Methoxylated Hexahydro-9 : 11-*dimethylcarbazoles.*

By M. F. Millson and Sir Robert Robinson.

[Reprint Order No. 6343.]

The hexahydro-*Bz*-methoxycarbazoles were found to be unsuitable as models for the colour reactions of indole alkaloids, doubtless because of oxidative changes. To avoid the latter the 3-position of the indole nucleus was fully substituted and the four hexahydro-*Bz*-methoxy-9 : 11-dimethylcarbazoles were prepared; their colour reactions and ultraviolet absorption spectra are described.

This investigation arose from a desire to facilitate comparisons of characteristic properties of certain indole alkaloids with model substances such that the position of a methoxyl group in the benzene nucleus could be virtually determined.

When we started the work it was thought that akuammine (Henry and Sharp, *J.*, 1927, 1950; Henry, *J.*, 1932, 2759) was a hydro-*Bz*-methoxyindole derivative, but it was later recognised as a phenol (Millson, Robinson, and Thomas, *Experientia*, 1953, **9**, 89). Nevertheless the oxidative reactions in acid solution and the ultraviolet absorption spectrum are quite close to those of bases derived from *p*-anisidine or *p*-phenetidine. Some notes on the chemistry of akuammine will, it is hoped, be submitted to the Society in a short time but the following Table and the light absorption data (see Fig. 1) suffice to make a good *prima facie* case for the *p*-aminophenol orientation. This is confirmed in the sequel.

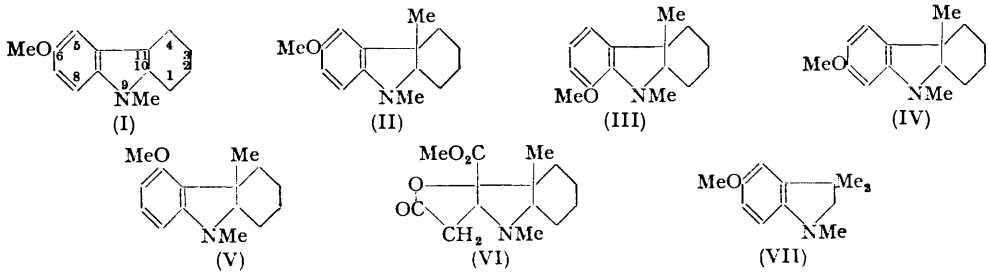
Substance	$FeCl_3$ in dil. HCl	$NaNO_2$ in acid soln. : original	on basification	Action of diazobenzenesulphonic acid
Akuammine ...	Orange-brown	Yellow-orange	Red	Does not form a methyl-orange
Strychnidine	Red	Red	Yellow	Forms a methyl-orange
Brucidine	Olive-green	Yellow-orange	Red	Does not form a methyl-orange
α-Colubridine (*m*-anisidine)	Red	Orange	Little change	Faint reaction
β-Colubridine (*p*-anisidine)	Orange	Yellow-orange	Darkens	Faint reaction
Eserethole	Orange-brown	Yellow	Red	No reaction
Hexahydro-9-methylcarbazole	Red	Red	Yellow	Forms a methyl-orange

One of the first substances we examined was 1 : 2 : 3 : 4 : 10 : 11-hexahydro-6-methoxy-9-methylcarbazole (I) which was prepared by standard methods. This substance resembled akuammine in its ultraviolet absorption spectrum and its failure to couple with diazobenzenesulphonic acid but under the influence of oxidising agents, even ferric chloride, a copious flocculent precipitate of the tetrahydrocarbazole was obtained. For this reason we turned to similar substances bearing a methyl group in position 11, as in (II). This substance was synthesised by two recognised methods, and then starting from *o*-anisidine we prepared (III).

From *m*-anisidine, two isomerides, one liquid and one crystalline, were obtained and separated by chromatography and distillation. The liquid isomer is 1 : 2 : 3 : 4 : 10 : 11-hexahydro-7-methoxy-9 : 11-dimethylcarbazole (IV), and the solid is the 5-methoxy-isomeride (V).

This conclusion follows from a study of the infrared absorption of the compounds (II)—(V) in the region 12—14 μ. The carbazoles (II) and (IV) are thus seen to be 1 : 2 : 4-unsubstituted [*i.e.*, unsubstituted at positions 5, 7, and 8 of (I)], whereas the isomers (III) and (V) contain three vicinal unsubstituted hydrogen atoms. In addition the phenol related to (IV) gives a rhodamine of normal type, whereas that derived from the solid isomer (V) gives a brilliant rhodamine exhibiting a quite different colour and fluorescence. A normal rhodamine is also obtained from α-colubridine, the benzene nucleus of which is known to be substituted as in (IV) (Warnat, *Helv. Chim. Acta*, 1931, **14**, 997). This was established by degradation to the related methoxyoxanthranilic acid. The yield was unfavourable, and in a similar permanganate oxidation of brucine, Späth and Bretschneider

(*Ber.*, 1930, **63**, 2997) obtained 4 : 5-dimethoxyoxanthranilic acid in a yield of only 0·23% of the theoretical. An attempt to distinguish between the isomers (IV) and (V) in this way was not made because it was found that the 6-methoxy-compound (II) was changed



by potassium permanganate into a product which was esterified by diazomethane and was then found to be neutral and to give analyses corresponding to the formula $C_{14}H_{21}O_4N$.

Absorption Spectra.

FIG. 1.

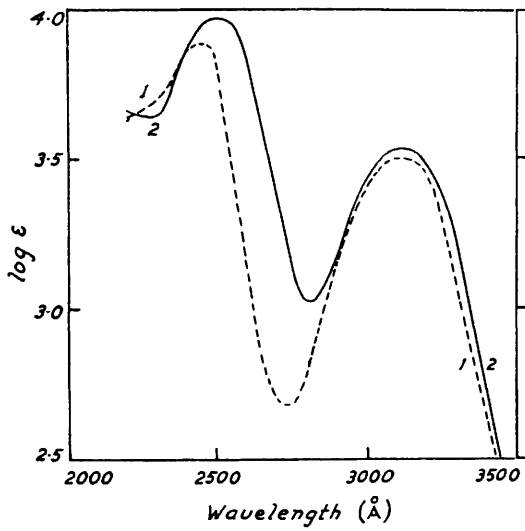


FIG. 2.

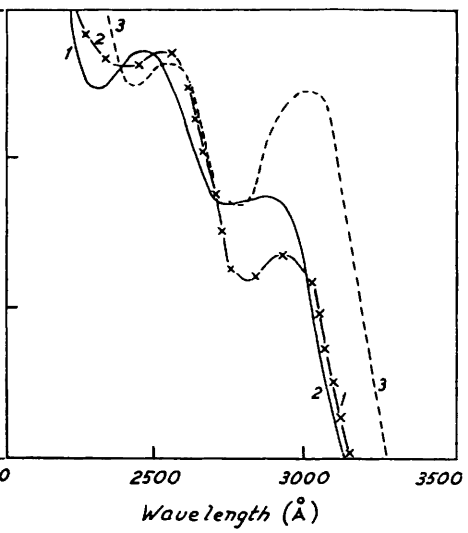


FIG. 1. 1, Akuammine.
2, 1 : 2 : 3 : 4 : 10 : 11-Hexahydro-6-methoxy-9 : 11-dimethylcarbazole (II).

