Studies in Pyrolysis. Part V. Pyrolysis of* 1-*Anilino*cyclo*alkanecarboxylic Acids.*

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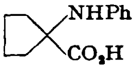
1-Anilino*cyclo*pentanecarboxylic acid, pyrolysed in the liquid phase (*ca.* 250°), yields not only aniline, water, and 1-(1-hydroxy*cyclo*pentanecarboxyanilido)*cyclo*pentanecarboxylic lactone (cf. Plant and Facer, *J.*, 1925, **127**, 2037), but also *cyclo*pent-1-enecarboxylic acid and 1-hydroxy*cyclo*pentanecarboxyanilide. Precisely parallel qualitative results are given by the homologous 1-anilino-*cyclo*hexane- and -*cyclo*heptane-carboxylic acids; the yield of olefinic acid increases, and that of lactone decreases, as the size of the *cyclo*alkane ring is increased. Reasons are adduced for believing that the hydroxy-anilides arise by primary thermal rearrangement of the isomeric parent anilino-acids rather than by secondary reactions of the primary products. In the gaseous phase (*ca.* 500—550°) all the above products are very largely decomposed, with formation of much carbon monoxide and dioxide.

Recent studies on the pyrolysis of a series of homologous 1-anilino*cyclo*alkanecarboxylic acids (I—III), and of the corresponding 1-anilino-1-cyano*cyclo*alkanes, have removed a number of apparent anomalies from the literature and brought to light some novel reactions. The present paper deals with the anilino-acids; the cyano-compounds will be dealt with in a future communication.



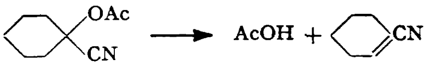
(I)

(II)

(III)

During a previous search for new general routes to polymerisable substituted olefins, of the acrylic and related types, it was found that vapour-phase pyrolysis (*ca.* 450—550°) of α-acyloxy-esters (*e.g.*, IV) and acylated cyanohydrins (*e.g.*, V) leads in general to smooth elimination of carboxylic acid, with formation of the desired olefinic ester (*e.g.*, VI) or nitrile (*e.g.*, VII) respectively (Burns, Jones, and Ritchie, *J.*, 1935, 400, 714; Ritchie, *J.*, 1935, 1054; Ritchie, Jones, Burns, and I.C.I., B.P. 425,885, U.S.P. 2,183,357, 2,265,184):

$$\text{(IV)}\quad BzO{\cdot}CMe_2{\cdot}CO_2Me \longrightarrow BzOH + CH_2{:}CMe{\cdot}CO_2Me \quad \text{(VI)}$$

(V)  (VII)

The method fails, however, when applied to α-acyloxy-acids (*e.g.*, VIII), which break down thermally by a more complex route and do not yield olefinic acids (Bagard, *Bull. Soc. chim. France*, 1907, **1**, 307):

$$\text{(VIII)}\quad AcO{\cdot}CHR{\cdot}CO_2H \longrightarrow AcOH + CO + R{\cdot}CHO$$

Nevertheless, it is recorded that the anilino-acid (II) breaks down, on distillation, to aniline and *cyclo*hex-1-enecarboxylic acid (Betts, Muspratt, and Plant, *J.*, 1927, 1310), which suggests that pyrolysis of suitable anilino- instead of acyloxy-compounds might provide a simple alternative route to olefinic acids, and perhaps to all the desired types of olefinic monomers. The possibility is attractive in view of the ready accessibility of many *x*-anilino-*x*-cyanoalkanes as a starting point (cf. Mulder, *Rec. Trav. chim.*, 1907, **26**, 180). Some complications seem likely, however. For example, the anilino-acid (I) is reported (Plant and Facer, *J.*, 1925, **127**, 2037) to break down thermally in quite a

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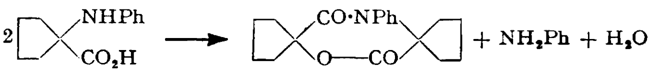
* Part IV, *J.*, 1955, 2717.

