obtained from benzene as short, pale greenish-yellow needles, m. p. 204—208° (6·1 g., 47%). The melting point was not raised by further crystallisation, so the product was dissolved in benzene–chloroform (3 : 1) and chromatographed on neutral alumina (300 g.). Elution with benzene–chloroform (3 : 2) furnished 3-*formyl*-1,4-*dimethylcarbazole* (5·5 g.) as long needles (from benzene), m. p. 215—216°; ν 3230, 1653, 888, and 735 cm.$^{-1}$ (Nujol suspension) (Found: C, 80·4; H, 5·7; N, 6·25. $C_{15}H_{13}NO$ requires C, 80·7; H, 5·9; N, 6·3%). The *dinitrophenylhydrazone* crystallised from pyridine as red needles, m. p. 326° (decomp.) (Found: C, 62·3; H, 4·3; N, 17·3. $C_{21}H_{17}N_5O_4$ requires C, 62·5; H, 4·2; N, 17·4%). The *oxime* crystallised from aqueous pyridine as prisms, m. p. 246—247·5° (Found: C, 75·45; H, 6·0; N, 11·5. $C_{15}H_{14}N_2O$ requires C, 75·6; H, 5·9; N, 11·8%).

3,6-*Diformyl*-1,4-*dimethylcarbazole*.—1,4-Dimethylcarbazole (2 g.) was added in portions to an ice-cooled mixture of *N*-methylformanilide (5·1 ml.) and phosphorus oxychloride (3·3 ml.). The mixture was then heated (steam-bath), gently at first, for 3½ hr. Water (150 ml.) was added, and the mixture was stirred and heated until the dark insoluble material solidified. When cold, the solid was dried, powdered, and extracted with chloroform. Removal of the solvent gave the crude dialdehyde (1·76 g., 69%), which was recrystallised from aqueous pyridine. 3,6-*Diformyl*-1,4-*dimethylcarbazole* (1 g., 40%) was obtained as pale yellow needles,

[10] Plancher, *Ber.*, 1902, **35**, 2606; Allen, Gilbert, and Young, *J. Org. Chem.*, 1938, **2**, 235; Robinson and Saxton, *J.*, 1950, 3136; 1953, 2596; Saxton, *J.*, 1951, 3239.

[11] Coulson and Longuet-Higgins, *Rev. sci.*, 1947, **85**, 929.

m. p. 264—267° (decomp.); ν 3175, 1658, 1646, 896, and 809 cm.$^{-1}$ (potassium chloride disc) (Found: C, 76·65; H, 5·15; N, 5·8. $C_{16}H_{13}NO_2$ requires C, 76·5; H, 5·2; N, 5·6%).

1,3,4-*Trimethylcarbazole*.—(*a*) A mixture of 3-formyl-1,4-dimethylcarbazole (0·7 g.), hydrazine hydrate (0·4 ml.), potassium hydroxide (0·6 g.), and diethylene glycol (6 ml.) was slowly distilled until the temperature of the solution reached 190°; it was then maintained at this temperature for 1¼ hr. The cooled solution was poured into water and the product was crystallised thrice from methanol. 1,3,4-*Trimethylcarbazole* (0·4 g.) was obtained as needles, m. p. 146—146·5°; ν 3425, 870, and 751 cm.$^{-1}$ (potassium chloride disc) (Found: C, 86·05; H, 7·15. $C_{15}H_{15}N$ requires C, 86·1; H, 7·2%).

(*b*) A solution of 2,4,5-trimethylphenylhydrazine [12] (0·8 g.) in acetic acid (9 ml.) was added slowly to a solution of cyclohexanone (0·6 ml.) in acetic acid (6 ml.), and the mixture was then heated (steam-bath) for 1½ hr. in an atmosphere of nitrogen. The solvent was removed, the residue was dissolved in ether, and washed with dilute hydrochloric acid and then water. The dried ethereal solution was evaporated, and the crude product was crystallised once from light petroleum (b. p. 60—80°). It was then mixed with 10% palladised charcoal (0·1 g.), and heated in an atmosphere of nitrogen at 200—220° for 1¼ hr. The product was crystallised twice from light petroleum (b. p. 60—80°) (charcoal), and 1,3,4-trimethylcarbazole (0·1 g.) was obtained as needles, m. p. 143—145·5° undepressed on admixture with the product obtained in procedure (*a*). The infrared spectra of the two specimens were identical.