FIG. 2. 1, 1 : 2 : 3 : 4 : 10 : 11-Hexahydro-8-methoxy-9 : 11-dimethylcarbazole (III).
2, 1 : 2 : 3 : 4 : 10 : 11-Hexahydro-5-methoxy-9 : 11-dimethylcarbazole (solid) (V)
3, 1 : 2 : 3 : 4 : 10 : 11-Hexahydro-7-methoxy-9 : 11-dimethylcarbazole (liquid) (IV).

It is possible to suggest several structures [of which (VI) is an example] for this substance but they are all based on the assumption that the benzene nucleus has been broken up. As our objective had been reached in another way it seemed unnecessary to carry the matter further. 5-Methoxy-1 : 3 : 3-trimethylindoline (VII) and some hexahydro-9-methylcarbazoles have been prepared for additional comparisons.

The following Table gives some of the colour reactions of the methoxylated bases and Figs. 1 and 2 show the ultraviolet absorptions.

In addition, only compounds (IV) and (V) give rise to rhodamines, and the isomer (II) gives an intense, stable, red-purple colour on the addition of a little dichromate to a solution in dilute sulphuric acid.

Dr. H. T. Openshaw has very kindly sent us details of quite similar results which he and Mr. J. R. Chalmers have obtained with the isomeric hexahydromethoxycarbazoles, studied in connexion with the constitution of aspidospermine.

Substance	$FeCl_3$ in dil. HCl	$NaNO_2$ in acid soln. : original	on basification	Action of diazobenzenesulphonic acid
(II)	Orange-brown	Yellow (dil. soln.)	Red	Does not form a methyl-orange
(III)	Magenta	Red	Yellow	Forms a methyl-orange
(IV)	Red	Red	Yellow	Forms a reddish colour in acid, but not a methyl-orange
(V)	Red	Red	Yellow	Forms a reddish colour in acid, but not a methyl-orange
(I)	Yellow-brown, rapidly fading	Yellow	Yellow	Does not form a methyl-orange
(VII)	Orange-brown	Yellow	Red	Does not form a methyl-orange

Experimental

N-Methyl-N-nitroso-p-anisidine (cf. Hodgson and Crook, *J.*, 1932, 1812).—Methyl sulphate (30 c.c.) was added with vigorous swirling during 15 min. to molten *p*-anisidine (50 g.). The mixture became hot and was kept for an hour, mixed with sodium hydroxide solution, and steam-distilled. The isolated, mixed bases were dissolved in hydrochloric acid (150 c.c.; *d* 1·16) and water (100 c.c.). Sodium nitrite (40 g.) in water (200 c.c.) was added to the stirred solution initially at 0° and always below 5°. The pale brown precipitate of *N*-methyl-*N*-nitroso-*p*-anisidine was collected, washed with water, and dried (20·5 g.); after crystallisation from light petroleum (b. p. 60—80°) it was obtained as colourless plates, m. p. 46—47° (15·9 g.).

The acid filtrate from the nitrosation mixture was treated with an excess of sodium nitrite solution and kept at the room temperature for 1 hr. The crystals that separated were recrystallised successively from ethanol, methanol, and aqueous methanol and obtained as almost colourless needles, m. p. 111·5°, insoluble in hot or cold dilute acid and alkali and showing a strong Liebermann reaction (Found : C, 37·8, 37·4; H, 3·7, 3·2; N, 21·8. Calc. for $C_8H_8O_6N_4$: C, 37·5; H, 3·1; N, 21·9%). The substance is therefore *N*-methyl-3 : 5-dinitro-*N*-nitroso-*p*-anisidine obtained by Hodgson and Crook (*J.*, 1933, 825) by the action of dilute nitric acid on *NN*-dimethyl-*p*-anisidine.

1 : 2 : 3 : 4-*Tetrahydro*-6-*methoxy*-9-*methylcarbazole*.—A solution of *N*-methyl-*N*-nitroso-*p*-anisidine (15·9 g.) in acetic acid (26·5 c.c.) was added slowly to a stirred suspension of zinc dust (26·5 g.) in water (40·5 c.c.), and stirring continued for 1½ hr.; the temperature was maintained at 10—15° throughout. *cyclo*Hexanone (9·8 c.c.) was added slowly, and the mixture heated to 80° for ½ hr. After the addition of hot dilute sulphuric acid (23 c.c. of *d* 1·84; water, 104 c.c.), the mixture was refluxed for 20 min. The cooled solution deposited a pink solid which was collected and extracted with boiling ethanol (4 × 40 c.c.). When the combined filtered extracts were poured into water (1500 c.c.) with stirring, 1 : 2 : 3 : 4-*tetrahydro*-6-*methoxy*-9-*methylcarbazole* (13·5 g.) was precipitated. It crystallised from aqueous ethanol as colourless needles, m. p. 88—89° (Found : C, 78·2; H, 9·0. $C_{14}H_{17}ON$ requires C, 78·1; H, 8·0%).

1 : 2 : 3 : 4 : 10 : 11-*Hexahydro*-6-*methoxy*-9-*methylcarbazole* (cf. Perkin and Plant, *J.*, 1924, 1512) (I).—A mixture of 1 : 2 : 3 : 4-tetrahydro-6-methoxy-9-methylcarbazole (5 g.), ethanol (8·6 c.c.), concentrated hydrochloric acid (8·6 c.c.), and granulated tin (8·6 g.) was refluxed for 3 hr. The hot solution was filtered, and the residue washed with a hot mixture of ethanol (3 c.c.) and concentrated hydrochloric acid (3 c.c.). The combined filtrates were cooled, made alkaline, and steam-distilled. The distillate was basified with ammonia and extracted with ether. The dark residual oil from the dried extract afforded 1 : 2 : 3 : 4 : 10 : 11-*hexahydro*-6-*methoxy*-9-*methylcarbazole* (3·2 g.) as a colourless oil, b. p. 188—189°/21 mm., which rapidly darkened in the air (Found : C, 77·6; H, 8·8; N, 6·5. $C_{14}H_{19}ON$ requires C, 77·4; H, 8·8; N, 6·5%); the *picrate* formed yellow plates (from ethanol), m. p. 132·5—133° (Found : C, 53·6; H, 4·8; N, 12·3. $C_{14}H_{19}ON,C_6H_3O_7N_3$ requires C, 53·8; H, 5·0; N, 12·6%).

