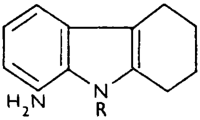
933. *Experiments on the Preparation of Indolocarbazoles. Part IX.* The Preparation of 9-Methylindolo(2′ : 3′-1 : 2)carbazole.*

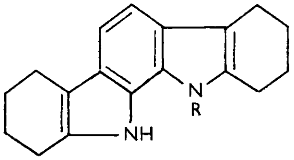
By R. J. Brunton, F. K. Drayson, (the late) S. G. P. Plant,
and Muriel L. Tomlinson.

The preparation of 9-methylindolo(2′ : 3′-1 : 2)carbazole is described. It has been shown that Brown and Nelson's method of reducing nitro-compounds with hydrazine and Raney nickel is very suitable for the preparation of aminotetrahydrocarbazoles.

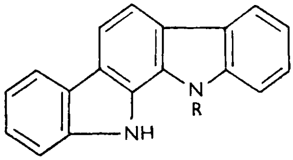
From 8-amino-1:2:3:4-tetrahydro-9-methylcarbazole (I; R = Me), 5 : 6 : 7 : 8 : 4′ : 5′ : 6′ : 7′-octahydro-9-methylindolo(2′ : 3′-1 : 2)carbazole (II; R = Me) has been prepared by condensation with 2-hydroxy*cyclo*hexanone; it has been successfully dehydrogenated to 9-methylindolo(2′ : 3′-1 : 2)carbazole (III; R = Me), the first derivative of the indolocarbazole (III; R = H) to be obtained. Derivatives of all but one, namely indolo(3′ : 2′-2 : 3)-carbazole (IV), of the five isomeric indolocarbazole systems, are therefore now known.[1,2,3,4]



(I)

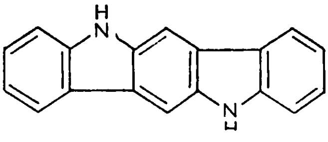


(II)

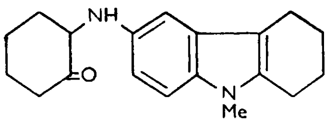


(III)

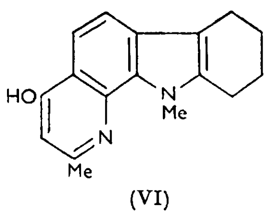
Attempts to prepare the parent substance (III; R = H) from 8-amino-1 : 2 : 3 : 4-tetrahydrocarbazole (I; R = H) failed: reaction took place between this amine and 2-hydroxy*cyclo*hexanone, but no crystalline material could be obtained, even after dehydrogenation of the crude product. It does not appear that failure to obtain the indolocarbazole was caused by the 8-aminotetrahydrocarbazole reacting as an *ortho*-diamine and producing a phenazine derivative with 2-hydroxy*cyclo*hexanone[5] for no basic material could be extracted from the reaction mixture, and unlike *o*-phenylenediamine 8-aminotetrahydrocarbazole gives a diacetyl-compound, and not a glyoxaline, on prolonged boiling with acetic anhydride. It was not possible to acetylate 1 : 2 : 3 : 4-tetrahydro-8-nitrocarbazole, and so the possibility of preparing the parent indolocarbazole (III; R = H) from 9-acetyl-8-amino-1 : 2 : 3 : 4-tetrahydrocarbazole could not be explored.



(IV)



(V)



(VI)

Attempts to prepare indolocarbazoles from 6-amino-1 : 2 : 3 : 4-tetrahydrocarbazole, from its 9-acetyl- and 9-methyl-derivative, and from 5-amino-8-chloro-1 : 2 : 3 : 4-tetrahydrocarbazole have all failed. In one case only was an intermediate, namely 1 : 2 : 3 : 4-tetrahydro-9-methyl-6-(2-oxo*cyclo*hexylamino)carbazole (V), obtained crystalline.

8-Amino-1 : 2 : 3 : 4-tetrahydrocarbazole and the corresponding 9-methyl derivative,

---

* Part VIII, *J.*, 1956, 1135.

[1] Clifton and Plant, *J.*, 1951, 461.

[2] Tomlinson, *J.*, 1953, 809.

[3] Hall and Plant, *J.*, 1953, 116.

[4] Swindells and Tomlinson, *J.*, 1956, 1135.

[5] Earle and Tomlinson, *J.*, 1956, 794.

6-amino-1 : 2 : 3 : 4-tetrahydrocarbazole, and 5-amino-8-chloro-1 : 2 : 3 : 4-tetrahydrocarbazole have all been condensed with ethyl acetoacetate to form the corresponding ethyl β-(1 : 2 : 3 : 4-tetrahydrocarbazolylamino)crotonates, but only one pyridinocarbazole, namely 5 : 6 : 7 : 8-tetrahydro-4′-hydroxy-9 : 6′-dimethylpyridino(2′ : 3′-1 : 2)carbazole (VI), could be obtained by further loss of water.