1,4,6-*Trimethylcarbazole*.—4-Methylcyclohexanone (7·9 g.) was added to a solution of *p*-xylylhydrazine (9·0 g.) in ethanol (30 ml.) containing one drop of glacial acetic acid. The solution was boiled for 40 min. and the solvent was then removed under reduced pressure. A solution of the residue in glacial acetic acid (40 ml.) was boiled for 1¼ hr. in an atmosphere of nitrogen. The solvent was removed under reduced pressure, the residue was dissolved in ether, and the ethereal solution was washed with dilute hydrochloric acid, then with dilute sodium carbonate solution, and finally with water. Evaporation of the dried ethereal solution gave a solid which was crystallised from light petroleum (b. p. 60—80°) (charcoal). Impure 5,6,7,8-tetrahydro-1,4,6-trimethylcarbazole (3·3 g.) was obtained as prisms, m. p. 98—104°. This was mixed with 10% palladised charcoal (0·2 g.) and heated at 210° for 2½ hr. in an atmosphere of nitrogen. The product was purified by chromatography on neutral alumina. Crystallisation from light petroleum (b. p. 60—80°) gave 1,4,6-*trimethylcarbazole* (1·7 g.) as prisms, m. p. 127—128°; ν 3400, 871, 808, and 796 cm.$^{-1}$ (potassium chloride disc) (Found: C, 85·95; H, 7·0. $C_{15}H_{15}N$ requires C, 86·1; H, 7·2%).

3-*Formyl*-1,4,6-*trimethylcarbazole*.—1,4,6-Trimethylcarbazole (2·1 g.) was added in portions to a mixture of *N*-methylformanilide (2·7 g.) and phosphorus oxychloride (1·7 g.); the reaction mixture was then heated (steam-bath) for 1½ hr. Dilute sodium hydroxide (50 ml.) was added, and the mixture was stirred and heated until the dark product solidified. When cold, the product was collected, dried, powdered, and extracted with benzene (charcoal). Removal of the solvent gave crude 3-*formyl*-1,4,6-*trimethylcarbazole* which was recrystallised twice from benzene, and obtained as needles (0·7 g.), m. p. 225·5—227°; ν 3195, 1656, 886, 862, 835, and 800 cm.$^{-1}$ (potassium chloride disc) (Found: C, 81·0; H, 6·3; N, 5·8. $C_{16}H_{15}NO$ requires C, 81·0; H, 6·3; N, 5·9%).

1,3,4,6-*Tetramethylcarbazole*.—(*a*) Wolff–Kishner reduction of 3,6-diformyl-1,4-dimethylcarbazole (0·57 g.) was carried out according to the conditions given above for the preparation of 1,3,4-trimethylcarbazole. 1,3,4,6-*Tetramethylcarbazole* (0·21 g.) was obtained from light petroleum (b. p. 60—80°) as needles, m. p. 190—191·5°; $\lambda_{max.}$ (in ethanol) 230—234sh, 238, 243, 267, 295, 323, and 334 mμ (log ε 4·51, 4·56, 4·58, 4.20, 4·20, 3·52, and 3·61, respectively); ν 3400, 877, 862, 859, and 806 cm.$^{-1}$ (potassium chloride disc) (Found: C, 85·8; H, 7·65. $C_{16}H_{17}N$ requires C, 86·1; H, 7·6%).