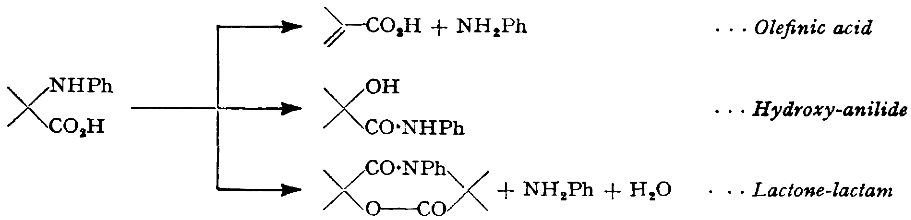
different way, yielding the curious " lactone-lactam " (IX), which suggests that the size of the *cyclo*alkane ring exerts some specific controlling influence on the degradation route.



(I) (IX)

Further, certain α-anilino-acids, on pyrolysis follow two competitive routes, dehydration to a dioxopiperazine and decarboxylation to an amine (cf. Hurd, " The Pyrolysis of Carbon Compounds," Chemical Catalog Co., New York, 1929, Chap. 15), so that interference by these routes might be expected.

For all these reasons, pyrolysis of the anilino-acids (I—III) merited detailed study; and the present work has now shown that the influence of ring size is merely quantitative. All three acids show precisely the same qualitative type of breakdown in the liquid phase at *ca.* 250° in a static reaction vessel (see Experimental section), yielding, not only aniline, water, olefinic acid, and lactone-lactam, but also a wholly unexpected minor product, the 1-hydroxy*cyclo*alkanecarboxyanilide isomeric with the parent anilino-acid. The results can be represented by the following generalised scheme of competitive pyrolytic changes :



As the size of *cyclo*alkane ring is increased ($C_5 \longrightarrow C_6 \longrightarrow C_7$) the yield of olefinic acid increases and that of lactone-lactam decreases, while the yield of hydroxy-anilide is not markedly affected. The three sets of figures quoted in Table 1 were obtained under strictly comparable conditions, and the trend is quite definite, though the yields should be regarded as minimum values because of slight manipulative losses.

TABLE 1.

Product (250°, 1 hr.)	Acid (I)	Acid (II)	Acid (III)
Aniline	17·5 (39)	23·2 (54)	26·0 (65)
Olefinic acid	3·9 (7)	21·5 (36)	31·1 (52)
Hydroxy-anilide	3·9 (4)	6·4 (6)	3·9 (4)
Lactone-lactam	15·0 (21)	10·1 (13)	8·0 (11)
Tars, water, losses	59·7	38·8	31·0

(Figures in parentheses represent % of theory based on conversion into a single constituent; the other figures represent % by wt. based on original acid.)

The yield of hydroxy-anilide from acid (II) varies with duration (*i.e.*, effective " contact-time ") and temperature of pyrolysis (13% at 160°, 48 hr.; 8% at 250°, ½ hr.).

Little gas is liberated during pyrolysis of acids (I—III) up to *ca.* 250°, though small amounts of carbon monoxide are evolved; but at *ca.* 500—550°, in a semimicro flow reaction vessel (see Experimental section), there is a large gaseous pyrolysate containing carbon monoxide and dioxide. It cannot be deduced from the gas analyses (Table 2)

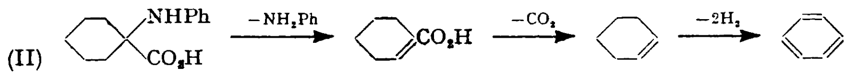
TABLE 2.

Gas produced (540°)	Anilino-acid (I)	Anilino-acid (II)	Olefinic-acid from (II)	Hydroxy-anilide from (II)	Lactone-lactam-from (II)
Yield of gas (%)	66 *	85 *	54 *	57 *	92 †
CO : CO_2 ratio (molar)	1·29	0·45	0·14	10·30	1·68

[Yields are calculated on assumption that one molecule of pyrolysand gives one (*) or two (†) molecules of gas.]