2 : 3 : 4 : 11-*Tetrahydro*-6-*methoxy*-9 : 11-*dimethylcarbazole and* 1 : 2 : 3 : 4-*Tetrahydro*-6-*methoxy*-1 : 9-*dimethylcarbazole*.—(i) *N*-Methyl-*N*-nitroso-*p*-anisidine (11·4 g.) was reduced as above with zinc dust (18·9 g.) in acetic acid (18·9 c.c.) and water (28·7 c.c.). 2-Methyl*cyclo*hexanone (8 c.c.) was introduced and the mixture kept at 80° for 30 min. Hot dilute sulphuric acid (16·4 c.c. of *d* 1·84; water, 74 c.c.) was then added and the mixture was refluxed for 20 min. The cooled solution was extracted several times with ether (A). The aqueous layer was mixed with saturated picric acid solution, and the *N*-methyl-*p*-anisidine picrate which separated was collected and crystallised from ethanol, forming yellow rods, m. p. 159° (Found : C, 46·3; H, 3·8; N, 15·1. Calc. for $C_8H_{11}ON,C_6H_3O_7N_3$: C, 45·9; H, 3·9; N, 15·3%).

On evaporation of the dried ethereal extract (A) 1 : 2 : 3 : 4-*tetrahydro*-6-*methoxy*-1 : 9-*dimethylcarbazole* was obtained as a colourless solid which crystallised from ethanol in needles

(1·9 g.), m. p. 75—76°, rapidly reddening in air (Found : C, 78·4; H, 8·4. $C_{15}H_{19}ON$ requires C, 78·6; H, 8·4%).

(ii) (cf. Plancher *et al.*, *Gazzetta*, 1929, **59**, 334). A mixture of 1 : 2 : 3 : 4-tetrahydro-6-methoxy-9-methylcarbazole (10·9 g.) and methyl iodide (55 g.) was heated in a sealed tube at 116° for 10 hr. The light brown crystalline mass was freed from methyl iodide and extracted with hot ethanol. The solution, on being kept in the dark for 3 days, deposited 2 : 3 : 4 : 11-*tetrahydro-6-methoxy-9 : 11-dimethylcarbazole hydriodide* as pale brown needles. Recrystallisation from ethanol gave colourless prisms, m. p. 186—187°, which became brown on exposure to air or daylight (Found : C, 50·4; H, 5·8; N, 3·8; I, 35·3. $C_{15}H_{19}ON$,HI requires C, 50·4; H, 5·6; N, 3·9; I, 35·5%). Most of the ethanol was removed from the solution of the crude hydriodide, and the residue was taken up in dilute hydrochloric acid. The aqueous solution was twice washed with ether and basified, and the liberated base isolated with ether and distilled. 2 : 3 : 4 : 11-*Tetrahydro-6-methoxy-9 : 11-dimethylcarbazole* was obtained as a pale yellow oil, b. p. 146—147°/0·5 mm. (Found : C, 79·0; H, 8·6; N, 6·0. $C_{15}H_{19}ON$ requires C, 78·6; H, 8·4; N, 6·1%). The picrate forms rosettes of fine, yellow needles, m. p. 140·5°, from ethanol (Found : C, 54·8; H, 4·5; N, 11·9. $C_{15}H_{19}ON,C_6H_3O_7N_3$ requires C, 55·0; H, 4·8; N, 12·2%).

(iii) *N*-Methyl-*N*-nitroso-*p*-anisidine (43·6 g.) was reduced with zinc dust and acetic acid as described above. The *N*-*p*-methoxyphenyl-*N*-methylhydrazine was isolated and distilled (20·5 g.). It was heated on the steam-bath with 2-methyl*cyclo*hexanone (15 c.c.), finally ***in vacuo*** until all the water was removed. After addition of acetic acid (250 c.c.) the mixture was refluxed for 30 min. Most of the acetic acid (190 c.c.) was removed under reduced pressure, and water (200 c.c.) and concentrated hydrochloric acid (20 c.c.) were added to the residue, after which the whole was several times washed with ether. The aqueous solution was made alkaline and the liberated bases were isolated with ether and distilled. The colourless oil, b. p. 60—115°/0·01 mm., was not further purified, but was immediately hydrogenated (see below).

1 : 2 : 3 : 4 : 10 : 11-*Hexahydro-6-methoxy-9 : 11-dimethylcarbazole* (II).—(*A*) A solution of 2 : 3 : 4 : 11-tetrahydro-6-methoxy-9 : 11-dimethylcarbazole (3·1 g.) (see ii, above) in ethanol (50 c.c.) was shaken under hydrogen at the room temperature and pressure in the presence of 10% palladised charcoal. Absorption of hydrogen ceased after 100 min., when 300 c.c. of hydrogen had been taken up (theor. for $1H_2$, 315 c.c.). The solution was filtered, concentrated, and distilled; 1 : 2 : 3 : 4 : 10 : 11-*hexahydro-6-methoxy-9 : 11-dimethylcarbazole* (2·9 g.) was collected at 148°/0·5 mm. as a colourless oil. This solidified, and crystallisation from a very small volume of light petroleum (b. p. 40—60°) gave colourless needles, m. p. 43—44° (Found : C, 78·1; H, 9·4; N, 5·9; *C*-Me, 3·7. $C_{15}H_{21}ON$ requires C, 77·9; H, 9·1; N, 6·1; *C*-Me, 6·5%). The base forms a *picrate*, pale yellow plates from ethanol (Found : C, 55·1; H, 5·1; N, 12·1. $C_{15}H_{21}ON,C_6H_3O_7N_3$ requires C, 54·8; H, 5·3; N, 12·2%), the m. p. (decomp.) of which varies over the range 155—169° according to the rate of heating; in a bath preheated to 155°, rapid heating results in decomposition at 169°.

(*B*) The colourless oil, b. p. 60—115°/0·01 mm. (see iii above), dissolved in ethanol (100 c.c.), was shaken under hydrogen with 10% palladised charcoal at the room temperature and pressure. No absorption of hydrogen occurred under these conditions, or at 50°. The solution was filtered and hydrogenation repeated using Raney nickel at 45°; 900 c.c. of hydrogen were absorbed in 12 hr. The filtered solution was concentrated, and the residual oil fractionated, giving : (*a*) *N*-methyl-*p*-anisidine, b. p. 48—57°/0·003 mm., m. p. 38°; (*b*) b. p. 88—90°/0·003 mm., a colourless oil which was again fractionated; then the oil, b. p. 85—88°/0·01 mm., solidified and had m. p. 42—43°. After crystallisation from light petroleum (b. p. 40—60°), it was obtained as colourless needles, m. p. 44—45°, identical with that obtained by the procedure (*A*) as shown by undepressed mixed m. p. and by the similar behaviour of the picrates.

1 : 2 : 3 : 4-*Tetrahydro-8-methoxy-9-methylcarbazole*.—*o*-Anisidine (100 g.) was methylated with methyl sulphate as described for *p*-anisidine. The mixture of bases obtained was dissolved in dilute sulphuric acid (65 c.c. of *d* 1·84; water, 1000 c.c.) and, while the solution was vigorously stirred with ether (200 c.c.), sodium nitrite (42 g.) in water (200 c.c.) was added at <5°. The ethereal layer was separated, and the aqueous solution extracted with ether. Removal of the solvent from the combined, dried, ethereal solutions left the nitrosamine as a dark oil (44 g.).