(*b*) Wolff–Kishner reduction of 3-formyl-1,4,6-trimethylcarbazole (0·48 g.) under similar conditions gave 1,3,4,6-tetramethylcarbazole (0·3 g.), obtained from light petroleum as prisms, m. p. 191·5—192·5° alone and 190—192° when mixed with the product from procedure (*a*) (Found: C, 86·35; H, 7·45%). The infrared spectra of the two specimens were identical.

3-(2,2-*Diethoxyethyliminomethyl*)-1,4-*dimethylcarbazole* [II; R = $CH{:}N{\cdot}CH_2{\cdot}CH(OEt)_2$].—A mixture of 3-formyl-1,4-dimethylcarbazole (5 g.) and 2,2-diethoxyethylamine (3·3 ml.) was

[12] Franzen, Onsager, and Faerden, *J. prakt. Chem.*, 1918, **97**, 336.

heated (steam-bath) for 2 hr. Benzene (50 ml.) was added, and the water formed in the reaction was removed by co-distillation. The viscous residue crystallised slowly, and was then recrystallised thrice from benzene. 3-(2,2-*Diethoxyethyliminomethyl*)-1,4-*dimethylcarbazole* (6·4 g., 85%) was obtained as needles, m. p. 129—130°; ν 3106, 1639, 1136, 1115, 1064, 1015, 879, and 746 cm.$^{-1}$ (Nujol suspension) (Found: C, 74·2; H, 7·75; N, 8·15. $C_{21}H_{26}N_2O_2$ requires C, 74·6; H, 7·7; N, 8·3%).

Attempts to convert this derivative directly into ellipticine by means of sulphuric or polyphosphoric acid failed; no trace of basic material was obtained. The use of the boron trifluoride–ether complex was also unsuccessful, and 3-formyl-1,4-dimethylcarbazole was recovered.

3-(2,2-*Diethoxyethylaminomethyl*)-1,4-*dimethylcarbazole* [II; R = CH_2·NH·CH_2·$CH(OEt)_2$].—3-(2,2-Diethoxyethyliminomethyl)-1,4-dimethylcarbazole (5 g.) in ethanol (80 ml.) was hydrogenated at a pressure of 5 atm. and room temperature, Raney nickel catalyst being used. The solution was filtered, the solvent was removed, and the residue was crystallised thrice from light petroleum (b. p. 60—80°). 3-(2,2-*Diethoxyethylaminomethyl*)-1,4-*dimethylcarbazole* (3·6 g.) was obtained as needles, m. p. 105—106° (Found: C, 73·95; H, 8·3; N, 8·0. $C_{21}H_{28}N_2O_2$ requires C, 74·1; H, 8·2; N, 8·2%).

Attempts to cyclise this compound by using sulphuric acid and arsenic pentoxide, or polyphosphoric acid, failed. Cyclisation by means of the boron trifluoride–ether complex gave an insoluble complex containing boron, which did not melt below 330°; attempts to decompose this complex by acidic (sulphuric acid) or basic (sodium hydroxide, ammonia, or pyridine) reagents failed.

Ellipticine.—A solution of 3-(2,2-diethoxyethylaminomethyl)-1,4-dimethylcarbazole (1 g.) in ethanol (25 ml.) was saturated with dry hydrogen chloride and boiled for 1¼ hr. When cold, the crude hydrochloride was collected, dissolved in water, and an excess of dilute sodium hydroxide was added. The base was extracted with chloroform, the extracts were washed with water, dried, and the solvent was removed. The residue (0·6 g.) was mixed with 10% palladised charcoal (0·2 g.) and heated at 225—235° in a stream of nitrogen for 2½ hr. The product was extracted with ethanol-free ethyl acetate (charcoal), and recrystallised thrice from the same solvent. Ellipticine (0·07 g.) was obtained as bright yellow needles, m. p. 309—313° (decomp.) alone and when mixed with authentic ellipticine; R_F, 0·71 [by using the upper phase of a butanol–acetic acid–water (4 : 1 : 5) mixture on Whatman No. 1 paper]; $\lambda_{max.}$ (in ethanol) 239, 277, 286, 294, 332, 340—345sh, 382, and 400 mμ (log ε 4·23, 4·61, 4·76, 4·74, 3·65, 3·47, 3·61, and 3·53, respectively) (Found: C, 82·6; H, 6·0; N, 11·4. Calc. for $C_{17}H_{14}N_2$: C, 82·9; H, 5·7; N, 11·35%). The infrared (potassium chloride disc) and ultraviolet spectra were identical with those of the authentic ellipticine. Ellipticine methiodide crystallised from methanol as orange needles, m. p. 348° (decomp.) alone or on admixture with authentic ellipticine methiodide (Found: C, 55·5; H, 4·55; I, 32·5. Calc. for $C_{18}H_{17}IN_2$: C, 55·65; H, 4·4; I, 32·7%). The infrared spectra (potassium chloride disc) of synthetic and authentic ellipticine methiodide were identical.

