CIX.—*Derivatives of Tetrahydrocarbazole. Part V. Carboxylic Acids.*

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THE tetrahydrocarbazolecarboxylic acids hitherto described have the carboxyl group either in the reduced portion of the carbazole molecule (Perkin, J., 1904, **85**, 418; Baeyer and Tutein, *Ber.*, 1889, **22**, 2184) or attached to the nitrogen atom (Perkin and Plant, J., 1923, **123**, 683). We have now prepared the four isomeric acids in which the carboxyl group is attached to the benzene nucleus (for the scheme of numbering the positions in tetrahydrocarbazole, see J., 1923, **123**, 677) by Fischer's method for the synthesis of indole derivatives. In this way, the hydrazones made by condensing *cyclo*hexanone with *o*- and *p*-hydrazinobenzoic acid lost ammonia and gave respectively *tetrahydrocarbazole*-8- and 6-*carboxylic acids*, whilst the hydrazone from *m*-hydrazinobenzoic acid by the same process gave a mixture of two acids, one of which must have the carboxyl group in the 5- and the other in the 7-position. This experience is contrary to that which was found in the case of *cyclo*hexanone-*m*-nitrophenylhydrazone, from which only one of the two possible isomeric nitrotetrahydrocarbazoles, assumed to be 7-nitrotetrahydrocarbazole, was obtained on closing the indole ring (Borsche, Witte, and Bothe, *Annalen*, 1908, **359**, 68; Perkin and Plant, J., 1921, **119**, 1828). Baeyer and Tutein (*loc. cit.*) prepared an acid which may be tetrahydrocarbazole-2 or 4-carboxylic acid from the phenylhydrazone of *cyclo*hexanone-3-carboxylic acid.

The constitutions of these four tetrahydrocarbazolecarboxylic acids are confirmed by the fact that they easily give tetrahydrocarbazole on distillation with soda-lime.

EXPERIMENTAL.

Tetrahydrocarbazole-6-*carboxylic Acid*.—The crude hydrochloride of *p*-hydrazinobenzoic acid, prepared from *p*-aminobenzoic acid (25 g.) by the method of Fischer (*Annalen*, 1882, **212**, 337), was dissolved in hot water (350 c.c.), treated with an excess of sodium acetate, and then with *cyclo*hexanone (18 c.c.); on shaking, cyclo*hexanone*-p-*carboxyphenylhydrazone* separated. It crystallised from glacial acetic acid in yellow prisms, m. p. 236° (decomp.) (Found: N, 12·5. $C_{13}H_{16}O_2N_2$ requires N, 12·1%).

The crude hydrazone was added to water (200 c.c.) and sulphuric acid (40 c.c.) and the mixture warmed to boiling. The *tetrahydrocarbazole*-6-*carboxylic acid* that separated crystallised from dilute alcohol in colourless plates, m. p. 282° (Found: N, 6·6. $C_{13}H_{13}O_2N$ requires N, 6·5%).

The *methyl* ester was produced by boiling the acid with methyl alcohol containing a little sulphuric acid for 4 hours, and precipitating by the addition of dilute aqueous ammonia. It crystallised from dilute acetic acid in colourless leaves, m. p. 158° (Found: N, 5·9. $C_{14}H_{15}O_2N$ requires N, 6·1%). The *ethyl* ester was prepared in a similar way and separated from dilute alcohol in small, colourless prisms, m. p. 119°.

Tetrahydrocarbazole-8-*carboxylic Acid*.—The hydrochloride of *o*-hydrazinobenzoic acid was converted by a process similar to that described above into cyclo*hexanone*-o-*carboxyphenylhydrazone*, which separated from benzene in pale yellow needles, m. p. 162° (Found: N, 12·0. $C_{13}H_{16}O_2N_2$ requires N, 12·1%). On warming the hydrazone (6 g.) with water (120 c.c.) and sulphuric acid (30 c.c.), *tetrahydrocarbazole*-8-*carboxylic acid* separated and, on recrystallisation from benzene, it was obtained in colourless prisms, m. p. 203° (Found: N, 6·5. $C_{13}H_{13}O_2N$ requires N, 6·5%).

The *methyl* ester crystallises from methyl alcohol in long, colourless prisms, m. p. 124° (Found: N, 5·9. $C_{14}H_{15}O_2N$ requires N, 6·1%). The *ethyl* ester separates from dilute alcohol in colourless needles, m. p. 76° (Found: N, 5·8. $C_{15}H_{17}O_2N$ requires N, 5·7%).

Tetrahydrocarbazole-5- and 7-*carboxylic Acids*.—cyclo*Hexanone*-m-*carboxyphenylhydrazone*, prepared from *m*-hydrazinobenzoic acid in the usual way, crystallised from dilute alcohol in orange prisms, m. p. 176° (decomp.) (Found: N, 11·9. $C_{13}H_{16}O_2N_2$ requires N, 12·1%). The crude hydrazone was converted into a mixture of *tetrahydrocarbazole*-5- and 7-*carboxylic acids* on warming with dilute sulphuric acid. The two acids were isolated from the product by fractional crystallisation from either glacial acetic acid or aqueous acetone, and purified by conversion into their methyl esters, from which they were readily obtained on saponification. The acid which separated first in both cases was finally recrystallised from glacial acetic acid and obtained in colourless prisms, m. p. 287° (Found: N, 6·6. $C_{13}H_{13}O_2N$ requires N, 6·5%). Its *methyl* ester crystallised from methyl alcohol in colourless needles, m. p.

155°, and its *ethyl* ester from dilute alcohol in small, colourless plates, m. p. 146°.

The isomeric *tetrahydrocarbazolecarboxylic acid* was ultimately obtained from glacial acetic acid in almost colourless prisms, m. p. 210° (Found : N, 6·1. $C_{13}H_{13}O_2N$ requires N, 6·5%). Its *methyl* ester separated from aqueous alcohol in colourless prisms, m. p. 93° (Found : N, 6·1. $C_{14}H_{15}O_2N$ requires N, 6·1%).

The higher-melting acid (m. p. 287°) is the main constituent of the product of this reaction and from 30 g. of the crude material 16 g. of this acid and 6 g. of the isomeride (m. p. 210°) were isolated in a pure condition.

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