Aminotetrahydrocarbazoles have previously been prepared by reduction of nitro-compounds with iron and hydrochloric acid;[6] zinc dust and aqueous alcoholic hydrogen chloride;[7] sodium hydrosulphite (dithionite) and alkali in alcohol;[3,9,10] and iron powder, alcohol, and a trace of hydrochloric acid;[8,10] but these substances, which are rather readily oxidised, are difficult to obtain pure and in quantity. It has now been found that Brown and Nelson's method[11] of reduction with hydrazine and Raney nickel in methanol solution will reduce tetrahydronitrocarbazoles to give good yields of the corresponding pure amines.

EXPERIMENTAL

9-*Methylindolo*(2′ : 3′-1 : 2)*carbazole*.—8-Amino-1 : 2 : 3 : 4-tetrahydro-9-methylcarbazole (0·25 g.) was heated with 2-hydroxy*cyclo*hexanone (0·15 g.) and a trace of anilinium bromide. Frothing began at 120° and the temperature was raised to 150° for 5 min. The resulting glass crystallised in contact with ethanol, and the product was crystallised from acetic acid, forming greyish needles (0·1 g.) of 5 : 6 : 7 : 8 : 4′ : 5′ : 6′ : 7′-*octahydro*-9-*methylindolo*(2′ : 3′-1 : 2)*carbazole*, m. p. 231° (Found : C, 81·8; H, 7·8. $C_{19}H_{22}N_2$ requires C, 82·0; H, 7·9%). Dehydrogenation of the crude product (0·5 g.) by heating it at 250—300° with palladium–charcoal (0·25 g.; containing 10% of Pd) under carbon dioxide, followed by sublimation *in vacuo* (210°/0·1 mm.) gave 9-*methylindolo*(2′ : 3′-1 : 2)*carbazole* as prisms (0·1 g.) (from alcohol), m. p. 243—244° (Found : C, 84·4; H, 5·5. $C_{19}H_{14}N_2$ requires C, 84·4; H, 5·2%); $\lambda_{max.}$ 2100 (log ε 4·2243), 2590 (4·7180), 2730 (4·7161), 2880 (4·4321), 3260 (4·5208), 3490 (3·8353), 3645 (3·6862) Å. The indolocarbazole dissolved in sulphuric acid forming a red-brown solution, changed to olive-green, fading to brown on addition of a little nitric acid. 1 : 2 : 3 : 4-*Tetrahydro*-9-*methyl*-6-(2-*oxo*cyclo*hexylamino*)-*carbazole* was prepared by heating equivalent quantities of 6-amino-1 : 2 : 3 : 4-tetrahydro-9-methylcarbazole and 2-hydroxy*cyclo*hexanone at 125° for 5 min. It crystallised from ethanol as needles, m. p. 133° (Found : C, 76·8; H, 8·1. $C_{19}H_{24}ON_2$ requires C, 76·9; H, 8·1%).

Ethyl β-(1 : 2 : 3 : 4-*Tetrahydro*-9-*methylcarbazol*-8-*ylamino*)*crotonate*.—8-Amino-1 : 2 : 3 : 4-tetrahydro-9-methylcarbazole (1·0 g.) was mixed to a paste with a little acetoacetic ester and treated with one drop of hydrochloric acid. Next day the solid was collected and *ethyl* β-(1 : 2 : 3 : 4-*tetrahydro*-9-*methylcarbazol*-8-*ylamino*)*crotonate* obtained as needles (1·1 g.), m. p. 135—136° (from alcohol) (Found : C, 72·8; H, 7·7. $C_{19}H_{24}O_2N_2$ requires C, 73·0; H, 7·7%). Prepared in a similar way, *ethyl* β-(1 : 2 : 3 : 4-*tetrahydrocarbazol*-8-*ylamino*)*crotonate* was obtained as prisms (0·8 g.), m. p. 133—134° (from ethanol) (Found : C, 72·5; H, 7·5. $C_{18}H_{22}O_2N_2$ requires C, 72·5; H, 7·4%), *ethyl* β-(1 : 2 : 3 : 4-*tetrahydrocarbozol*-6-*ylamino*)*crotonate* as needles (0·8 g.), m. p. 140—141° (from ethanol) (Found : C, 72·4; H, 7·3%), and *ethyl* β-(8-*chloro*-1 : 2 : 3 : 4-*tetrahydrocarbazol*-5-*ylamino*)*crotonate* as prisms (1·2 g.), m. p. 149—150° (from ethanol) (Found : C, 64·8; H, 6·5. $C_{18}H_{21}O_2N_2Cl$ requires C, 65·0; H, 6·3%).

5 : 6 : 7 : 8-*Tetrahydro*-4′-*hydroxy*-9 : 6′-*dimethylpyridino*(2′ : 3′-1 : 2)*carbazole*.—The corresponding ethyl β-aminocrotonate (1·1 g.) was powdered and mixed with diphenyl (15 g.) and boiled under reflux for 10 min. Extraction with sodium hydroxide and subsequent acidification gave a solid which crystallised from aqueous alcohol to give 5 : 6 : 7 : 8-*tetrahydro*-4′-*hydroxy*-9 : 6′-*dimethylpyridino*(2′ : 3′-1 : 2)*carbazole* (0·2 g.), m. p. 256—258° (decomp.) (Found : C, 71·5; H, 7·1. $C_{17}H_{18}ON_2,H_2O$ requires C, 71·6; H, 7·0%).