The crude nitrosamine was reduced as was *N*-nitroso-*p*-anisidine (above), with zinc dust and acetic acid. *cyclo*Hexanone (27 c.c.) was added to the stirred suspension, and the mixture was heated at 80° during 1 hr. and then refluxed with dilute sulphuric acid (88 c.c. of *d* 1·84; water, 420 c.c.) for 20 min. The acidic suspension, containing a red oil, was extracted with ether,

and the extract was washed with dilute sodium hydroxide solution and water, and dried ($MgSO_4$). After evaporation of the ether, most of the *cyclo*hexanone was removed *in vacuo*. The residue partly crystallised overnight, and the crystals were collected; by further concentration of the mother-liquors a second crop was obtained. Recrystallisation of the combined crops from ethanol furnished pure 1 : 2 : 3 : 4-*tetrahydro*-8-*methoxy*-9-*methylcarbazole* (4·0 g.), colourless needles, m. p. 100—101° (Found: C, 78·4; H, 8·2; N, 6·8. $C_{14}H_{17}ON$ requires C, 78·1; H, 8·0; N, 6·5%).

In a later preparation the reaction mixture from the reduction of the nitrosamine and treatment with *cyclo*hexanone was heated on the steam-bath for 2 hr., cooled, and extracted with ether. The ether was removed from the undried extract, and the resultant black oil (*e.g.*, 20 g.) was added to acetic acid (50 c.c.), concentrated sulphuric acid (2 c.c.), and water (160 c.c.), and the whole was refluxed for 35—45 min. The cooled suspension was extracted with ether, and the extract freed from acetic acid with dilute sodium hydroxide solution and washed with water. The residue from the dried extract was distilled, giving 1 : 2 : 3 : 4-tetrahydro-8-methoxy-9-methylcarbazole, b. p. 180—210°/15 mm. Attempts to methylate this base with methyl iodide were unsuccessful.

2 : 3 : 4 : 11-*Tetrahydro*-8-*methoxy*-9 : 11-*dimethylcarbazole*.—Crude *N*-methyl-*N*-nitroso-*o*-anisidine (48·5 g.) was reduced in the usual manner. The product was heated with 2-methyl-*cyclo*hexanone (34 c.c.) on the steam-bath for 2 hr., cooled, and extracted with ether. The oily residue (66 g.) from the dried extract was divided into three equal portions. One portion was refluxed with a mixture of acetic acid and dilute sulphuric acid, another with acetic acid (above). Extraction of the diluted and basified solutions with ether afforded small quantities of yellow oils, b. p. 200—210°/2 mm. and 140—160°/1 mm., respectively.

The third portion of the crude hydrazone was heated at 60—80° with 10% sulphuric acid (200 c.c.) for 11 hr. After being washed with ether the solution was basified and again extracted and the product distilled. Recovered *N*-methyl-*o*-anisidine, b. p. 103—105°/10 mm., m. p. 31—33°, was followed by an almost colourless oil, b. p. 140—170°/2 mm., which solidified on keeping at −5° in about 3 weeks (m. p. 45—61°).

The small higher-boiling fractions from the first two portions of crude hydrazone were cooled to −5° and seeded with this solid; they partly crystallised, but were liquid at the room temperature. This product (1·2 g.) was triturated with a small volume of light petroleum (b. p. 40—60°), cooled in carbon dioxide–ethanol. The crystals so obtained were combined with the material, m. p. 45—61°, and recrystallised from light petroleum (b. p. 40—60°), to give 2 : 3 : 4 : 11-*tetrahydro*-8-*methoxy*-9 : 11-*dimethylcarbazole* (*ca.* 250 mg.) as colourless needles, m. p. 79—80° (Found: C, 78·6; H, 8·1; N, 6·3. $C_{15}H_{19}ON$ requires C, 78·6; H, 8·4; N, 6·1%). The *picrate*, yellow rods from ethanol, had m. p. 215° (decomp.) (Found: C, 55·1; H, 4·7. $C_{15}H_{19}ON,C_6H_3O_7N_3$ requires C, 55·0; H, 4·8%). A specimen of this picrate was oxidised by air during recrystallisations from ethanol, giving a *picrate* which formed green rods, m. p. 210—212° (Found: C, 53·6; H, 4·3; N, 11·9. $C_{15}H_{17}O_2N,C_6H_3O_7N_3$ requires C, 53·4; H, 4·3; N, 11·9%).

1 : 2 : 3 : 4 : 10 : 11-*Hexahydro*-8-*methoxy*-9 : 11-*dimethylcarbazole* (III).—Crude *N*-methyl-*N*-nitroso-*o*-anisidine (46 g.) was reduced and the product treated with 2-methyl*cyclo*hexanone (30 c.c.) as described above. The dark oil (75 g.) was heated at 80° with 10% sulphuric acid (500 c.c.) for 11 hr. and worked up as already described. The product, b. p. 140—145°/1 mm., was a thick yellow oil (1·75 g.) which largely solidified when seeded with 2 : 3 : 4 : 11-tetrahydro-8-methoxy-9 : 11-dimethylcarbazole. It was dissolved in ethanol (40 c.c.) and shaken under hydrogen with Raney nickel at 60°. After 12 hr., about 150 c.c. of hydrogen had been absorbed. The filtered solution was distilled and 1 : 2 : 3 : 4 : 10 : 11-*hexahydro*-8-*methoxy*-9 : 11-*dimethylcarbazole* (1 g.) was obtained as a colourless viscous oil, b. p. 103—105°/0·06 mm. (Found: C, 78·1; H, 9·2. $C_{15}H_{21}ON$ requires C, 77·9; H, 9·1%).

m-*Anisidine*.—A solution of *m*-nitroanisole (160 g.) (cf. *Org. Synth.*, Coll. Vol. I, 2nd edn., p. 404; Hodgson and Nixon, *J.*, 1930, 2166) in ethanol (400 c.c.) was shaken with Raney nickel under hydrogen at 95°/90 atm.; after removal of the solvent the base was purified by dissolution in dilute hydrochloric acid, washing with ether, basification, isolation with ether, and distillation. *m*-Anisidine (121 g.) was obtained as a colourless oil, b. p. 123—125°/15 mm.

N-*Methyl*-m-*anisidine*.—(*a*) An attempted methylation of *m*-anisidine with methyl iodide in ether resulted in the separation of *m*-anisidine hydriodide which crystallised from methanol–ether in colourless needles, m. p. 175—177° (Found: C, 33·9; H, 4·0. Calc. for C_7H_9ON,HI: C, 33·5; H, 4·0%).

