CLVI.—*Some Reactions of* 1-p-*Toluidino*cyclo*pentane*-1-*carboxylic Acid. A New Carbazole Synthesis.*

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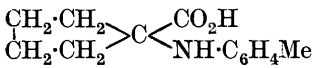
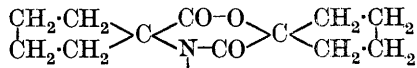
The reaction whereby 1-anilino*cyclo*pentane-1-carboxylic acid, on fusion with a mixture of sodium ethoxide and potassium hydroxide, gives carbazole (Plant and Facer, J., 1925, **127**, 2037), may follow one of two courses: either the *cyclo*pentane ring may open and form with the carboxyl group the second benzene nucleus of carbazole, or, alternatively, the carbazole may be produced entirely from the anilino-group. It is possible to decide this point by an investigation of 1-*p*-toluidino*cyclo*pentane-1-carboxylic acid (I), which, if the former view is correct, ought to give 3-methylcarbazole as opposed to 3 : 6-dimethylcarbazole, in accordance with the latter view, on fusion under the same conditions.

We have now condensed *p*-toluidine with *cyclo*pentanone cyanohydrin and have converted the 1-p-*toluidino*-1-*cyano*cyclo*pentane* so obtained into the corresponding *amide*, which can be hydrolysed to 1-p-*toluidino*cyclo*pentane*-1-*carboxylic acid*. On heating this acid with a mixture of sodium ethoxide and potassium hydroxide, 3-methylcarbazole was obtained. Its identity was established by careful comparison of the substance obtained and its picrate with 3-methylcarbazole and 3 : 6-dimethylcarbazole, which we find can be obtained most conveniently by oxidising the corresponding methyl derivatives of tetrahydrocarbazole with sulphur, and their respective picrates. It seems clear now that the production of carbazole from 1-anilino*cyclo*pentane-1-carboxylic acid involves the enlargement of the carbocyclic system, probably by absorption of

the carboxyl group. A further investigation of this reaction has shown that it proceeds quite as well in the absence of sodium ethoxide and that the sodium or potassium salt of the acid can be used.



(I.)



(II.)

1-*p*-Toluidino*cyclo*pentane-1-carboxylic acid is comparatively unstable and loses *p*-toluidine and water on heating above its melting point with the formation of the *lactone* of 1-1′-*hydroxy*cyclo*pentane*-1′-*carboxylyl*-p-*toluidino*cyclo*pentane*-1-*carboxylic acid* (II), showing a behaviour similar to that of 1-anilino*cyclo*pentane-1-carboxylic acid in this respect.

EXPERIMENTAL.

1-p-*Toluidino*-1-*cyano*cyclo*pentane*.—*cyclo*Pentanone cyanohydrin will condense with *p*-toluidine when a solution of these substances in benzene is boiled for 12 hours, but conditions similar to those used by Walther and Hübner (*J. pr. Chem.*, 1916, **93**, 124) for the preparation of 1-anilino-1-cyano*cyclo*hexane were found to be more convenient. To a solution of *cyclo*pentanone (21 g.) and *p*-toluidine (27 g.) in glacial acetic acid (100 c.c.), cooled in ice, potassium cyanide (18 g.), dissolved in a little water, was added. 1-p-*Toluidino*-1-*cyano*cyclo*pentane* separated in good yield and was washed with water. It crystallised from low-boiling petroleum in colourless needles, m. p. 55° (Found : N, 14·2. $C_{13}H_{16}N_2$ requires N, 14·0%). The *nitrosoamine*, prepared from an alcoholic solution of the nitrile, dilute hydrochloric acid, and aqueous sodium nitrite, separated from methyl alcohol in yellow prisms, m. p. 58°.

A solution of 1-*p*-toluidino-1-cyano*cyclo*pentane in cold sulphuric acid was kept for 2 days, poured on to ice and the mixture made alkaline with ammonia; the *amide* of 1-p-*toluidino*cyclo*pentane*-1-*carboxylic acid* was then precipitated. It separated from aqueous methyl alcohol in colourless plates, m. p. 120°. Its *nitrosoamine*, prepared by adding sodium nitrite to the amide dissolved in alcoholic hydrochloric acid, separated from aqueous methyl alcohol in yellow needles, m. p. 132°.

