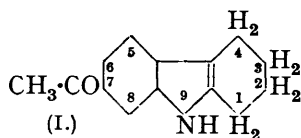


8. Tetrahydrocarbazoles with Substituents in the 7-Position.

By S. G. P. PLANT and (MISS) K. M. ROGERS.

CONSIDERABLE uncertainty attaches to the structure assigned to several tetrahydrocarbazole derivatives with substituents in the 5- or the 7-position (numbering as in I), mainly through the failure of Fischer's indole synthesis to give unambiguous results when applied to *m*-substituted phenylhydrazones of cyclohexanone (see, e.g., J., 1921, 119, 1825; 1923, 123, 2393; 1926, 808, 2260; 1928, 2454). A recent investigation of the course of the Friedel-Crafts reaction in the carbazole series (Plant, Rogers, and Williams, J., 1935, 741) indicated that ketones with the side chain in the 7-position, which might be used in



elucidating the structure of some of the above derivatives, might result from the action of acid chlorides on the 9-acetyltetrahydrocarbazoles, and this has been shown to be the case. The 7-acetyl derivatives of 9-acetyl- and 9-benzoyl-tetrahydrocarbazole have been obtained by the use of acetyl bromide and aluminium chloride, and the constitution of the 7-acetyltetrahydrocarbazole (I) derived from them by hydrolysis has been established by oxidation with sulphur to 2-acetylcarbazole (D.R.-P. 555,312; *Chem. Zentr.*, 1932, ii, 2532; Plant and Williams, J., 1934, 1142). Owing to the difficulty of effecting complete purification of the 2-acetylcarbazole prepared by this process, confirmation of the structure was obtained by reducing (I) to 7-ethyltetrahydrocarbazole, which was satisfactorily oxidised to 2-ethylcarbazole (Plant and Williams, *loc. cit.*). The 7-benzoyl derivatives of the two 9-acyltetrahydrocarbazoles have been similarly prepared by the use of benzoyl chloride and hydrolysed to 7-benzoyltetrahydrocarbazole, which has been oxidised to 2-benzoylcarbazole, the identity of the latter being confirmed by conversion into its 9-acetyl derivative (Plant, Rogers, and Williams, *loc. cit.*). The observation has also been made that, although 3-acetylcarbazole can readily be obtained by the action of aluminium chloride on 9-acetylcarbazole in nitrobenzene, 9-acetyltetrahydrocarbazole gives under similar conditions an unsatisfactory product from which a small amount of 7-acetyltetrahydrocarbazole can be isolated.

EXPERIMENTAL.

7-Acetyltetrahydrocarbazole.—(a) A mixture of 9-acetyltetrahydrocarbazole (5 g., prepared from tetrahydrocarbazole and acetic anhydride as described by Perkin and Plant, J., 1921, 119, 1832), carbon disulphide (50 c.c.), acetyl bromide (8 g.), and aluminium chloride (10 g.) was refluxed for 2½ hours, and the solvent allowed to evaporate. When the residue was scraped on to ice-dilute hydrochloric acid, 7 : 9-diacetyltetrahydrocarbazole, pale yellow prisms, m. p. 110°, from alcohol, was obtained (Found : C, 75.5; H, 6.6. C₁₈H₁₇O₂N requires C, 75.3; H, 6.7%). Hydrolysis of the latter was effected by refluxing with aqueous-alcoholic potassium hydroxide for ½ hour, and 7-acetyltetrahydrocarbazole, pale yellow prisms, m. p. 206–208°, from alcohol, was precipitated by the addition of water (Found : C, 78.9; H, 7.1. C₁₄H₁₅ON requires C, 78.9; H, 7.0%).

(b) Prepared similarly from 9-benzoyltetrahydrocarbazole (Perkin and Plant, J., 1923, 123, 676), 9-benzoyl-7-acetyltetrahydrocarbazole separated from alcohol in colourless plates, m. p. 149° (Found : C, 79.4; H, 6.0. C₂₁H₁₉O₂N requires C, 79.5; H, 6.0%), and gave 7-acetyltetrahydrocarbazole, identical with the above product (mixed m. p.), on hydrolysis.