Ethyl N-(1,4-*Dimethyl*-3-*carbazolylidene*)*aminoacetate*.—A mixture of 3-formyl-1,4-dimethylcarbazole (3·5 g.) and ethyl aminoacetate (1·7 g.) was heated (steam-bath) for 2 hr. Benzene (25 ml.) was added, and the water removed by co-distillation. Crystallisation of the residue twice from benzene gave *ethyl* N-(1,4-*dimethyl*-3-*carbazolylidene*)*aminoacetate* (3·7 g.) as prisms, m. p. 167—169°; ν 3280, 1730, 1631, 890, 754, and 743 cm.$^{-1}$ (potassium chloride disc) (Found: C, 74·05; H, 6·4; N, 9·25. $C_{19}H_{20}N_2O_2$ requires C, 74·0; H, 6·5; N, 9·1%).

N-(1,4-*Dimethyl*-3-*carbazolylmethyl*)*aminoacetic Acid*.—Ethyl *N*-(1,4-dimethyl-3-carbazolylidene)aminoacetate (0·55 g.) was hydrogenated at room temperature and 5 atm. in ethanol (40 ml.), Raney nickel catalyst being used. The filtered solution was concentrated to 10 ml., sodium hydroxide (0·06 g.) in water (6 ml.) was added, and the mixture was boiled for 2½ hr. The solvent was removed, water (25 ml.) added, and the solution acidified to pH 5·5 with dilute acetic acid. N-(1,4-*Dimethyl*-3-*carbazolylmethyl*)*aminoacetic acid* (0·39 g., 75%) crystallised from water as prisms, m. p. 191—192·5° (Found: C, 68·5; H, 6·7; N, 9·6. $C_{17}H_{18}N_2O_2,H_2O$ requires C, 68·0; H, 6·7; N, 9·3%).

The *toluene*-p-*sulphonate* crystallised from ethanol as prisms, m. p. 188·5—190° (decomp.) (Found: C, 66·25; H, 5·65; N, 6·35; S, 7·35. $C_{24}H_{24}N_2O_4S$ requires C, 66·05; H, 5·5; N, 6·4; S, 7·3%).

Attempts to cyclise the above acid by means of sulphuric or polyphosphoric acid failed. When the toluene-*p*-sulphonate was treated with sulphuric acid the only product isolated was

N-toluene-*p*-sulphonylaminoacetic acid, m. p. 145—146°, identical (mixed m. p. and infrared spectrum) with authentic material.