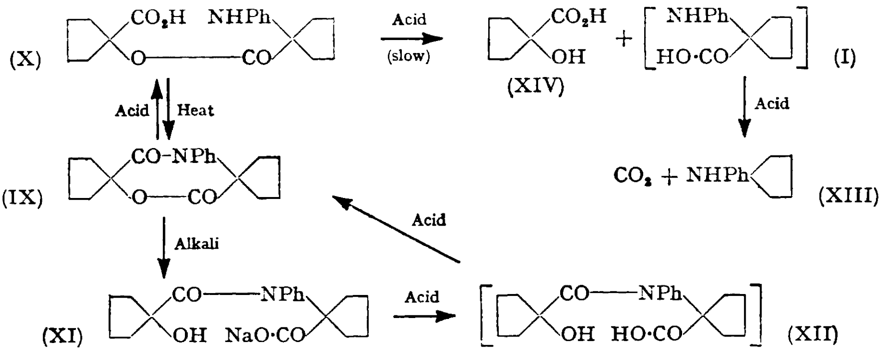
whether the gases produced from acids (I) and (II) arise in part directly from the acids themselves, or whether they are wholly due to secondary pyrolysis of the various primary breakdown products. It can, however, reasonably be concluded from the $CO : CO_2$ ratios that at 500—550° most of the carbon monoxide from acid (II) arises *via* the hydroxy-anilide (with the lactone-lactam as a subsidiary source), in sharp contrast to the fact that this hydroxy-anilide remains completely unchanged after 1 hr. at 250°.

In a vapour-phase flow vessel, at *ca.* 500° with a short contact time, the acid (II) gives a gaseous pyrolysate consisting of carbon monoxide (43%), carbon dioxide (40%), and hydrogen (17%), and a liquid pyrolysate containing aniline, *cyclo*hexene, and benzene. No hydroxy-anilide is obtained, though it may have been a transient precursor of at least part of the carbon monoxide. The constituents of the pyrolysate suggest that at high temperatures a major breakdown-route is the following :



A similar partial dehydrogenation of *cyclo*hexene to benzene has been observed in the pyrolysis of *cyclo*hexyl acetate at *ca.* 550° (Burns, Jones, and Ritchie, *J.*, 1935, 400).

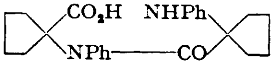
Since steam is formed during pyrolysis of acids (I—III), information is desirable on the mode of hydrolysis of the lactone-lactams. The hydrolysis of substance (IX) has therefore been studied in some detail, and occurs according to the following scheme :

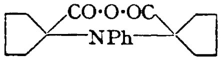


It is very difficult to hydrolyse both the lactone (ester) and lactam (anilido) linkages of the lactone-lactam (IX), presumably because these bonds are formally due to the interaction of a carboxyl group, directly linked to a tertiary carbon atom, with a similarly attached hydroxyl or anilino-group respectively. Prolonged alkaline hydrolysis, followed by acidification of the solution, yields a sticky precipitate which slowly solidifies to regenerated lactone-lactam (95%) and probably consists of the unstable hydroxy-acid (XII) released from the salt (XI). Prolonged acidic hydrolysis leaves much of the original material unchanged; but some of the anilino-acid (X) is produced, which at 250° evolves water and regenerates the original substance (IX). Traces of 1-hydroxy*cyclo*pentanecarboxylic acid (XIV) and *N*-*cyclo*pentylaniline (XIII) are also formed, but none of the acid (I). Separate experiments showed that this anilino-acid is readily decarboxylated when heated with mineral acid.

Origin and Constitution of Lactone-lactams.—The structure (IX), proposed by Plant and Facer (*loc. cit.*) for the lactonic product from acid (I), lacks rigid experimental confirmation; and their simple equation (see above) representing the conversion of the acid (I) into the lactone-lactam (IX), aniline, and water is clearly a summation of two or more stages and does not indicate the immediate precursor of the lactone-lactam. If the first stage is formation of the anilino-acid (XV) by intermolecular elimination of water, it is not obvious why the second stage should be ring closure to lactone-lactam by elimination of aniline rather than to a dioxopiperazine by further elimination of water. On the other hand, since a major primary scission of acid (I) leads to aniline and an olefinic acid, it is possible to formulate other plausible routes on the assumption that the first stage is addition of an amino-compound to an activated double bond, and the second a ring closure by loss of water, or *vice versa.* These routes should lead to one of the lactone-lactams (XVII) or (XVIII), in which there is a central seven-membered ring.