(c) A solution of 9-acetyltetrahydrocarbazole (3.5 g.) in nitrobenzene (30 c.c.) was treated with aluminium chloride (2.5 g.) and kept at 120–125° for 15 minutes. The cooled solution was poured into dilute hydrochloric acid, the nitrobenzene removed in steam, and the residual solid boiled in alcohol with charcoal. When the product obtained by adding dilute hydrochloric acid to the filtered solution was distilled under reduced pressure and crystallised from acetic acid and then alcohol, a small quantity (about 0.2 g.) of 7-acetyltetrahydrocarbazole (mixed m. p.) was isolated.

A solution of the latter substance (4.1 g.) and sulphur (1.25 g.) in quinoline (50 c.c.) was boiled for an hour and poured into ice-dilute hydrochloric acid, and the product extracted with ether. The dried extract was evaporated, and the residue distilled, with the addition of iron filings, under reduced pressure. After the distillate had been crystallised twice from toluene

and then twice from acetic acid, 2-acetylcarbazole was obtained in colourless plates, m. p. 225° (after softening at 218°), and identified by mixed m. p. with an authentic specimen, m. p. 227°.

7-Acetyltetrahydrocarbazole (5.4 g.) was shaken with amalgamated granulated zinc (400 g.) and concentrated hydrochloric acid (100 c.c.), and left for several hours. After the addition of anisole (10 c.c.) and more hydrochloric acid (30 c.c.), the whole was refluxed for 12 hours, and the product extracted with ether. The extract was washed with water and evaporated, and anisole removed from the residue by distillation in steam. The less volatile product was again collected in ether and 7-ethylhexahydrocarbazole, m. p. 44–46°, was extracted with dilute sulphuric acid; it was recovered by the addition of sodium hydroxide and purified by distillation under reduced pressure (Found: C, 83.9; H, 9.5. $C_{14}H_{19}N$ requires C, 83.6; H, 9.5%). When this base was oxidised with sulphur in boiling quinoline as described above, and the product distilled with iron filings under reduced pressure, 2-ethylcarbazole, yellow plates, m. p. 223° (after two crystallisations from acetic acid), was obtained and identified by a mixed m. p. with an authentic specimen.

7-Benzoyltetrahydrocarbazole.—A mixture of 9-acetyltetrahydrocarbazole (5 g.), carbon disulphide (35 c.c.), benzoyl chloride (10 g.), and aluminium chloride (10 g.) was refluxed for 4 hours, most of the solvent allowed to evaporate, and the residue poured on ice—dilute hydrochloric acid. The more volatile material was removed in steam and the solid residue was collected, washed free from benzoic acid with aqueous sodium carbonate, and crystallised from alcohol and then acetic acid; 7-benzoyl-9-acetyltetrahydrocarbazole was obtained in yellow plates, m. p. 126° (Found: C, 78.8; H, 5.9%). Prepared similarly from 9-benzoyltetrahydrocarbazole, 7:9-dibenzoyltetrahydrocarbazole separated from glacial acetic acid in almost colourless prisms, m. p. 121° (Found: C, 81.8; H, 5.6. $C_{26}H_{21}O_2N$ requires C, 82.3; H, 5.5%). Both these compounds gave 7-benzoyltetrahydrocarbazole, yellow needles, m. p. 165°, from glacial acetic acid, on hydrolysis with alkali as above (Found: C, 82.9; H, 6.3. $C_{19}H_{17}ON$ requires C, 82.9; H, 6.2%). This substance was oxidised with sulphur in quinoline, and the product distilled with iron filings under 0.7 mm. pressure. When the distillate was crystallised from acetic acid, it gave 2-benzoylcarbazole, m. p. 153°, after softening from 143°, which was purified by conversion into 2-benzoyl-9-acetylcarbazole by refluxing with acetic anhydride and a drop of sulphuric acid for 2 hours. The product obtained by precipitation with water then separated from alcohol in brown needles, m. p. 137°, and was identified by mixed m. p.

THE DYSON PERRINS LABORATORY, OXFORD.

[Received, November 21st, 1935.]