3-*Aminomethyl*-1,4-*dimethylcarbazole*.—A solution of the oxime of 3-formyl-1,4-dimethylcarbazole (2·5 g.) in tetrahydrofuran (70 ml.) was added dropwise to a stirred, boiling solution of lithium aluminium hydride (0·8 g.) in tetrahydrofuran (20 ml.) at such a rate that gentle refluxing was maintained. The solution was boiled for a further 4 hr. When cold, water was cautiously added, followed by dilute sodium hydroxide solution (20 ml.). The solution was filtered, the organic layer was separated, and the aqueous layer was extracted with chloroform. The combined organic extracts were evaporated, and the residue was crystallised from benzene (charcoal). 3-*Aminomethyl*-1,4-*dimethylcarbazole* (1 g.) was obtained as prisms, m. p. 205—208° (Found: C, 80·8; H, 7·15; N, 12·15. $C_{15}H_{16}N_2$ requires C, 80·4; H, 7·1; N, 12·5%). The condensation product of this base with glyoxal monoacetal gave no basic product on being treated with sulphuric acid, or with sulphuric acid and hydrogen chloride.[7]

1,4,7,10-*Tetramethyl*-5H-*benzo*[b]*carbazole*.—(*a*) A rapid stream of dry hydrogen chloride was passed into a solution of indole (40 g.) and hexane-2,5-dione (80 g.) in ethanol (130 ml.) for 30 min. The solution was then boiled for 45 min., and the solvent was removed under reduced pressure. The tarry residue was extracted with light petroleum (b. p. 60—80°), and then with benzene (3 × 30 ml.). The crystalline material which separated from the benzene extracts on cooling was recrystallised several times from benzene (charcoal). 1,4,7,10-*Tetramethyl*-5H-*benzo*[b]*carbazole* (0·5 g.) was obtained as clusters of needles, m. p. 219·5—221·5°; $\lambda_{max.}$ (in ethanol) 237, 260infl., 272, 282, 307, 320, 335, 376, 395 mμ (log ε 4·48, 4·48, 4·71, 4·95, 3·68, 3·85, 3·89, 3·64, and 3·68); ν 3460, 873, 840, 805, and 796 cm.$^{-1}$ (potassium chloride disc) (Found: C, 88·0; H, 6·8; N, 5·2. $C_{20}H_{19}N$ requires C, 87·9; H, 6·95; N, 5·1%).

(*b*) A rapid stream of dry hydrogen chloride was passed into a solution of 1,4-dimethylcarbazole (2·0 g.) and hexane-2,5-dione (4 g.) in ethanol (10 ml.) for 20 min. The solution was then boiled for 1 hr., the solvent removed, and the residue extracted with light petroleum (b. p. 60—80°) and then with cyclohexane. The light-petroleum extracts yielded a small amount of 1,4,7,10-tetramethyl-5*H*-benzo[*b*]carbazole, m. p. 215—218° after recrystallisation from cyclohexane (charcoal). The cyclohexane extracts yielded a crude solid (1 g.), which was redissolved in cyclohexane and chromatographed on neutral alumina. The product was eluted with cyclohexane, and recrystallised from the same solvent. 1,4,7,10-Tetramethyl-5*H*-benzo[*b*]carbazole was thus obtained as feathery needles, m. p. 215—218° undepressed on admixture with the by-product from the reaction of indole and hexane-2,5-dione. The infrared spectra of these specimens were also identical.

1,2,4,7,10-*Pentamethyl*-5H-*benzo*[b]*carbazole*.—The condensation of 1,3,4-trimethylcarbazole (1 g.) with hexane-2,5-dione (1·1 ml.) was carried out according to the conditions described in the preceding experiment. Chromatography of the crude product on neutral alumina gave, on elution with benzene, 1,3,4-trimethylcarbazole (0·1 g.), followed by 1,2,4,7,10-*pentamethyl*-5H-*benzo*[b]*carbazole* (0·2 g.) which was obtained from cyclohexane as prisms, m. p. 252·5—254·5° (decomp.); $\lambda_{max.}$ (in ethanol) 238, 262infl., 273, 285, 323, 337, 380, and 400 mμ (log ε 4·49, 4·51, 4·71, 4·94, 3·92, 3·94, 3·65, and 3·70, respectively); ν 3400, 870, and 837 cm.$^{-1}$ (potassium chloride disc) (Found: C, 87·5; H, 7·35; N, 5·05. $C_{21}H_{21}N$ requires C, 87·8; H, 7·3; N, 4·9%).

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