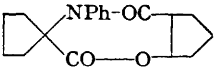
(XV)

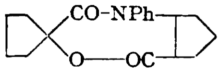




(XVI)

(XVII)





(XVIII)

The anhydride structure (XVI) has been discussed and rejected by Plant and Facer. This rejection is confirmed by the presence of 1-hydroxy*cyclo*pentanecarboxylic acid (XIV) in the acidic hydrolysate from the lactone-lactam; and the same fact appears to rule out structure (XVII). The presence of *N*-*cyclo*pentylaniline (XIII) in this acidic hydrolysate is probably due to decarboxylation of anilino-acid (I); but only isolation of this acid could conclusively eliminate structure (XVIII), since the amine (XIII) might equally well arise by decarboxylation of the isomeric 2-anilino*cyclo*pentanecarboxylic acid. The fact, however, that an equimolecular mixture of the appropriate hydroxy-anilide and olefinic acid fails to interact at 250° argues against the formation of structure (XVIII) by addition *plus* dehydration of these two intermediates.

The new evidence now available therefore supports the double *spiro*-structure (IX) proposed by Plant and Facer, and suggests that it is formed *via* the precursor (XV). It is clear from their infrared spectra that all three lactone-lactams have the same type of double *spiro*-structure.

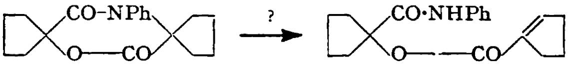
Origin of Hydroxy-anilides.—Three possible routes suggest themselves.

(i) There may be a direct thermal rearrangement of the parent anilino-acid; for, whatever the mechanism, the net result is an interchange of hydroxyl and anilino-groups. In this, the change formally resembles the pinacol–pinacone and benzil–benzilic acid rearrangements; in both of these, one stage in the accepted sequence is a catalysed interchange of hydroxyl and aryl (or alkyl) groups, though attempts to rearrange the acid (II) catalytically at room temperature (*e.g.*, by ethereal phosphoric acid, or boron trifluoride–ether complex) were unsuccessful.

(ii) Steam, present in the reaction vessel as a result of lactone-lactam formation, may conceivably hydrolyse part of the lactone-lactam to anilino-acid and hydroxy-acid, followed by reaction of the latter with free aniline to give hydroxy-anilide. However, complete hydrolysis of the lactone-lactam (IX) is extraordinarily difficult (see above); hydrolysis of one anilido-link followed by formation of another is a most unlikely sequence; and no hydroxy-anilide is formed (see Experimental section) when the lactone-lactam (IX) is heated with aniline and water (bath-temperature 260°).

(iii) There may be pyrolytic rupture of the lactone-lactam ring (IX), as shown below, followed by hydrolysis of the remaining ester linkage by the steam in the vessel, yielding hydroxy-anilide and olefinic acid:

(IX)

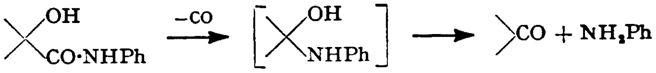


While there is nothing inherently improbable in this idea, it seems to be ruled out by the negative result of the test described in the previous section.

Of the three alternative routes, only direct thermal rearrangement of anilino-acid remains without contrary experimental evidence, though lacking direct proof; and this apparently novel reaction is being investigated further.

Since the hydroxy-anilide from acid (II) remains unchanged at 250°, this substance clearly cannot be the sole primary product from pyrolysis of the acid, leading to the other observed products by secondary reactions at the same temperature. It seems clear, therefore, that pyrolysis of the anilino-acids (I—III) must proceed by several concurrent competitive routes.

Origin of Carbon Monoxide.—Plausible schemes can be advanced, based on known analogous pyrolyses, to account for the formation of carbon monoxide from the substances mentioned in Table 2. For example, just as thermal decarboxylation of benzoic acid (*ca.* 370—400°) is accompanied by a minor scission to carbon monoxide and phenol (Moser, *Helv. Chim. Acta,* 1931, **14**, 971), *cyclo*hex-1-enecarboxylic acid might be expected to give a small amount of carbon monoxide and the enol of *cyclo*hexanone. Similarly, just as a lactide breaks down thermally very largely to carbon monoxide and an aldehyde or ketone (Blaise, *Compt. rend.*, 1904, **138**, 697; cf. Hurd, *op. cit.*, p. 426), the somewhat analogous lactone-lactams might be expected to yield carbon monoxide, a ketone, and the anil of the latter. Finally, the hydroxy-anilides might formally undergo primary conversion into aniline and a lactide, followed by pyrolysis of the latter as described above, or they might even lose carbon monoxide directly by the route:



All these tentative explanations suggest that the pyrolysate from acids (I—III) should contain the appropriate cyclic ketone or its anil; but there was no sign of either in two cases studied particularly [acid (I) at 250°; acid (II) at 500°; see Experimental section]. A control experiment showed that *cyclo*hexanone, intentionally added to the pyrolysand, is not completely destroyed under these conditions; and this argues against the correctness of the above explanations. The carbon monoxide in the various pyrolysates therefore remains for the present unaccounted for.

EXPERIMENTAL

Light petroleum was the fraction of b. p. 60—80°. Aniline was determined as described by Siggia, "Quantitative Organic Analysis," Wiley, New York, 1st Ed., 1949, p. 71. Solid products were identified by mixed m. p., supplemented in some cases by infrared spectra. Gas analyses are reported on a nitrogen-free basis.

Pyrolysis: Macro-method (Static Reaction Vessel).—The pyrolysand (50—80 g.) was heated under reflux in a small flask, immersed in a bath of Wood's metal. Temperatures were controlled to within ±5°. To prevent oxidation during pyrolysis, the system was thoroughly flushed with nitrogen before each run. The pyrolysate was fractionally distilled.

Pyrolysis: Macro-method (Flow Reaction Vessel).—In one run (see Table 3) at 500° (vapour phase) a flow reaction vessel of the type described by Allan, Forman, and Ritchie (*J.*, 1955, 2717) was used; here, also, the system was flushed with nitrogen before use.

Pyrolysis: Semi-micro Method (Flow Reaction Vessel).—The Pyrex-glass apparatus shown in Fig. 1 was used primarily for the collection and study of gaseous pyrolysates (see Table 2). The pyrolysand (300 mg.) was placed in bulb *A*; bulb *B* was then filled with glass beads (diam. *ca.* 3 mm.) up to a constriction at *C*, and the whole repeatedly evacuated and filled with nitrogen *via* inlets *D* and *E*. A short cylindrical electric furnace *F*, and the similar furnace *G* (in position 1), were raised to 540°; after 2 hr., *G* was moved to position 2, enclosing bulb *A*. The barometric leg *H* was adjusted during the run so as to collect the gaseous pyrolysate at approximately atmospheric pressure. Any non-gaseous pyrolysate was removed at the leg *J*, or the cold trap *K*. After pyrolysis (10 min.) the vessel was removed from the furnace and cooled (15 min.): the total gas evolved was measured by the difference between the initial and final volume readings on the gas-burette. By lowering the mercury level of the collecting limb of the burette before closing the stopcock, *ca.* 80% of the gas in the system can be collected for analysis; Sleigh's method (*J. Soc. Chem. Ind.*, 1937, **56**, 430) was a particularly suitable analytical method. From the capacity of the reaction vessel (29 ml.) the total gas evolved can be calculated.

*Preparation of 1-Anilino*cyclo*alkanecarboxylic Acids* (I—III).—These were prepared from the corresponding anilino-nitriles (cf. Plant and his co-workers, *locc. cit.*) by hydrolysis of the nitrile to the amide by concentrated sulphuric acid, followed by hydrolysis of the amide to the acid by concentrated hydrochloric acid. Thus were obtained:

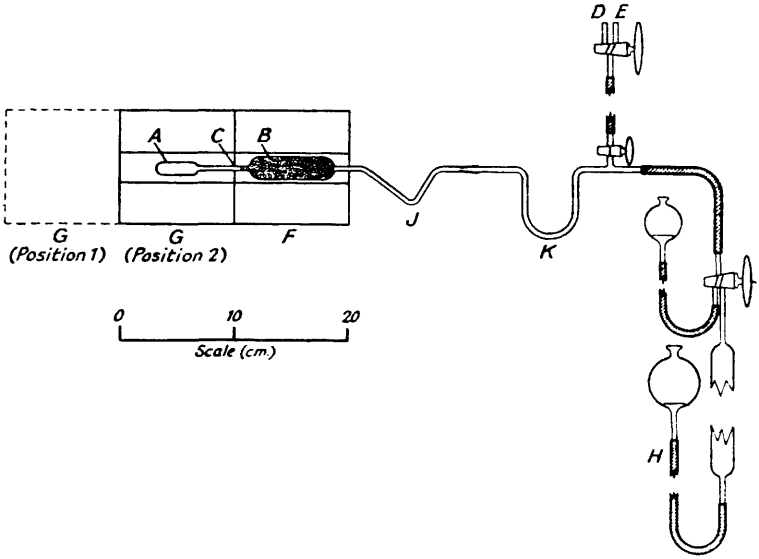
(*a*) 1-Anilino*cyclo*pentanecarboxylic acid (I) (63%), prisms (from xylene), m. p. 150—162° (decomp.) (Found: C, 70·4; H, 7·4; N, 6·8%; equiv., 205. Calc. for $C_{12}H_{15}O_2N$: C, 70·2;

H, 7·4; N, 6·8%; equiv., 205) [Plant and Facer, *loc. cit.*, give m. p. 162°. The acid gave the *N*-acetyl derivative, m. p. 183—194° (decomp.), in very poor yield (0·4%; 7 hr., acetic anhydride: 0·2%; 7 hr., acetyl chloride); Plant and Facer, *loc. cit.*, give m. p. 195° (yield not stated)].

(*b*) 1-Anilino*cyclo*hexanecarboxylic acid (II) (55%), fine needles (from benzene), m. p. 123—140° (decomp.) (Found: C, 71·4; H, 7·7; N, 6·3%; equiv., 218. Calc. for $C_{13}H_{17}O_2N$: C, 71·2; H, 7·8; N, 6·4%; equiv., 219) [Betts *et al.*, *loc. cit.*, give m. p. 142°; Bucherer and Barsch, *J. prakt. Chem.*, 1934, **140**, 151, give m. p. 158°. A sample, kept at 160° for 30 min., lost 25% in wt., indicating marked decomposition just above the m. p.].

(*c*) 1-*Anilino*cyclo*heptanecarboxylic acid* (III) (78%), prisms (from benzene), m. p. 143—158° (decomp.) (Found: C, 72·0; H, 8·0; N, 6·3%; equiv., 234. $C_{14}H_{19}O_2N$ requires C, 72·1; H, 8·2; N, 6·0%; equiv., 233). The intermediate 1-*anilino*cyclo*heptanecarboxyamide* crystallised from ethanol as needles, m. p. 141—142° (Found: C, 72·2; H, 9·1; N, 12·0. $C_{14}H_{20}ON_2$ requires C, 72·4; H, 8·7; N, 12·1%).

Semimicro flow reaction vessel.



Although previous workers have reported a sharp m. p. for acids (I) and (II), it was observed that even after rigorous purification all three acids (I—III) melted indefinitely over a range of some 12° to 17°, indicating decomposition at the m. p.

Pyrolysis of 1-*Anilino*cyclo*alkanecarboxylic Acids* (*Macro-method*: *Static Reaction Vessel*).—(a) 1-*Anilino*cyclo*pentanecarboxylic acid* (I). Acid (50 g.), pyrolysed for 1 hr. at 250°, yielded (i) a fraction (9·9 g.), b. p. 150—210°, containing aniline (7·0 g.), *cyclo*pent-1-enecarboxylic acid (0·36 g.), and water, and (ii) a residue (39·4 g.). *cyclo*Pentanone and *cyclo*pentylideneaniline were absent from both (i) and (ii) (tested by 2 : 4-dinitrophenylhydrazine in dilute hydrochloric acid–ethanol). Residue (ii), extracted with aqueous sodium carbonate, yielded *cyclo*pent-1-ene-carboxylic acid (1·76 g.), crystallising from light petroleum as prisms, m. p. 120—121° (Cook and Linstead, *J.*, 1934, 956, give m. p. 121°), and giving a dibromo-derivative, crystallising from acetic acid–water as prisms, m. p. 133—134° [Urion, *Ann. Chim.* (*France*), 1934, **1**, 5, gives m. p. 133°]. The alkali-insoluble residue from (ii), extracted with hydrochloric acid, yielded aniline (2·95 g.); the neutral residue gave 1-*hydroxy*cyclo*pentanecarboxyanilide* (1·55 g.), recrystallising from benzene as plates, m. p. 169—170° (Found: C, 69·9; H, 7·4; N, 7·1. $C_{12}H_{15}O_2N$ requires C, 70·2; H, 7·4; N, 6·8%). The identity of the anilide was confirmed by hydrolysis by concentrated hydrochloric acid to aniline hydrochloride and 1-hydroxy*cyclo*pentanecarboxylic acid, the latter recrystallising from benzene as plates, m. p. and mixed m. p. 103—104° (von Auwers and Krollpfeiffer, *Ber.*, 1915, **48**, 1389, give m. p. 103°), and by a mixed m. p. with synthetic anilide prepared by refluxing the hydroxy-acid with aniline. The liquors from the anilide, treated with light petroleum, yielded 12·4 g. of the crude lactone-lactam,

