

177. *Experiments on the Preparation of Indolocarbazoles.
Part IV. The Preparation of Indolo(3' : 2'-1 : 2)carbazole.*

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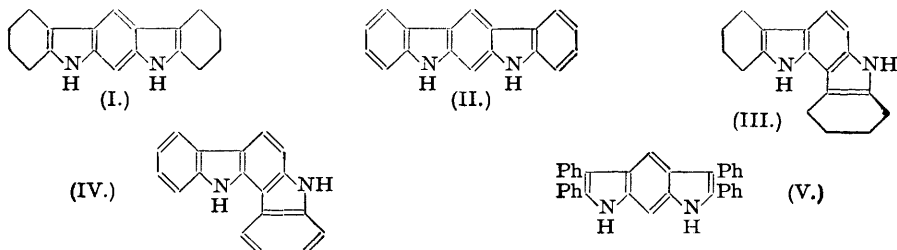
Biscyclohexanone *m*-phenylenedihydrazone has been made and converted, by treatment with acetic acid, into 5 : 6 : 7 : 8 : 4' : 5' : 6' : 7'-octahydro-indolo(3' : 2'-1 : 2)carbazole which has been dehydrogenated to give indolo-(3' : 2'-1 : 2)carbazole.

NONE of the five isomeric indolocarbazoles appears to have been made*, and in previous attempts to prepare them and their simple derivatives (*e.g.*, Manjunath, *J. Indian Chem. Soc.*, 1927, **4**, 271; Bond, Deegan, and Plant, *J.*, 1949, S 160; Coker, Plant, and Turner, *J.*, 1950, 110), the

* *Added in proof.*—I am indebted to Mr. J. D. Bu'Lock for calling my attention to the recent paper by Fearon and Boggust (*Biochem. J.*, 1950, **46**, 62). These authors suggest that urorosein base is indolo(3' : 2'-2 : 3)carbazole, but the composition they give, C₁₈H₁₆N₂, corresponds to a dehydro-indolocarbazole.

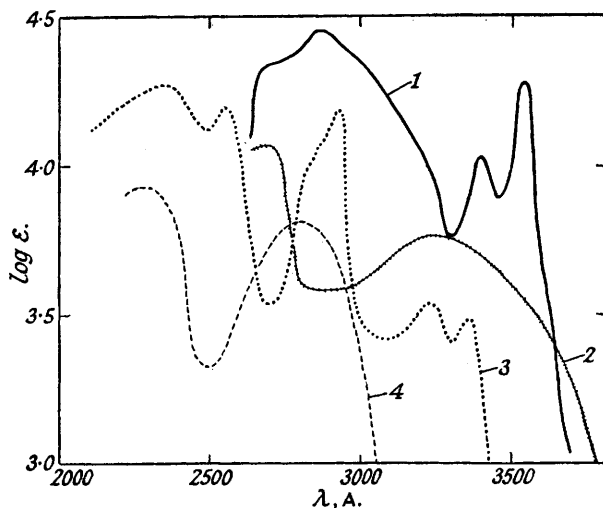
only success was that of Clifton and Plant (*J.*, 1950, 461) who obtained 6-cyanoindolo(2' : 3' : 4)carbazole by pyrolysis of 1-3'-carbazolyl-5-cyanobenzotriazole.

Biscyclohexanone *m*-phenylenedihydrazone (*N'N'''*-dicyclohexylidene-*m*-phenylenedihydrazine) has now been made and converted into an octahydroindolocarbazole which has been dehydrogenated to the corresponding indolocarbazole by heating it with palladium-charcoal. This dihydrazone is extremely easily decomposed by acids which immediately colour it red and, of the many different conditions investigated for bringing about a Fischer indole synthesis with it, only two were in any way successful. Its alcoholic solution, containing slightly more than the requisite amount of 2*N*-aqueous sulphuric acid, deposits ammonium sulphate in considerable



quantity after being brought to boiling point and cooled, but only a small amount of the indole can be isolated; a more satisfactory yield is obtained by using acetic acid.

Two structures are possible for indolocarbazoles prepared from *m*-phenylenedihydrazone: investigation has revealed the presence of only one product in the present work, and the octahydro-compound and the indolocarbazole obtained from it must be respectively either (I) and (II), or (III) and (IV). Of these 5 : 6 : 7 : 8 : 4' : 5' : 6' : 7'-octahydroindolo(3' : 2' : 1 : 2)carbazole (III) and indolo(3' : 2' : 1 : 2)carbazole (IV) are preferred, both on theoretical



1. Indolo(3' : 2' : 1 : 2)carbazole. 2. 5 : 6 : 7 : 8 : 4' : 5' : 6' : 7'-Octahydroindolo(3' : 2' : 1 : 2)carbazole.
(1 and 2 in dioxan solution.)
3. Carbazole. 4. 1 : 2 : 3 : 4-Tetrahydrocarbazole. (3 and 4 in methanol solution.)

grounds and from analogy with such reactions as the Skraup reaction with *m*-phenylenediamine (Smith, *J. Amer. Chem. Soc.*, 1930, 52, 397). In this connection, however, it should be noted that Ruggli and Petitjean (*Helv. Chim. Acta*, 1936, 19, 928) prefer the "linear" structure (V) for the compound, m. p. 279°, which they prepared from bisdeoxybenzoin *m*-phenylenedihydrazone and identified as the substance, m. p. 282°, obtained by Japp and Meldrum (*J.*, 1899, 75, 1044) from *m*-phenylenediamine and benzoin. They base their preference on analogy with the compound that Japp and Meldrum (*loc. cit.*, p. 1039) made from resorcinol and benzoin and from which Dischendorfer (*Monatsh.*, 1933, 62, 263) has obtained 4 : 6-dibenzoylresorcinol by oxidation and hydrolysis.