(*b*) Methyl sulphate (49·2 c.c.) was added dropwise and with swirling to *m*-anisidine (82 g.)

initially at 60°. The hot products were cooled, poured into an excess of sodium hydroxide solution, and steam-distilled. The bases were isolated from the distillate with ether, and distilled; crude *N*-methyl-*m*-anisidine (80 g.) was obtained as a pale yellow oil, b. p. 118—119·5°/8 mm.

(*c*) Benzene (300 c.c.) was added to an intimate mixture of powdered sodamide (17·6 g.) and powdered *N*-acetyl-*m*-anisidine (71 g.). When the evolution of ammonia slackened, the mixture was refluxed until it suddenly became a gel. The benzene was then removed under diminished pressure and ether (300 c.c.) added to the hard white residue. Methyl iodide (61 g.) was added and the mixture kept for 2 hr. and then refluxed for 11 hr. After addition of water (400 c.c.) the ethereal layer was washed with dilute acid and water, and evaporated, giving *N-acetyl-N-methyl*-m-*anisidine* as a colourless solid; crystallisation from light petroleum (b. p. 40—60°) gave colourless prisms (48 g.), m. p. 64° (Found : C, 67·0; H, 7·4; N, 7·5. $C_{10}H_{13}O_2N$ requires C, 67·0; H, 7·3; N, 7·8%). This derivative (19·6 g.) was refluxed with 25% sulphuric acid (400 c.c.) for 2 hr. The cooled solution was basified, and the base isolated with ether and distilled. *N-Methyl*-m-*anisidine* (13·8 g.) was obtained as a colourless oil, b. p. 131°/17 mm. (Found : C, 70·2; H, 8·2; N, 10·3. $C_8H_{11}ON$ requires C, 70·0; H, 8·1; N, 10·2%). The picrate formed yellow or red-brown prisms (from ethanol), m. p. 147° (decomp.) (Found : C, 46·0, 46·2; H, 3·9, 3·7; N, 15·6, 15·1. $C_8H_{11}ON,C_6H_3O_7N_3$ requires C, 45·9; H, 3·9; N, 15·3%).

N-*Methyl*-N-*nitroso*-m-*anisidine*.—A solution of *N*-methyl-*m*-anisidine (15 g.) in 6% hydrochloric acid (65 c.c.) was vigorously agitated with ether (50 c.c.) at 5—10° during the addition of a solution of sodium nitrite (8 g.) in water (20 c.c.) until the aqueous layer gave an immediate colour with starch–cadmium iodide paper. The ethereal layer was separated, washed with sodium hydrogen carbonate solution, and with water, and dried. On evaporation of the ether, the crude *nitrosamine* remained as a golden-yellow oil; a portion was distilled as a yellow oil, b. p. 98°/0·1 mm. (Found : C, 57·6; H, 6·4; N, 16·9. $C_8H_{10}O_2N_2$ requires C, 57·8; H, 6·1; N, 16·9%).

2-*Methyl*cyclo*hexanone* N-m-*Methoxyphenyl*-N-*methylhydrazone and* 2 : 3 : 4 : 11-*Tetrahydro*-5- *and* -7-*methoxy*-9 : 11-*dimethylcarbazole*.—Crude *N*-methyl-*N*-nitroso-*m*-anisidine (14 g.) was reduced to *N*-*m*-methoxyphenyl-*N*-methylhydrazine (8 g. crude, distilled) by the method of Kermack, Perkin, and Robinson (*J.*, 1922, **121**, 1872). The crude hydrazine was heated on the steam-bath with 2-methyl*cyclo*hexanone (9 c.c.), first at atmospheric pressure for ½ hr., and then under reduced pressure until no more water was evolved. A portion of the *hydrazone* was distilled, and again was a colourless liquid, b. p. 90—95°/0·005 mm., rapidly darkening in air (Found : C, 73·0; H, 9·1; N, 11·4. $C_{15}H_{22}ON_2$ requires C, 73·1; H, 9·0; N, 11·4%).

The remainder of the crude hydrazone was refluxed with acetic acid (100 c.c.) for 30 min., and the mixture then evaporated under reduced pressure. The residue was taken up in dilute hydrochloric acid, the solution was washed with ether and basified with ammonia, and the liberated bases were isolated with ether and distilled. The fraction of b. p. 95—110°/0·005 mm. was redistilled, yielding a mixture of 2 : 3 : 4 : 11-tetrahydro-5- and -7-methoxy-9 : 11-dimethylcarbazole as a colourless liquid, b. p. 94—95° (bath)/0·001 mm., rapidly becoming yellow in air (Found : C, 78·3; H, 8·8; N, 6·2. Calc. for $C_{15}H_{19}ON$: C, 78·6; H, 8·4; N, 6·2%).

1 : 2 : 3 : 4-*Tetrahydro*-5- *or* -7-*methoxy*-1 : 9-*dimethylcarbazole*; 1 : 2 : 3 : 4 : 10 : 11-*Hexahydro*-5- *and* -7-*methoxy*-9 : 11-*dimethylcarbazoles* (V and IV, respectively).—(*a*) A solution of crude *N*-methyl-*N*-nitroso-*m*-anisidine (17·2 g.) (from 40 g. of *N*-methyl-*m*-anisidine) in acetic acid (35 c.c.) was added dropwise to a stirred suspension of zinc dust (28 g.) in water (50 c.c.) at <10°; stirring was continued for a further 3 hr. The mixture was heated on the steam-bath, then filtered, and the residue washed with hot water and ether. The combined filtrate and washings were basified with sodium hydroxide solution and extracted with ether. Distillation of the very dark residue from the dried extract furnished a colourless oil (11 g.), b. p. 150°/8 mm., rapidly darkening in air. This crude hydrazine (10 g.) was heated on the steam-bath with 2-methyl*cyclo*hexanone (12 c.c.) and 30% acetic acid (1 c.c.) during 2 hr. A solution of concentrated sulphuric (11 c.c.) in water (180 c.c.) was added and the mixture heated on the steam-bath for 13 hr., cooled, and extracted with ether (A). The aqueous layer was basified and the liberated bases were extracted with ether (B). The residue from the dried and evaporated extract A was distilled, and the pale yellow oil (*ca.* 1 g.), b. p. 100—170°/0·5 mm., so obtained, was dissolved in light petroleum (b. p. 60—80°), passed through an alumina column (25 g.) and eluted with the same solvent. On evaporation, the eluates all afforded colourless crystals contaminated with a little oil. Recrystallisation from light petroleum gave 1 : 2 : 3 : 4-*tetrahydro*-5(or 7)-*methoxy*-1 : 9-*dimethylcarbazole* as colourless prisms, m. p. 107—108° (Found :

C, 78·3; H, 8·2. $C_{15}H_{19}ON$ requires C, 78·6; H, 8·4%). The dried extract B was distilled, giving a colourless oil, b. p. 85—130°/1 mm. (identified as *N*-methyl-*m*-anisidine) and a viscous oil (*ca.* 2 g.), b. p. 130—200°/1 mm. A solution of this product in ethanol (50 c.c.) was shaken under hydrogen at 40° with Raney nickel; 180 c.c. of hydrogen were absorbed. The ethanol was removed from the filtered solution, and the dark purple residue, in light petroleum (b. p. 40—60°), was chromatographed on alumina (60 g.). The eluate was collected in 50-c.c. portions, which were separately evaporated in a nitrogen stream. The first two fractions yielded small amounts (*ca.* 30 mg. each) of colourless crystals, m. p. 71—78°. Recrystallisation from light petroleum (b. p. 40—60°) furnished 1 : 2 : 3 : 4 : 10 : 11-*hexahydro-5-methoxy*-9 : 11-*dimethylcarbazole*, colourless plates, m. p. 83—84° (Found : C, 77·9; H, 9·3. $C_{15}H_{21}ON$ requires C, 77·9; H, 9·1%). The base, in dilute hydrochloric acid, gives a blood-red colour on addition of ferric chloride. Successive portions of the eluate, from the third to the tenth, provided decreasing quantities of a colourless oil, which gave a blood-red ferric reaction in dilute hydrochloric acid.

