

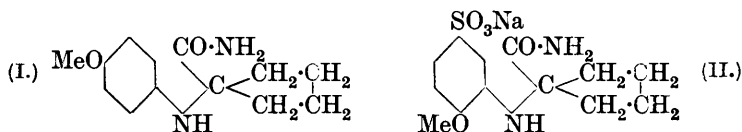
LXXI.—*The Condensation of Substituted Anilines with cyclopentanone Cyanohydrin. Derivatives of 1-Anilinocyclopentane-1-carboxylic Acid.*

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It has already been shown that 1-anilinocyclopentane-1-carboxylic acid and the corresponding 1-*p*-toluidino-compound give carbazole and 3-methylcarbazole, respectively, on fusion with a mixture of potassium hydroxide and sodium ethoxide (Plant and Facer, J., 1925, 127, 2037; Oakeshott and Plant, J., 1926, 1210). With a view to extend this reaction and establish the structures of some carbazole compounds, the preparation of a number of derivatives of 1-anilinocyclopentane-1-carboxylic acid has been investigated. The general method of procedure has been to prepare the corresponding nitrile by mixing the required amine with *cyclopentanone* (rather more than 1 mol.) in glacial acetic acid with the subsequent addition of aqueous potassium cyanide (about 1½ mols.) (compare the preparation of 1-anilino-1-cyanocyclohexane, Walther and Hübner, *J. pr. Chem.*, 1916, 93, 124). The direct hydrolysis of the nitrile to the corresponding acid in several cases was difficult, but an almost quantitative conversion could be obtained if the nitrile was first converted into the amide and subsequently into the acid. It was observed in some instances that the nature and position of the substituent in the aniline molecule considerably retarded the formation of the corresponding nitrile, and a detailed study of this was undertaken. The presence of a methyl or methoxyl group in the benzene ring, whatever its position with respect to the amino-group, did not influence the condensation, the reaction being completed during the course of an hour at room temperature. The nitro-group had the greatest effect, this being most pronounced when the nitro-group was in the ortho-position, and least when it was in the meta-position, to the amino-group. Thus *o*-nitroaniline could not be made to condense at all, even when the mixture was heated in a sealed tube at 100° for 5 days, *p*-nitroaniline reacted during 2 days if the temperature was kept at 40–45°, while the reaction with *m*-nitroaniline took place slowly at room temperature, several hours being required for its completion. The effect of the carboxyl group was similar, but not so pronounced, anthranilic acid requiring a few days at 40–45°, *p*-aminobenzoic acid 24 hours at this temperature, whilst *m*-aminobenzoic acid reacted completely in a few hours at room temperature. The retarding effect of chlorine and bromine was negligible, except when the group was

ortho to the amino-group, in which case several hours were required at room temperature for the completion of the reaction.

The formation of the amide from the corresponding nitrile proceeded smoothly, by keeping in concentrated sulphuric acid solution for 2 days, in all cases except some in which a methoxyl group was present. It was possible to convert 1-*p-anisidino*-1-cyanocyclopentane into the *amide* (I), but with the corresponding *o-anisidino*- and *m-anisidino*-compounds sulphonation took place at the same time. From 1-*o-anisidino*-1-cyanocyclopentane the sodium salt of a monosulphonic acid was isolated, and, since no apparent sulphonation takes place with the *p-anisidino*-compound or in the absence of the methoxyl group, it seems certain that the sulphonyl group enters the position para to the methoxyl group to give *sodium 1-o-anisidinocyclopentane-1-carboxamide-5'-sulphonate* (II).



1-*Veratrylamino*-1-cyanocyclopentane and 1-*mm'-dimethoxyanilino*-1-cyanocyclopentane were prepared from veratrylamine and 3:5-dimethoxyaniline, respectively, in order to investigate the possibility of obtaining the corresponding dimethoxy-derivatives of ψ -indoxyl-*spirocyclopentane* (compare Perkin and Plant, J., 1923, 123, 676) by interaction of the cyano-group and the hydrogen atom in the ortho-position in the benzene nucleus under conditions similar to those used by Hoesch (*Ber.*, 1915, 48, 1122) for condensing nitriles with certain hydroxybenzene compounds. Several attempts to bring about this reaction in dry ether in the presence of zinc chloride or aluminium chloride and dry hydrogen chloride were unsuccessful, the nitriles being recovered unchanged. The failure of this reaction may be accounted for by the absence of an unmethylated hydroxyl group in the benzene nucleus or by the basic nature of the substance.