8-*Amino*-1 : 2 : 3 : 4-*tetrahydrocarbazole*.—Powdered 1 : 2 : 3 : 4-tetrahydro-8-nitrocarbazole (5 g.) and Raney nickel (2—3 g.) in methanol (250 c.c.) were heated under reflux and hydrazine (60% aqueous solution; 50 c.c.) mixed with methanol (100 c.c.) was added slowly during ½ hr. by which time the solution had become colourless. Nickel was removed by filtration and the solution was concentrated under slightly reduced pressure. Dilution with water then precipitated the amine, needles (2·5 g.) (from benzene), m. p. 162° (Edwards and Plant[7] give

---

[6] Perkin and Plant, *J.*, 1921, 1825.

[7] Edwards and Plant, *J.*, 1923, 2393.

[8] Fawcett and Robinson, *J.*, 1927, 2254.

[9] Perkin and Riley, *J.*, 1923, 2399.

[10] Robinson and Tomlinson, *J.*, 1934, 1524.

[11] Brown and Nelson, *J. Amer. Chem. Soc.*, 1954, **76**, 5149.

m. p. 159—160°) (Found : C, 77·1; H, 7·5. Calc. for $C_{12}H_{14}N_2$: C, 77·4; H, 7·5%). Boiled with acetic anhydride (1½ hr.) it gave 8-*acetamido*-9-*acetyl*-1 : 2 : 3 : 4-*tetrahydrocarbazole*, needles (from ethanol), m. p. 201—202° (Found : C, 71·2; H, 6·7. $C_{16}H_{18}O_2N_2$ requires C, 71·1; H, 6·7%). The following amines were prepared from the nitro-compound (5 g.) in a similar way : 6-amino-1 : 2 : 3 : 4-tetrahydrocarbazole (3·6 g.) m. p. 151—152° (from light petroleum) ; 8-*amino*-1 : 2 : 3 : 4-*tetrahydro*-9-*methylcarbazole* (2·9 g.) (from aqueous ethanol), m. p. 116° after further recrystallisation from benzene (Found: C, 77·9; H, 7·9. $C_{13}H_{16}N_2$ requires C, 78·0; H, 8·0%) ; 6-amino-1 : 2 : 3 : 4-tetrahydro-9-methylcarbazole (2·4 g.), m. p. 97—98° (from light petroleum) (Found : C, 77·9; H, 8·2. Calc. for $C_{13}H_{16}N_2$: C, 78·0; H, 8·0%); 6-amino-9-ethyl-1 : 2 : 3 : 4-tetrahydrocarbazole, an oil, which gave, with acetic anhydride, 6-*acetamido*-9-*ethyl*-1 : 2 : 3 : 4-*tetrahydrocarbazole*, m. p. 183—184° (from benzene) (Found : C, 75·1; H, 7·8. $C_{16}H_{20}ON_2$ requires C, 75·0; H, 7·8%) ; 9-acetyl-6-amino-1 : 2 : 3 : 4-tetrahydrocarbazole (1·6 g.), m. p. 138° (from light petroleum) (Robinson and Tomlinson gave m. p. 140°) ; and 5-amino-8-chloro-1 : 2 : 3 : 4-tetrahydrocarbazole (3·8 g.), decomp. at 160° without melting (from ethanol).

1 : 2 : 3 : 4-*Tetrahydro*-9-*methyl*-8-*nitrocarbazole*.—1 : 2 : 3 : 4-Tetrahydro-8-nitrocarbazole (5 g.) and powdered potassium hydroxide (7 g.) were boiled in acetone (100 c.c.) while dimethyl sulphate (7 c.c.) was slowly added during 1 hr. After it had been boiled for a further hour, the mixture was diluted with water and the precipitate was recrystallised from acetic acid from which 1 : 2 : 3 : 4-*tetrahydro*-9-*methyl*-8-*nitrocarbazole* (4·5 g.) separated as needles, m. p. 106° (Found : C, 67·7; H, 6·3. $C_{13}H_{14}O_2N_2$ requires C, 67·8; H, 6·1%). Alkylation of the corresponding 6-nitro-compound proceeded more readily : potassium hydroxide was used in concentrated aqueous solution and the reaction was complete in an hour. 1 : 2 : 3 : 4-Tetrahydro-6-nitrocarbazole (10 g.) afforded 1 : 2 : 3 : 4-tetrahydro-9-methyl-6-nitrocarbazole (9 g.), m. p. 183°, previously obtained by nitrating 1 : 2 : 3 : 4-tetrahydro-9-methylcarbazole, and 1 : 2 : 3 : 4-*tetrahydro*-9-*ethyl*-6-*nitrocarbazole* (7·2 g.) as yellow needles, m. p. 136°, from acetic acid (Found : C, 68·7; H, 6·5. $C_{14}H_{16}O_2N_2$ requires C, 68·8; H, 6·6%).

THE DYSON PERRINS LABORATORY,
OXFORD UNIVERSITY.

[*Received, July* 23*rd*, 1956.]