Fractions 11—19 inclusive did not contain any such base and the eluant was changed to light petroleum (b. p. 40—60°)–benzene (10 : 1).

Fractions 20—24 contained a trace of an oil which gave a bright red ferric reaction in dilute hydrochloric acid, but was insufficient for further investigation. The only other material eluted from the column was dark oil, obtained by the use of chloroform–benzene (1 : 1) as eluant. The residues from fractions 3—10 were combined and chromatographed from light petroleum (b. p. 40—60°) on alumina (*ca.* 20 g.), and eluted with the same solvent. The eluate was collected in 50-c.c. portions, which were evaporated in a nitrogen stream. Only two (successive) portions afforded any appreciable residues. These were combined and distilled; 1 : 2 : 3 : 4 : 10 : 11-*hexahydro-7-methoxy*-9 : 11-*dimethylcarbazole* was obtained as a colourless oil, b. p. 90—100° (bath)/0·05 mm. (Found : C, 78·2; H, 9·2. $C_{15}H_{21}ON$ requires C, 77·9; H, 9·1%).

(*b*) Similarly *N*-methyl-*m*-anisidine (75 g.) gave nitrosamine (90 g.), *N*-*m*-methoxyphenyl-*N*-methylhydrazine (48 g., crude, distilled) which was condensed with 2-methyl*cyclo*hexanone (30 c.c.) as above. The product was refluxed with acetic acid (350 c.c.) during 30 min. Acetic acid (280 c.c.) was removed by distillation under reduced pressure, and the residue added to 10% hydrochloric acid (550 c.c.). The ether extracts A and B were made as under (*a*), and A gave the tetrahydromethoxydimethylcarbazole, m. p. 107—108°, as before. The bases from extract B were distilled and gave liquid fractions, (i) b. p. 75—100°/0·1 mm., and (ii) b. p. 100—104°/0·1 mm. which were separately hydrogenated in ethanol at 50°, over Raney nickel. The solution of (i) absorbed 140 c.c. of hydrogen, and that of (ii) 830 c.c., and the products were isolated as oils. The product from (ii) was distilled and collected in two fractions, (iii) b. p. 75—95°/0·1 mm. (11·9 g.), and (iv) b. p. 95—115°/0·1 mm. (5·4 g.). The hydrogenation product of (i) (8·1 g.) was chromatographed on alumina (120 g.) and fractionally eluted with light petroleum (b. p. 40—60°). The eluate was collected in 50-c.c. fractions which were evaporated in a nitrogen stream. The 3rd, 4th, and 5th fractions left small amounts of solid residue, m. p. 72—80°. Succeeding fractions, to the 17th, gave a bright red colour with dilute hydrochloric acid and ferric chloride solution and left oils on evaporation. Fractions (iii) and (iv) from the distillation described above were treated in a manner similar to that described for fraction (i), and gave essentially similar results.

The crystals obtained from the first few portions of eluate from each of the three chromatograms were freed from adhering oil and washed with a little light petroleum (b. p. 40—60°). Crystallisation from the same solvent furnished 1 : 2 : 3 : 4 : 10 : 11-hexahydro-5-methoxy-9 : 11-dimethylcarbazole (2·3 g.), colourless prisms, m. p. 83—84°. The *picrate* formed yellow-green prisms, m. p. 152° (decomp.), from ethanol (Found : C, 55·4; H, 5·3; N, 11·9. $C_{15}H_{21}ON,C_6H_3O_7N_3$ requires C, 54·8; H, 5·3; N, 12·2%).

The oil and washings from the crystalline base, and the mother-liquors from its crystallisation, were combined with the oily residues from those fractions of the eluates which gave red colours in the ferric chloride tests. From the solution, by chromatographic methods similar to those described above, with activated alumina (200 g.) in a column 160 cm. in length, a small amount of the crystalline solid, m. p. 83—84°, was obtained and also a colourless oil, which was converted into a *picrate*, which formed yellow prisms (5·3 g.), m. p. 134—135° (decomp.), from ethanol (Found : C, 54·9; H, 5·1; N, 12·3. $C_{15}H_{21}ON,C_6H_3O_7N_3$ requires C, 54·8; H, 5·3; N, 12·2%). It was decomposed with ammonia and the liberated base isolated with ether, and twice distilled. 1 : 2 : 3 : 4 : 10 : 11-Hexahydro-7-methoxy-9 : 11-dimethylcarbazole (220 g.) was obtained as a colourless oil, b. p. 95—96°/0·03 mm. (Found : C, 78·0; H, 9·2; N, 6·4%).

Rhodamines.—The methoxylated bases were refluxed with concentrated aqueous hydrobromic acid for 2 hr. and the solution concentrated under diminished pressure to small volume.

Addition of water usually gave an oily, sometimes a crystalline, precipitate of a hydrobromide. The supernatant liquid was poured away and the salt (a very small portion sufficed) boiled with phthalic anhydride for about a minute. The melt was dissolved in alcohol. The liquid hexahydro-7-methoxy-9 : 11-dimethylcarbazole gave a dye which in colour and fluorescence closely matched Rhodamine B. The solid 5-methoxy-analogue gave a dye which was much bluer (purple) in acid alcoholic solution and exhibited a most intense *red* fluorescence, even on great dilution. Comparisons, which will be submitted later, indicate that this remarkable change in colour and fluorescence is probably due to the bulky (quaternary) group in the 2-position (vicinal to oxygen and nitrogen) of the *m*-aminophenol nucleus.

Rhodamine dyes are obtained in the manner described above from α-colubridine, strychnospermine, and dimethylharmine chloride after hydrogenation at an Adams catalyst, but not from β-colubridine, eserine, vomicidine, aspidospermine, or akuammine.