Fusion of 1-*o-toluidinocyclopentane-1-carboxylic acid* with a mixture of potassium hydroxide and sodium ethoxide has given rise to 1-methylcarbazole, which was identified by comparison with a specimen of 1-methylcarbazole prepared by oxidising 8-methyl-tetrahydrocarbazole. The fact that this fusion gives rise to 1-methylcarbazole and not to 1:8-dimethylcarbazole confirms our previous evidence for the view that the formation of carbazole from 1-anilino-*cyclopentane-1-carboxylic acid* involves the enlargement of the *cyclopentane* ring (*loc. cit.*).

E X P E R I M E N T A L.

1-o-Toluidinocyclopentane-1-carboxylic Acid.—*o*-Toluidine (27.5 g.) and cyclopentanone (21 g.) were mixed in glacial acetic acid (200 c.c.) and then treated at room temperature with potassium cyanide (20 g.), dissolved in water (60 c.c.). After a short time, the product separated as an oil which, on stirring, solidified, and, after crystallisation from low-boiling petroleum, *1-o-toluidino-1-cyanocyclopentane* was obtained in good yield as colourless prisms, m. p. 68°. A solution of this in concentrated sulphuric acid was kept for 2 days and poured on to ice, and the liquid made alkaline with ammonia. *1-o-Toluidinocyclopentane-1-carboxyamide*, which was precipitated, separated from petroleum in colourless prisms, m. p. 122°. The amide, on being rubbed with concentrated hydrochloric acid, gave its *hydrochloride*, which was added to an excess of hydrochloric acid and the mixture boiled to dryness. The residue was dissolved in aqueous sodium hydroxide, and the filtered solution treated with an excess of glacial acetic acid. This precipitated *1-o-toluidinocyclopentane-1-carboxylic acid*, which separated from xylene in colourless needles, m. p. 128° (Found : N, 6.5. $C_{13}H_{17}O_2N$ requires N, 6.4%). The acid was unaltered by heating with an excess of potassium hydroxide up to 300°. From an aqueous solution of the cooled mixture, the substance was recovered by the addition of acetic acid.

1-Methylcarbazole.—*1-o*-Toluidinocyclopentane-1-carboxylic acid (16 g.) was mixed with potassium hydroxide (35 g.) and sodium ethoxide (40 g.) and heated from 270° to 320° during $\frac{1}{2}$ hour. After cooling, the pulverised product was treated with water, and the insoluble portion dried and distilled. The colourless distillate was crystallised from petroleum, *1-methylcarbazole* separating in colourless plates, m. p. 117° (compare Ullmann, *Annalen*, 1903, 332, 87). Its picrate separated from hot alcohol in scarlet needles, m. p. 144° (compare Ullmann, *loc. cit.*). The *1-methylcarbazole* obtained in this way dissolved in concentrated sulphuric acid to give a pale green solution, the colour of which faded in 30 seconds to straw-yellow. The addition of a drop of concentrated nitric acid to this solution produced an intense green colour.

1-Methylcarbazole was also synthesised in the following way : *o*-Tolyldiazine (12.2 g.) and cyclohexanone (9.8 g.) were heated together on the steam-bath for a short time, and, on cooling, *cyclohexanone-o-tolyldiazine* was obtained as a solid mass. The crude hydrazone was heated to boiling with dilute sulphuric acid for a few minutes ; the *8-methyltetrahydrocarbazole* which separated crystallised from aqueous alcohol in colourless plates, m. p. 98°. *8-Methyltetrahydrocarbazole* has previously been prepared by the

interaction of chlorocyclohexanone and *o*-toluidine, and found to melt at 98° (D.R.-P. 374,098). A solution of 8-methyltetrahydrocarbazole (6 g.) and sulphur (2.1 g.) in pure quinoline (20 c.c.) was boiled for 20 minutes and then poured into a mixture of dilute hydrochloric acid and ice. The oil which separated gradually solidified, and was collected, dried, and distilled with an equal volume of iron powder. The distillate, m. p. 110°, was converted into its picrate, which separated from hot alcohol in scarlet needles, m. p. 144°. On warming the picrate with aqueous sodium hydroxide, 1-methylcarbazole, m. p. 117°, was obtained. The fact that this product was identical with that obtained from 1-*o*-toluidinocyclopentane-1-carboxylic acid was established by a mixed m. p. determination, by the colour changes in concentrated sulphuric acid solution, and by the melting points of their picrates.