1-p-*Toluidino*cyclo*pentane*-1-*carboxylic Acid*.—A mixture of the crude amide and concentrated hydrochloric acid was boiled under reflux for 2 hours, evaporated to dryness, the residue treated with an excess of aqueous sodium hydroxide, and the solution boiled and filtered. The addition of glacial acetic acid to the cold filtrate precipitated 1-p-*toluidino*cyclo*pentane*-1-*carboxylic acid*, which separated from benzene–petroleum in colourless leaves, m. p. 144°

(Found: N, 6·6. $C_{13}H_{17}O_2N$ requires N, 6·4%). 1-*p*-Toluidino-*cyclo*pentane-1-carboxylic acid is soluble in dilute aqueous sodium hydroxide and in dilute hydrochloric acid and gives a *nitrosoamine*, which separates from aqueous methyl alcohol in pale yellow plates, m. p. 114° (decomp.).

On heating 1-*p*-toluidino*cyclo*pentane-1-carboxylic acid in a small distillation flask, water and *p*-toluidine, which was identified by converting it into its acetyl derivative, were evolved. The remainder distilled at a higher temperature, leaving no residue, and, on recrystallisation from petroleum, the *lactone* of 1-1'-*hydroxy*cyclo-*pentane*-1'-*carboxylyl*-p-*toluidino*cyclo*pentane*-1-*carboxylic acid* separated in colourless needles, m. p. 151° (Found: N, 4·7. $C_{19}H_{23}O_3N$ requires N, 4·5%). This lactone dissolves slowly in cold aqueous sodium hydroxide and is reprecipitated unchanged by the addition of dilute hydrochloric acid. It is not soluble in dilute acids and is unchanged by heating with aniline at 170° or dry ammonia at 200°.

3-*Methylcarbazole.*—An intimate mixture of 1-*p*-toluidino*cyclo*-pentane-1-carboxylic acid (16 g.), potassium hydroxide (36 g.), and sodium ethoxide (40 g.) was heated at 350° for 30 minutes. The product was pulverised and added to water, when 3-methylcarbazole separated. It was purified by distillation and subsequent recrystallisation from glacial acetic acid and obtained in colourless, glistening plates, m. p. 207° (compare Ullmann, *Ber.*, 1898, **31**, 1697). Its picrate separated from benzene in scarlet needles, m. p. 179° (compare Ullmann, *Annalen*, 1904, **332**, 88). The 3-methylcarbazole prepared in this way dissolved in concentrated sulphuric acid to give a pale green solution, which became intensely green on addition of a few drops of nitric acid.

3-Methylcarbazole was also synthesised very conveniently by boiling a solution of 6-methyltetrahydrocarbazole (3 g.; prepared from *p*-tolylhydrazine and *cyclo*hexanone; Borsche, Witte, and Bothe, *Annalen*, 1908, **359**, 62) and sulphur (1·05 g.) in pure quinoline (10 c.c.) for 25 minutes and then pouring it into dilute hydrochloric acid–ice. The 3-methylcarbazole which separated, after distillation with a small quantity of iron powder and recrystallisation of the distillate from glacial acetic acid, was obtained in colourless plates, m. p. 207°. Mixed with the product derived from 1-*p*-toluidino-*cyclo*pentane-1-carboxylic acid, it showed no depression of m. p., and its colour reactions with concentrated sulphuric acid and nitric acid were as above (compare Ullmann, *loc. cit.*). The picrate of this specimen of 3-methylcarbazole, crystallised from benzene, melted at 180°.

3 : 6-*Dimethyltetrahydrocarbazole.*—A mixture of 4-methyl*cyclo*-hexanone (5·5 g.), *p*-tolylhydrazine (6 g.), and alcohol (5 c.c.) was

gently warmed; on cooling, 4-*methyl*cyclo*hexanone*-p-*tolylhydrazone* separated. It was warmed to boiling with dilute sulphuric acid and heated on the steam-bath for an hour. The 3 : 6-*dimethyltetrahydrocarbazole* that separated crystallised from petroleum in small, colourless needles, m. p. 112° (Found : N, 7·0. $C_{14}H_{17}N$ requires N, 7·0%). Its *picrate* separated from benzene in dark red prisms, m. p. 147°.

3 : 6-*Dimethylcarbazole* was prepared from 3 : 6-dimethyltetrahydrocarbazole (3·2 g.) and sulphur (1 g.) in quinoline (5 c.c.) as described above. The oily product, which gradually solidified, was distilled with iron powder and thereafter crystallised from benzene, dimethylcarbazole being thus obtained in colourless needles, m. p. 219° (compare Täuber and Loewenherz, *Ber.*, 1891, **24**, 1033). 3 : 6-Dimethylcarbazole gives a faintly brown solution in concentrated sulphuric acid, the colour being intensified on addition of nitric acid. The picrate of 3 : 6-dimethylcarbazole separated from benzene in red needles, m. p. 192° (compare Täuber and Loewenherz, *loc. cit.*). A mixture of this 3 : 6-dimethylcarbazole with the 3-methylcarbazole obtained from 1-*p*-toluidino*cyclo*pentane-1-carboxylic acid melted completely below 197°.

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