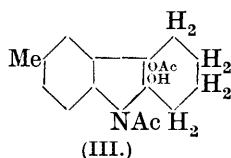
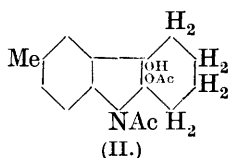
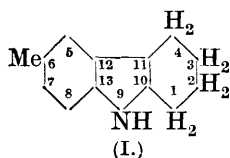


CCXCVIII.—*Derivatives of Tetrahydrocarbazole. Part VI. Compounds Derived from 6-Methyltetrahydrocarbazole.*

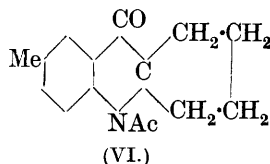
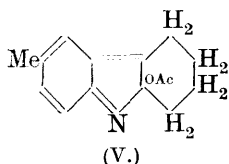
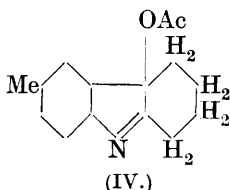
By BASAVALINGAIAH LINGAIAH MANJUNATH and SYDNEY GLENN PRESTON PLANT.

THIS investigation was undertaken with a view to study the possibility of obtaining, from a derivative of tetrahydrocarbazole which contains a substituent in the benzenoid part of the molecule, a series of compounds similar to those obtained from tetrahydrocarbazole by Perkin and Plant (J., 1923, **123**, 676), and for this purpose 6-methyltetrahydrocarbazole (I) was selected.

This substance was prepared from *p*-tolylhydrazine and cyclohexanone by Fischer's method for synthesising indole derivatives (compare Borsche, Witte, and Bothe, *Annalen*, 1908, **359**, 62). Its 9-acetyl derivative, on treatment with nitric acid in glacial acetic acid solution, gave three substances, *viz.*, a nitro-compound, presumably 5-nitro-9-acetyl-6-methyltetrahydrocarbazole, and 9-acetyl-10:11-dihydroxy-6-methylhexahydrocarbazole, corresponding to the products of Perkin and Plant, and also a compound, $C_{17}H_{21}O_4N$, which appears to be 9-acetyl-10-acetoxy-11-hydroxy-6-methylhexahydrocarbazole (II). An isomeric structure (III) is possible for this derivative, but (II) is considered to be the more probable. The latter two substances, on treatment with potassium hydroxide, gave the same bright yellow product, $C_{13}H_{15}ON$, apparently 11-hydroxy-6-methyltetrahydrocarbazolenine, which, like 11-hydroxytetrahydrocarbazolenine, gives a colourless acetyl derivative (IV).



9-Acetyl-10-acetoxy-11-hydroxy-6-methylhexahydrocarbazole, on treatment with sodium hydroxide under rather different conditions, gave a bright orange-red substance, $C_{15}H_{17}O_2N$, which on account of its colour is probably 10-acetoxy-6-methyltetrahydrocarbazolenine (V), being isomeric with the colourless acetyl derivative of 11-hydroxy-6-methyltetrahydrocarbazolenine.



Attempts to prepare 6-acetyl-9-methyl- ψ -indoxylspirocyclopentane from 9-acetyl-10 : 11-dihydroxy-6-methylhexahydrocarbazole gave products which could not be crystallised, but 9-acetyl-10-acetoxy-11-hydroxy-6-methylhexahydrocarbazole, on heating, gave acetic acid and a substance, $C_{15}H_{17}O_2N$, which appears to be the desired compound (VI).

The action of nitric acid on 9-benzoyl-6-methyltetrahydrocarbazole has been investigated, but the products have not been obtained crystalline.

EXPERIMENTAL.

9-Acetyl-6-methyltetrahydrocarbazole.—6-Methyltetrahydrocarbazole, prepared by warming cyclohexanone-*p*-tolylhydrazone with dilute sulphuric acid (Borsche, Witte, and Bothe, *loc. cit.*), was boiled with acetic anhydride (3 parts) for 3 hours. The product which separated on cooling, after being washed with acetic acid and with alcohol, was pure 9-acetyl-6-methyltetrahydrocarbazole (yield 75%). It separated from glacial acetic acid in colourless prisms, m. p. 145° (Found : N, 6.3. $C_{15}H_{17}ON$ requires N, 6.2%).

Action of Nitric Acid on 9-Acetyl-6-methyltetrahydrocarbazole.—The tetrahydrocarbazole (18 g.) was dissolved in glacial acetic acid (45 c.c.) at 80° , and nitric acid (5.2 c.c.; *d* 1.42), dissolved in acetic acid (12 c.c.), was added gradually with vigorous stirring, the temperature rising to 105° and nitrous fumes being evolved. The product, which separated slowly on frequent rubbing, after being washed with a little alcohol, melted at 150 – 200° (yield 6 g.). It was dissolved in hot alcohol (750 c.c.), and from the filtered solution long, yellow needles (3 g.) of 5-nitro-9-acetyl-6-methyltetrahydrocarbazole, m. p. 165° , slowly separated (Found : N, 10.4. $C_{15}H_{16}O_3N_2$ requires N, 10.3%). The filtrate from this solution on being stirred, slowly deposited small, colourless prisms (2 g.), m. p. 220° , of

9-acetyl-10 : 11-dihydroxy-6-methylhexahydrocarbazole (Found : C, 68.6; H, 7.3; N, 5.6. $C_{15}H_{19}O_3N$ requires C, 68.9; H, 7.3; N, 5.4%). Like 9-acetyl-10 : 11-dihydroxyhexahydrocarbazole, it is coloured red by sulphuric acid and dissolves to give a yellow solution.