1-*m*-Toluidinocyclopentane-1-carboxylic Acid.—*m*-Toluidine (10 c.c.) and cyclopentanone (8.5 c.c.), dissolved in glacial acetic acid (50 c.c.), were treated at room temperature with potassium cyanide (7 g.), in a little water; an oily product gradually separated. After 2 hours, the mixture was poured into an excess of water, the oily nitrile gradually solidified, and 1-*m*-toluidino-1-cyanocyclopentane was obtained as a colourless solid, m. p. 53°, on rubbing with petroleum. This nitrile was hydrolysed in the same way as the corresponding *o*-toluidino-compound and the 1-*m*-toluidinocyclopentane-1-carboxamide obtained separated from aqueous alcohol in colourless prisms, m. p. 145°. The clear solution of the amide in concentrated hydrochloric acid was boiled under reflux for 1 hour and evaporated to dryness, the residue was dissolved in aqueous sodium hydroxide, and the filtered solution acidified with acetic acid. The product was crystallised from aqueous alcohol and 1-*m*-toluidinocyclopentane-1-carboxylic acid obtained in colourless needles, m. p. 123—124° (Found: N, 6.5. C₁₃H₁₇O₂N requires N, 6.4%).

Condensation of the Methoxyanilines with cyclopentanone Cyanohydrin.

1-*o*-Anisidino-1-cyanocyclopentane.—The reaction mixture was kept at room temperature for 2 hours and then poured into water, the oily product was extracted with ether, and the ethereal solution shaken twice with water and then with dilute aqueous sodium carbonate. On drying the solution with calcium chloride and removing the ether, 1-*o*-anisidino-1-cyanocyclopentane remained as a brown syrup. Its solution in concentrated sulphuric acid was kept for 2 days and then poured into ice-water. Calcium carbonate was added to the hot solution until effervescence ceased, and, after filtering, it was treated with a slight excess of sodium carbonate to precipitate the

calcium, again filtered, and evaporated to dryness. The residue was extracted with hot alcohol, acetone was added to the clear alcoholic solution, and, on standing, *sodium 1-o-anisidino-cyclopentane-1-carboxyamide-5'-sulphonate* separated in colourless prisms (Found: S, 9.6. $C_{13}H_{17}O_5N_2SNa$ requires S, 9.5%). This sodium salt is very soluble in water.

1-m-Anisidino-1-cyanocyclopentane.—From the reaction mixture at room temperature, the oily product gradually separated during 1 hour. After dilution with water, the oil solidified on being rubbed with alcohol, and, on crystallisation from this solvent, *1-m-anisidino-1-cyanocyclopentane* separated in colourless prisms, m. p. 132°. The solution of this product in concentrated sulphuric acid became dark green, and was poured into ice-water after 2 days; from the intense purple solution produced, nothing separated on addition of ammonia.

1-p-Anisidino-cyclopentane-1-carboxylic Acid.—The reaction mixture was treated as described for *o*-anisidine, *1-p-anisidino-1-cyanocyclopentane* being obtained as a brown syrup. By treatment with concentrated sulphuric acid for 2 days, pouring into ice-water, making alkaline with ammonia, and crystallising the product from benzene-petroleum, *1-p-anisidino-cyclopentane-1-carboxyamide* was obtained in almost colourless prisms, m. p. 81–82°. The amide was hydrolysed by boiling its clear solution in concentrated hydrochloric acid for $\frac{1}{2}$ hour; this was then evaporated to dryness, the residue dissolved in dilute aqueous sodium hydroxide, and the filtered solution acidified with acetic acid. *1-p-Anisidino-cyclopentane-1-carboxylic acid* separates from alcohol in colourless prisms, m. p. 160° (Found: N, 6.0. $C_{13}H_{17}O_3N$ requires N, 5.9%).

1-Veratrylamino-1-cyanocyclopentane.—From the reaction mixture, after a short time, the addition of ammonia precipitated *1-veratrylamino-1-cyanocyclopentane*, which separated from benzene-petroleum in colourless plates, m. p. 98° (Found: N, 11.3. $C_{14}H_{18}O_2N_2$ requires N, 11.4%). When this nitrile dissolves in concentrated sulphuric acid, sulphonation apparently takes place, since dilution of the solution after 2 days and treatment with ammonia gives no precipitate.