Oxidation of 1 : 2 : 3 : 4 : 10 : 11-*Hexahydro-6-methoxy-9* : 11-*dimethylcarbazole.*—1 : 2 : 3 : 4 : 10 : 11-Hexahydro-6-methoxy-9 : 11-dimethylcarbazole (2·0 g.) was dissolved in a mixture of water (150 c.c.) and 10% sulphuric acid (7 c.c.), and dilute sodium hydroxide solution was added to faint turbidity. The mixture was stirred at 50°, and a solution of potassium permanganate (6·5 g.) in water (110 c.c.), heated to 50°, was added during 15 min. Stirring was continued and after ½ hr., anhydrous sodium carbonate (1·0 g.) was added, and then a warm solution of potassium permanganate (5·0 g.) in water (100 c.c.) during 2 hr.; the permanganate colour then persisted. Anhydrous sodium carbonate (1·0 g.) was added, and stirring was continued at 50° for a further 2 hr. Sodium sulphite (0·2 g.) was added, and the mixture filtered; the manganese precipitate was washed with boiling water (250 c.c.). The combined filtrates were concentrated under reduced pressure to about 90 c.c., acidified with concentrated hydrochloric acid, and extracted with ether (8 × 15 c.c.). The ethereal solution was washed with water, dried, and concentrated. The residue was treated with ethereal diazomethane (from 5 g. of nitrosomethylurea) and kept overnight. The ether was evaporated, and the residue triturated with methanol, and filtered. The colourless residue was polymethylene, softening point 270°, insoluble in all the usual solvents (Found : C, 85·4; H, 13·9. Calc. for $[CH_2]_n$: C, 85·6; H, 14·4%). The filtrate was concentrated and the residue distilled, giving *substances* (*a*) b. p. 60—70°/0·03 mm. (Found : C, 59·1; H, 8·8; N, 2·4%), (*b*) b. p. 70—102°/0·03 mm. (Found : C, 60·5; H, 8·7; N, 4·0%), (*c*) b. p. 102—125° (bath)/0·03 mm. (Found : C, 62·5; H, 7·9; N, 5·4; OMe, 11·7; NMe, 6·0; *C*-Me, 4·7. $C_{14}H_{21}O_4N$ requires C, 62·9; H, 7·9; N, 5·2; OMe, 11·6; NMe, 10·9; *C*-Me, 5·8%).

γ-Methyl-α-oxobutyric Acid p-*Methoxyphenylhydrazone* (cf. Robinson and Suginome, *J.*, 1932, 298).—A solution of ethyl *iso*propylacetoacetate (20·6 g.) in ethanol (150 c.c.) at 0° was mixed with one of sodium hydroxide (12 g.) in water (30 c.c.). A solution of *p*-methoxybenzenediazonium chloride prepared from *p*-anisidine (12·4 g.), hydrochloric acid (50 c.c. of concentrated acid in 60 c.c. of water), and sodium nitrite (6·9 g.) in water (20 c.c.) was added immediately to the swirled and cooled (ice-bath) mixture. The heavy red oil which separated was isolated with ether after 6—7 min. and hydrolysed under reflux for 1 hr. with alcoholic 5% sodium hydroxide (165 c.c.). The solution was concentrated under diminished pressure, diluted with water (charcoal), washed twice with ether, boiled, cooled to 0°, and acidified with dilute hydrochloric acid. The yellow *hydrazone* was collected and dried (7·5 g.). It formed bright yellow needles, m. p. 129°, from light petroleum (b. p. 60—80°) or aqueous methanol (Found : C, 60·9; H, 6·9; N, 11·5. $C_{12}H_{16}O_3N_2$ requires C, 61·0; H, 6·8; N, 11·9%).

5-*Methoxy*-3 : 3-*dimethylindolenine and* 5-*Methoxy*-3 : 3-*dimethylindolenine*-2-*carboxylic Acid.*—A solution of γ-methyl-2-oxobutyric acid *p*-methoxyphenylhydrazone (3·6 g.) in ethanol (36 c.c.) was saturated with hydrogen chloride at 0°. The greenish-black mixture was refluxed for 5 min., and the ethanol was then removed at the room temperature under diminished pressure in a stream of nitrogen. The residue was shaken with ether and sodium carbonate solution. The aqueous layer was washed with ether, freed from ether under reduced pressure, cooled in ice, and acidified. The flocculent, colourless precipitate was collected, thoroughly washed with water, and dried (550 mg.). Three crystallisations from methanol, finally cooled to −40°, gave the *indolenine-acid* as colourless needles, m. p. 138—139° (Found : C, 65·3; H, 6·0. $C_{12}H_{13}O_3N$ requires C, 65·7; H, 6·0%).

The ethereal layer was washed with sodium carbonate solution and water, dried, and concentrated. The dark viscous residue was mixed with a few drops of methanol and kept at −5° for 4 days. The greenish solid was collected, washed with methanol and ether, and dried (1·3 g.). The product is very sparingly soluble in hot or cold methanol, ethanol, ether, and

light petroleum (b. p. 40—60°) but is easily soluble in benzene. Crystallisation from the latter solvent furnished *5-methoxy-3 : 3-dimethylindolenine* as colourless prisms, m. p. 123—124° (Found : C, 75·7; H, 7·5; N, 8·0. $C_{11}H_{13}ON$ requires C, 75·4; H, 7·5; N, 8·0%).

The attempted preparation of the methoxy-3 : 3-dimethylindolenine methiodide gave stout rods, m. p. 140—147°, which could not be recrystallised.

5-Methoxy-3 : 3-dimethylindolenine Methochloride.—A solution of the above indolenine (1·0 g.) and methyl sulphate (0·6 c.c.) in benzene (10 c.c.) was heated on the steam-bath for 15 min. The heavy brown oil which separated was washed with ether and treated with cold dilute potassium hydroxide, and the liberated base taken up in ether. The ethereal solution was washed with water, dried ($MgSO_4$), and filtered, and dry hydrogen chloride was passed in. The *methochloride* separated in large faintly brown prisms (0·78 g.), m. p. 166—167° (Found : C, 59·9; H, 7·7; N, 5·7; Cl, 14·4. $C_{12}H_{18}O_2NC$ lrequires C, 59·1; H, 7·5; N, 5·7; Cl, 14·5%)

5-Methoxy-1 : 3 : 3-trimethylindoline (VII).—A solution of the above methochloride (0·76 g.) and palladium chloride (1·3 c.c. of 1% solution) in methanol (40 c.c.) and concentrated hydrochloric acid (4 drops) was shaken in an atmosphere of hydrogen at room temperature and pressure. After 15 min. the solution had absorbed 73 c.c. of hydrogen, and in a further 30 min. 4 c.c. more of hydrogen were taken up, and absorption ceased. The filtered solution was concentrated to 10 c.c. under reduced pressure and then evaporated to dryness over concentrated sulphuric acid and potassium hydroxide in a vacuous desiccator. The residual mixture of crystals and a small amount of a yellow oil was washed with methanol, leaving *5-methoxy-1 : 3 : 3-trimethylindoline hydrochloride* (0·65 g.), colourless prisms, m. p. 207—208° (Found : C, 63·7; H, 8·1; N, 6·4. $C_{12}H_{17}ON,HCl$ requires C, 63·3; H, 8·0; N, 6·2%). The hydrochloride (0·61 g.) was dissolved in water and basified with ammonia, and the liberated *base* isolated with ether and distilled as a colourless oil, b. p. 118° (bath)/5 mm. (Found : C, 75·7; H, 9·0; N, 7·2. $C_{12}H_{17}ON$ requires C, 75·4; H, 9·0; N, 7·3%).