In some experiments the alcoholic filtrate from the 5-nitro-9-acetyl-6-methyltetrahydrocarbazole, on being stirred, slowly deposited an entirely different product consisting of colourless prisms, m. p. 210°. Analysis suggested that this substance is 9-acetyl-10-acetoxy-11-hydroxy-6-methylhexahydrocarbazole (Found : C, 67.2; H, 7.0; N, 4.6. $C_{17}H_{21}O_4N$ requires C, 67.3; H, 6.9; N, 4.6%), and like the above derivative it is coloured red by sulphuric acid and dissolves to give a yellow solution. The formation of this derivative was assisted by using a suspension of 9-acetyl-6-methyltetrahydrocarbazole in acetic acid at 50°, only a small amount of the nitro-compound then being formed.

The acetyl group was removed from 5-nitro-9-acetyl-6-methyltetrahydrocarbazole by boiling it with potassium hydroxide in aqueous alcohol for an hour. 5-Nitro-6-methyltetrahydrocarbazole, obtained on diluting the solution with water, crystallised from alcohol in large, brown plates, m. p. 181—182° (Found : N, 12.1. $C_{13}H_{14}O_2N_2$ requires N, 12.2%).

Action of Potassium Hydroxide on 9-Acetyl-10 : 11-dihydroxy-6-methylhexahydrocarbazole.—A deep red solution was produced on boiling the dihydroxy-derivative (3 g.) with alcohol (45 c.c.) and a solution of potassium hydroxide (10 g.) in water (30 c.c.). After $\frac{1}{2}$ hour, it was poured into cold water, and the sticky solid precipitated was crystallised from light petroleum; 11-hydroxy-6-methyltetrahydrocarbazolenine then separated in long yellow needles, m. p. 130° (Found : C, 77.8; H, 7.4; N, 7.3. $C_{13}H_{15}ON$ requires C, 77.6; H, 7.4; N, 7.0%). This substance shows properties similar to those of 11-hydroxytetrahydrocarbazolenine (Perkin and Plant, *loc. cit.*). Its solution in methyl alcohol shows a strong fluorescence, which is destroyed on addition of a drop of ferric chloride.

The substance was boiled with an excess of acetic anhydride for 2 hours, and the solution shaken with a large bulk of water. The 11-acetoxy-6-methyltetrahydrocarbazolenine thus obtained crystallised from petroleum in colourless prisms, m. p. 116—117° (Found : C, 74.5; H, 7.1; N, 5.8. $C_{15}H_{17}O_2N$ requires C, 74.1; H, 7.0; N, 5.7%).

Action of Alkalis on 9-Acetyl-10-acetoxy-11-hydroxy-6-methylhexahydrocarbazole.—On treating 9-acetyl-10-acetoxy-11-hydroxy-6-methylhexahydrocarbazole with potassium hydroxide under the conditions described above, 11-hydroxy-6-methyltetrahydrocarbazolenine was again the product obtained, but when the substance

(3 g.) was boiled with alcohol (45 c.c.) and a solution of sodium hydroxide (10 g.) in water (25 c.c.), a deep red solution was obtained, which, on dilution with water, yielded a sticky solid. This, after being crystallised twice from petroleum, was obtained in orange-red needles (0.3 g.), m. p. 79°. It has been suggested (p. 2261) that this product is 10-acetoxy-6-methyltetrahydrocarbazolenine (Found : C, 73.8; H, 7.1; N, 5.8. $C_{15}H_{17}O_2N$ requires C, 74.1; H, 7.0; N, 5.7%).

Action of Heat on 9-Acetyl-10-acetoxy-11-hydroxy-6-methylhexahydrocarbazole.—When this hexahydrocarbazole derivative (10 g.) was heated for a minute at 240° it decomposed, acetic acid being evolved. The residue was distilled and the oil, b. p. 220—240°/13 mm., was crystallised several times from petroleum; colourless needles (0.3 g.) of 6-acetyl-9-methyl- ψ -indoxylspirocyclopentane, m. p. 174° were thus obtained (Found : C, 74.5; H, 7.1; N, 5.8. $C_{15}H_{17}O_2N$ requires C, 74.1; H, 7.0; N, 5.7%).

9-Benzoyl-6-methyltetrahydrocarbazole.—Magnesium (4.8 g.) was dissolved in a mixture of ethyl iodide (32 g.) and dry ether (450 c.c.), and 6-methyltetrahydrocarbazole (37 g.) was gradually added. A vigorous reaction took place with the evolution of ethane and the formation of 6-methyltetrahydrocarbazyl-9-magnesium iodide, and it was completed by warming for a few minutes. Benzoyl chloride (28.5 g.) was then added in small quantities at a time; much heat was evolved and a heavy viscous layer separated. After some time, the mixture was treated with ice and water, the ethereal layer shaken with dilute hydrochloric acid and dried over calcium chloride, and the ether removed. The oily residue was dissolved in boiling alcohol with the addition of animal charcoal, and, after filtration, 9-benzoyl-6-methyltetrahydrocarbazole separated, on cooling, in colourless prisms, m. p. 118° (yield 50%) (Found : N, 4.8. $C_{20}H_{19}ON$ requires N, 4.8%). Attempts to obtain a crystalline product by the interaction of 9-benzoyl-6-methyltetrahydrocarbazole with nitric acid under various conditions were unsuccessful.

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