1-mm'-Dimethoxyanilino-1-cyanocyclopentane. — 3 : 5-Dimethoxynitrobenzene was obtained from trinitrobenzene by the steps described by Vermeulen (*Rec. trav. chim.*, 1906, 25, 26), although the following conditions for the methylation of 5-nitro-3-hydroxyanisole were found to be more satisfactory than those given. The anisole (8 g.), methyl sulphate (7.4 g.), and potassium carbonate (8 g.) were mixed in toluene (200 c.c.) and boiled for 4 hours. The toluene was removed in steam and, on cooling the residue, 3 : 5-dimethoxynitro-

benzene solidified; after recrystallisation from ethyl acetate, it melted at 89°.

The most convenient conditions for reducing this compound are similar to those used by Hope and Robinson (J., 1911, 99, 1159) for reducing anhydrocotarnine-5-nitrophthalide. 3 : 5-Dimethoxy-nitrobenzene (10 g.) was dissolved in a mixture of glacial acetic acid (100 c.c.) and water (100 c.c.), tin (1 g.) was added, followed by a solution of stannous chloride (6 g.) in hydrochloric acid (60 c.c.), the mixture being then stirred vigorously and maintained at 40° for a few hours. After being made alkaline with sodium hydroxide, the product was extracted with ether and the ethereal solution was shaken with water and dried over sodium sulphate. The ether was removed, and 3 : 5-dimethoxyaniline (3.5 g.) obtained on distillation, b. p. 178°/20 mm. On treating the amine with an excess of acetic anhydride and then mixing the product with benzene-petroleum, a solid was obtained. This was crystallised from water, 3 : 5-dimethoxyacetanilide separating in colourless needles, m. p. 157° (Found : N, 7.3. $C_{10}H_{13}O_3N$ requires N, 7.2%).

A mixture of 3 : 5-dimethoxyaniline (5 g.), *cyclopentanone* (3 c.c.), and concentrated aqueous potassium cyanide (3 g.) in glacial acetic acid (30 c.c.), after standing at room temperature for a short time, was partly neutralised with ammonia. The dark-coloured oil that separated was extracted with ether, the extract was twice shaken with water and dried over sodium sulphate, and the solvent removed. The dark oily residue was obtained in colourless plates after successive treatments with low-boiling petroleum. 1-mm' *Dimethoxyanilino-1-cyanocyclopentane* melts at 150° (Found : N, 11.1. $C_{14}H_{18}O_2N_2$ requires N, 11.4%).

Condensation of the Chloroanilines with cyclopentanone Cyanohydrin.

1-o-Chloroanilinocyclopentane-1-carboxylic Acid.—The reaction mixture was left at room temperature for 12 hours, and then poured into dilute hydrochloric acid to remove any unchanged *o*-chloroaniline, but the oily product which separated did not solidify after several hours. The mixture was shaken with ether and the ethereal solution was washed with water and dilute aqueous sodium carbonate and dried over calcium chloride. After removal of the ether, *1-o-chloroanilino-1-cyanocyclopentane* remained as a yellow oil. This was dissolved in concentrated sulphuric acid and the solution was kept for 2 days and poured on to ice. Dilution with water, without the addition of ammonia, caused the separation of the product as a sticky solid, which hardened on being rubbed with petroleum. After crystallisation from petroleum, *1-o-chloroanilino-cyclopentane-1-carboxamide* was obtained in colourless prisms,

m. p. 113° (Found : N, 11.6. $C_{12}H_{15}ON_2Cl$ requires N, 11.7%). The amide was hydrolysed by boiling its solution in concentrated hydrochloric acid for an hour, and the product isolated by the method employed in the previous cases. After crystallisation from aqueous alcohol, 1-*o*-chloroanilinocyclopentane-1-carboxylic acid was obtained in colourless needles, m. p. 145° (Found : N, 5.8. $C_{12}H_{14}O_2NCl$ requires N, 5.8%).

1-*m*-Chloroanilinocyclopentane-1-carboxylic Acid.—The reaction mixture was kept for 1 hour at room temperature and then poured into water; the product separated as an oil which slowly solidified on stirring. After crystallisation from low-boiling petroleum, 1-*m*-chloroanilino-1-cyanocyclopentane was obtained in colourless prisms, m. p. 47°. Its solution in concentrated sulphuric acid, after 2 days, was poured on to ice, and the product isolated by making it alkaline with ammonia; the 1-*m*-chloroanilinocyclopentane-1-carboxyamide obtained crystallised from aqueous alcohol in colourless prisms, m. p. 118°. A solution of this in concentrated hydrochloric acid was boiled for $\frac{1}{2}$ hour, the product isolated as before, and, after crystallisation from aqueous alcohol, 1-*m*-chloroanilinocyclopentane-1-carboxylic acid was obtained in colourless prisms, m. p. 112° (Found : N, 5.8. $C_{12}H_{14}O_2NCl$ requires N, 5.8%).