1 : 2 : 3 : 4 : 10 : 11-Hexahydro-9 : 11-dimethylcarbazole.—(i) *as*-Methylphenylhydrazine (4·4 g.) was heated on a steam-bath with 2-methyl*cyclo*hexanone (5·5 c.c.), first at atmospheric pressure for ½ hr., and then under reduced pressure until no more water was removed. The product was refluxed with acetic acid (90 c.c.) during ½ hr., and most of the acetic acid (71 c.c.) was then removed under reduced pressure. Water (100 c.c.) and concentrated hydrochloric acid (7 c.c.) were added, the solution was extracted with ether and basified, and the liberated bases were isolated with ether and distilled *in vacuo*. A solution of the colourless oily distillate in ethanol (40 c.c.) was shaken in hydrogen at 40° with Raney nickel. Absorption ceased after about 500 c.c. of hydrogen had been taken up in 76 hr. Ethanol was removed from the filtered solution under diminished pressure and the residue was fractionated, giving a colourless oil (1·2 g.), b. p. 58—61°/2 mm., rapidly darkening in air, and then a colourless oil (4·3 g.), b. p. 122—124°/2 mm. The latter was converted into the *picrate* (8·4 g.) in ethanolic picric acid. After recrystallisation from ethanol, the derivative (7·8 g.) formed bright orange prisms, m. p. 135—136° (Found : C, 56·0; H, 5·1. $C_{14}H_{19}N,C_6H_3O_7N_3$ requires C, 55·8; H, 5·2%). The picrate (6·25 g.) was decomposed with ammonia solution, and the liberated *base* was isolated with ether and twice distilled; it was a colourless liquid (2·7 g.), b. p. 65°/0·005 mm. (Found : C, 83·8; H, 9·6. $C_{14}H_{19}N$ requires C, 83·5; H, 9·5%).

(ii) A mixture of 2 : 3 : 4 : 11-tetrahydro-11-methylcarbazole (1·0 g.), ether (10 c.c.), and methyl iodide (2 c.c.) was kept for 2 weeks. The brown prismatic crystals which separated were collected, once crystallised from ethanol, and dissolved in dilute hydrochloric acid. The solution was washed with ether and basified with ammonia, and the base isolated with ether and distilled as a colourless oil, b. p. 93—95° (bath)/0·05 mm. Its solution in ethanol (40 c.c.) was shaken for 4 days under hydrogen with Raney nickel. Working up as above gave a picrate which, once crystallised from ethanol, had m. p. 135—136°, unchanged on admixture with that obtained in (i) above.

1 : 2 : 3 : 4 : 10 : 11-Hexahydro-11-methylcarbazole.—A solution of 2 : 3 : 4 : 11-tetrahydro-11-methylcarbazole (1·15 g.) in ethanol (40 c.c.) was shaken under hydrogen at 35° with Raney nickel. After 3 days 160 c.c. of hydrogen had been taken up and absorption ceased. Ethanol was removed from the filtered solution under reduced pressure, and the residual *base* was distilled as a colourless oil (1·05 g.), b. p. 80—85° (bath)/0·03 mm. (Found : C, 83·4; H, 9·1; N, 7·7. $C_{13}H_{17}N$ requires C, 83·4; H, 9·2; N, 7·5%).

1 : 2 : 3 : 4-Tetrahydro-1 : 9-dimethylcarbazole.—*as*-Methylphenylhydrazine (10 c.c.) was heated on the steam-bath with 2-methyl*cyclo*hexanone (12 c.c.) for 1 hr. The product was refluxed with 10% sulphuric acid (200 c.c.) for 20 min., and allowed to cool. An ethereal solution of the oily layer was washed with dilute sulphuric acid and water. The oil from the dried extract

solidified on scratching and, twice crystallised from ethanol, the 1 : 2 : 3 : 4-*tetrahydro*-1 : 9-*dimethylcarbazole* (6·55 g.) formed colourless plates, m. p. 57—59° (Found : C, 84·3; H, 8·7; N, 6·6. $C_{14}H_{17}N$ requires C, 84·4; H, 8·6; N, 7·0%).

1 : 2 : 3 : 4 : 10 : 11-*Hexahydro*-1 : 9-*dimethylcarbazole*.—A mixture of the tetrahydrodimethylcarbazole (5 g.), ethanol (40 c.c.), concentrated hydrochloric acid (20 c.c.), and granulated tin (25 g.) was refluxed on a steam-bath for 12 hr. The mixture was filtered hot, and the residue was washed with a hot mixture of ethanol (10 c.c.) and concentrated hydrochloric acid (10 c.c.). The combined filtrates and washings were cooled, basified with sodium hydroxide solution, and steam-distilled. The distillate was acidified with concentrated hydrochloric acid, filtered, twice washed with ether, and basified with ammonia, and the liberated *base* was isolated with ether and distilled, forming a colourless oil (2·3 g.), b. p. 100° (bath)/0·1 mm. (Found : C, 83·8; H, 9·6. $C_{14}H_{19}N$ requires C, 83·5; H, 9·5%). The *picrate*, yellow needles from ethanol, had m. p. 151—153° (Found : C, 55·9; H, 5·2; N, 13·4. $C_{14}H_{19}N,C_6H_3O_7N_3$ requires C, 55·8; H, 5·2; N, 13·0%).

1 : 2 : 3 : 4 : 10 : 11-*Hexahydro*-1-*methylcarbazole*.—A solution of 1 : 2 : 3 : 4-tetrahydro-1-methylcarbazole (10 g.) (from phenylhydrazine and 2-methyl*cyclo*hexanone) in ethanol (40 c.c.) and concentrated hydrochloric acid (25 c.c.) along with granulated tin (20 g.) was refluxed for 12 hr. The *base* was isolated as a colourless oil (4·3 g.), b. p. 85° (bath)/0·05 mm. (Found : C, 83·7; H, 9·3. $C_{13}H_{17}N$ requires C, 83·4; H, 9·2%). The *picrate* crystallised from benzene in bright, orange-red prisms, m. p. 151—153° (Found : C, 54·5; H, 5·1. $C_{13}H_{17}N,C_6H_3O_7N_3$ requires C, 54·8; H, 4·8%).

The authors are grateful to the Department of Scientific and Industrial Research for a Maintenance Grant awarded to one of them (M. F. M.). They thank Dr. T. A. Henry and Dr. T. M. Sharp of the Wellcome Foundation Limited for a specimen of akuammine hydrochloride.

DYSON PERRINS LABORATORY, OXFORD. [*Received, April 20th*, 1955.]