The identity of the substances prepared by Japp and Meldrum and by Ruggli and Petitjean has been confirmed: the product of each reaction has now been obtained, by sublimation in hydrogen, as colourless plates, m. p. 287°, which show a violet fluorescence, intense in ultra-violet light and visible even in daylight, but the structure of this compound is not considered to have been finally settled.

The ultra-violet absorption spectra of indolo(3':2'-1:2)carbazole and its octahydro-compound have been determined (in dioxan solution because a solution of the latter in alcohol darkens) and these are shown in the figure, in comparison with the ultra-violet absorption spectra of carbazole and 1:2:3:4-tetrahydrocarbazole.

In the light of experience with *biscyclohexanone m*-phenylenedihydrazone further attempts have been made to convert *biscyclohexanone p*-phenylenedihydrazone (Clifton and Plant, *loc. cit.*) into an octahydroindolocarbazole. The observations of the original workers have been confirmed and these attempts were also unsuccessful. The compound decomposed with brisk effervescence in cold glacial acetic acid, and, although application of the above alcohol-sulphuric acid method to this substance yielded ammonium sulphate, the desired octahydroindolocarbazole was not obtained. The hydrazone has been treated with very dilute acetic and sulphuric acids under a variety of conditions. The product was generally a brown amorphous powder that did not crystallise from any of the common solvents and gave considerable quantities of carbazole, but no indolocarbazole, on dehydrogenation.

EXPERIMENTAL.

Biscyclohexanone m-Phenylenedihydrazone.—*cycloHexanone* (6.0 c.c.) was dissolved in a solution of *m*-phenylenedihydrazine hydrochloride (Schoutissen, *Rec. Trav. chim.*, 1935, **54**, 253) (4.3 g.) in water (300 c.c.), and the mixture was treated gradually, with thorough shaking, with crystalline sodium acetate (6.0 g.). The *dihydrazone* thus obtained was recrystallised from alcohol and it separated as orange-yellow prisms, m. p. 155° (2.5 g.) (Found: C, 72.9; H, 9.2; N, 18.4. $C_{18}H_{26}N_4$ requires C, 72.5; H, 8.7; N, 18.8%). It decomposes to a black resinous mass when kept and some decomposition seems to occur on recrystallisation.

5:6:7:8:4':5':6':7'-*Octahydroindolo*(3':2'-1:2)*carbazole*.—The above dihydrazone (1.0 g.) was mixed with glacial acetic acid (5 c.c.) and the deep-red solution so formed was carefully warmed over a steam-bath for a few minutes until it became brown. It was then set aside for 24 hours, whereupon a crystalline solid separated from the dark brown solution. This was collected and washed, first with acetic acid and then with water (yield, 0.4 g.). Recrystallisation from glacial acetic acid afforded 5:6:7:8:4':5':6':7'-*octahydroindolo*(3':2'-1:2)*carbazole* as pale grey prisms, m. p. 228° (Found: C, 81.7; H, 7.9; N, 10.5. $C_{18}H_{20}N_2$ requires C, 81.8; H, 7.6; N, 10.6%). It is insoluble in dilute acids, and in concentrated sulphuric acid it forms a colourless solution, not coloured by addition of nitric acid. In benzene solution it shows a weak grey-blue fluorescence in ultra-violet light, and its solutions in alcohol and benzene darken fairly rapidly.

Indolo(3':2'-1:2)*carbazole*.—The above octahydro-compound was mixed with about half its volume of palladium-charcoal and gradually heated in an atmosphere of hydrogen. After being kept at 240° for 20 minutes the temperature was slowly raised to 320° and heating was continued for a further 30 minutes. *Indolo*(3':2'-1:2)*carbazole* sublimed as colourless plates, m. p. 299–300° (Found: C, 84.5; H, 4.8. $C_{18}H_{12}N_2$ requires C, 84.4; H, 4.7%). Extraction of the catalyst with acetic acid or benzene afforded more indolocarbazole, m. p. 295°, which was purified by sublimation in hydrogen. The yield was nearly theoretical. In concentrated sulphuric acid this substance forms a yellow solution that is changed, by nitric acid, to a deep green, fading to red-brown; nitric acid alone converts it into a green solid. In the solid state, and in benzene solution, it shows a brilliant violet fluorescence in ultra-violet light. It was recovered essentially unchanged after being boiled with acetic anhydride for 5 hours.

Dehydrogenation of the dried amorphous solid, obtained by adding water to the dark brown solution from which the octahydro-compound first separated, afforded a small quantity (about 0.1 g.) of indolo-(3':2'-1:2)carbazole, m. p. 295°, raised to 298° by admixture with the above. Resublimation in hydrogen gave the pure indolocarbazole, m. p. 299–300°.

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