1-*p*-Chloroanilinocyclopentane-1-carboxylic Acid.—The reaction mixture was treated exactly as described for *m*-chloroaniline, and the condensation was complete after 15 minutes. From aqueous alcohol, 1-*p*-chloroanilino-1-cyanocyclopentane separated in long, colourless prisms, m. p. 73°. The hydrolysis of this nitrile proceeded exactly as with the *m*-chloroanilino-compound; the 1-*p*-chloroanilinocyclopentane-1-carboxyamide obtained crystallised from aqueous alcohol in colourless needles, m. p. 132°. 1-*p*-Chloroanilinocyclopentane-1-carboxylic acid crystallised from benzene in colourless prisms, m. p. 144° (Found : N, 5.5. $C_{12}H_{14}O_2NCl$ requires N, 5.8%).

Condensation of the Bromoanilines with cyclopentanone Cyanohydrin.

1-*o*-Bromoanilinocyclopentane-1-carboxylic Acid.—The preparation of this acid followed exactly the same course as that described for the *o*-chloroanilino-derivative. 1-*o*-Bromoanilino-1-cyanocyclopentane was obtained as a yellowish-brown oil, but its complete formation required about 24 hours at room temperature. 1-*o*-Bromoanilinocyclopentane-1-carboxyamide separated from petroleum in colourless prisms, m. p. 128°, and 1-*o*-bromoanilinocyclopentane-1-carboxylic acid from aqueous alcohol in colourless prisms, m. p. 140° (Found : N, 4.9. $C_{12}H_{14}O_2NBr$ requires N, 4.9%).

1-*m*-Bromoanilinocyclopentane-1-carboxylic Acid.—The formation

of 1-*m*-bromoanilino-1-cyanocyclopentane took place under the conditions described for the corresponding *m*-chloroanilino-compound, but the product separated as an oil and, after extraction with ether, it was ultimately obtained as a yellowish-brown syrup. 1-*m*-Bromoanilinocyclopentane-1-carboxyamide separated from aqueous alcohol in colourless plates, m. p. 126°, and 1-*m*-bromoanilinocyclopentane-1-carboxylic acid in colourless needles, m. p. 130° (Found : N, 4.9. $C_{12}H_{14}O_2NBr$ requires N, 4.9%).

1-*p*-Bromoanilinocyclopentane-1-carboxylic Acid.—The formation of this compound followed the course described for the *p*-chloroanilino-derivative. 1-*p*-Bromoanilino-1-cyanocyclopentane separated from petroleum in colourless plates, m. p. 69°, 1-*p*-bromoanilinocyclopentane-1-carboxyamide from aqueous alcohol in colourless plates, m. p. 145°, and 1-*p*-bromoanilinocyclopentane-1-carboxylic acid from aqueous alcohol in colourless prisms, m. p. 130° (Found : N, 5.2. $C_{12}H_{14}O_2NBr$ requires N, 4.9%).

Condensation of the Nitroanilines with cyclopentanone Cyanohydrin.

1-*m*-Nitroanilinocyclopentane-1-carboxylic Acid.—The appropriate mixture was kept at room temperature, the course of the reaction being followed by taking advantage of the fact that *m*-nitroaniline dissolves in dilute hydrochloric acid, whilst the condensation product remains undissolved. On pouring the product into water after 1 hour, it was found that about 80% of the mixture was unchanged *m*-nitroaniline; but after 18 hours the reaction had proceeded practically to completion. 1-*m*-Nitroanilino-1-cyanocyclopentane separates from aqueous alcohol in yellow prisms, m. p. 95° (Found : N, 18.0. $C_{12}H_{13}O_2N_3$ requires N, 18.2%). The hydrolysis of this nitrile was carried out in the usual way, and the 1-*m*-nitroanilinocyclopentane-1-carboxyamide obtained separated from aqueous alcohol in orange prisms, m. p. 144° (Found : N, 16.8. $C_{12}H_{15}O_3N_3$ requires N, 16.9%). 1-*m*-Nitroanilinocyclopentane-1-carboxylic acid was obtained, after crystallisation from aqueous alcohol, in long, yellow prisms, m. p. 137° (Found : N, 11.4. $C_{12}H_{14}O_4N_2$ requires N, 11.2%).

1-*p*-Nitroanilinocyclopentane-1-carboxylic Acid.—As in the case of the *m*-nitroanilino-derivative, the course of the condensation may be followed easily, since the product is insoluble in dilute hydrochloric acid, in which *p*-nitroaniline dissolves. After standing at room temperature for 15 hours, the mixture had undergone very little change, the product being almost entirely soluble in dilute hydrochloric acid. When the reaction mixture was kept in a water-bath at 40–45°, 1-*p*-nitroanilino-1-cyanocyclopentane gradually separated in yellow plates during 2 days. A further

quantity of the nitrile was obtained by diluting the mother-liquor with water and crystallising the product from glacial acetic acid. The nitrile separated from this solvent in yellow plates, m. p. 165° (Found: N, 18.2. $C_{12}H_{13}O_2N_3$ requires N, 18.2%). 1-p-Nitroanilinocyclopentane-1-carboxyamide was obtained by pouring a solution of this nitrile in concentrated sulphuric acid into water after 2 days, without making it alkaline, and separated from alcohol in yellow plates, m. p. 231°. 1-p-Nitroanilinocyclopentane-1-carboxylic acid, obtained in the usual way, separated from aqueous alcohol in yellow plates, m. p. 187° (Found: N, 11.2. $C_{12}H_{14}O_4N_2$ requires N, 11.2%).

*Condensation of the Aminobenzoic Acids with cyclopentanone
Cyanohydrin.*

The Amide of 1-o-Carboxyanilinocyclopentane-1-carboxylic Acid.—The reaction mixture was kept for 5 days at 40—45°, and poured into water, and the solid product crystallised from benzene-petroleum, from which 1-o-carboxyanilino-1-cyanocyclopentane separated in colourless needles, m. p. 122°. Its solution in concentrated sulphuric acid, after being kept for 2 days and then poured into much ice-water, yielded the *amide* of 1-o-carboxyanilinocyclopentane-1-carboxylic acid, which separated from alcohol in colourless prisms, m. p. 225° (after prolonged drying). An attempt to hydrolyse this amide to the corresponding acid by boiling with concentrated hydrochloric acid for 1 hour and isolating the product in the usual way yielded 1-anilinocyclopentane-1-carboxylic acid, m. p. 160—161° (compare Plant and Facer, *loc. cit.*). The identity of this acid was established by analysis (Found: N, 7.0. Calc.: N, 6.8%) and by a mixed m. p. determination. Other attempts to obtain 1-o-carboxyanilinocyclopentane-1-carboxylic acid have so far been unsuccessful.

The Amide of 1-m-Carboxyanilinocyclopentane-1-carboxylic Acid.—The reaction mixture was kept for 4 hours at room temperature, and the product was isolated by pouring the mixture into water, *m*-aminobenzoic acid being soluble in dilute acetic acid. After crystallisation from toluene, 1-m-carboxyanilino-1-cyanocyclopentane was obtained in colourless needles, m. p. 153°. The solution of the nitrile in concentrated sulphuric acid was kept for 2 days and poured into ice-water, and the mixture was made alkaline with ammonia and then acidified with acetic acid; the *amide* of 1-m-carboxyanilinocyclopentane-1-carboxylic acid that separated crystallised from water in colourless prisms, m. p. 215° (Found: N, 11.2. $C_{13}H_{16}O_3N_2$ requires N, 11.3%).

When the amide (20 g.) was heated with a mixture of potassium

hydroxide (36 g.) and sodium ethoxide (40 g.) at 270—320° for $\frac{1}{2}$ hour and the product, after cooling, was treated with water, a small quantity of carbazole remained. This was distilled and subsequently crystallised from toluene and was then identified by a mixed m. p. determination and by conversion into its picrate, m. p. 186°.

1-p-Carboxyanilinocyclopentane-1-carboxylic Acid.—The reaction mixture was kept at 40°, and, during the course of 24 hours, colourless prisms separated. After recrystallisation from glacial acetic acid, *1-p-carboxyanilino-1-cyanocyclopentane* was obtained in colourless prisms, m. p. 189—190°. Hydrolysis was carried out as described for the *m*-carboxyanilino-derivative and, on crystallisation from alcohol, the *amide* of *1-p-carboxyanilinocyclopentane-1-carboxylic acid* separated in colourless prisms, m. p. 272°. The formation of the acid proceeded in the usual way and *1-p-carboxyanilinocyclopentane-1-carboxylic acid* was obtained, after crystallisation from aqueous alcohol, in colourless prisms, m. p. 225° (decomp.) (Found: N, 5.6. $C_{13}H_{15}O_4N$ requires N, 5.6%).

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