m. p. 130—144°; recrystallisation from benzene–light petroleum yielded 1-(1-hydroxy*cyclo*pentanecarboxyanilido)*cyclo*pentanecarboxylic lactone (IX) as prisms, m. p. 143—144° [Found: C, 72·4; H, 7·1; N, 4·7%; *M* (cryoscopic in benzene), 295. Calc. for $C_{18}H_{21}O_3N$: C, 72·2; H, 7·1; N, 4·7%; *M*, 299]. Plant and Facer (*loc. cit.*) give m. p. 142°. The equivalent weight, determined by back-titration of an alkaline hydrolysate, was 306.

(b) 1-*Anilino*cyclo*hexanecarboxylic acid* (II). This acid was pyrolysed, and the products isolated and identified, as for acid (I). The products were as follows (see Table 1 for yields): (i) *cyclo*Hex-1-enecarboxylic acid, b. p. 123—126°/7 mm., m. p. 29—31° [Found: equiv. (titration), 125. Calc. for $C_7H_{10}O_2$: equiv., 126], which gave a dibromo-derivative crystallising from benzene as plates, m. p. 144—145°. Betts *et al.* (*loc. cit.*) give m. p. 29—31° and 144° respectively. (ii) 1-Hydroxy*cyclo*hexanecarboxyanilide, crystallising from benzene as plates, m. p. 174—175° [Found: C, 71·3; H, 7·8; N, 6·5%; *M* (ebullioscopic in benzene), 214, 216. Calc. for $C_{13}H_{17}O_2N$: C, 71·2; H, 7·8; N, 6·4%; *M*, 219]. Bucherer and Barsch (*loc. cit.*) give m. p. 175°, and Passerini (*Gazzetta*, 1923, **53**, 410), m. p. 167°. Its identity was confirmed by hydrolysis (as above) to aniline hydrochloride and 1-hydroxy*cyclo*hexanecarboxylic acid, the latter crystallising from benzene as plates, m. p. and mixed m. p. 107—108° (Bucherer and Brandt, *J. prakt. Chem.*, 1934, **140**, 129, give m. p. 108°), and by comparison of the infrared spectra of synthetic and pyrolytic anilides. (iii) The lactone-lactam, 1-(1-*hydroxy*cyclo*hexanecarboxyanilido*)cyclo*hexanecarboxylic lactone*, crystallising from light petroleum as prisms, m. p. 157—158°, less readily soluble than compound (IX) in warm dilute alkali [Found: C, 73·7; H, 7·7; N, 4·5%; *M* (cryoscopic in benzene), 330, 331. $C_{20}H_{25}O_3N$ requires C, 73·4; H, 7·7; N, 4·3%; *M*, 327].

(c) 1-*Anilino*cyclo*heptanecarboxylic acid* (III). This acid was pyrolysed, and the products isolated and identified, as for acid (I). The products were as follows (see Table 1 for yields): (i) *cyclo*Hept-1-enecarboxylic acid, needles, m. p. 50—51°, from light petroleum [Found: C, 68·4; H, 8·9%; equiv. (titration), 140. Calc. for $C_8H_{12}O_2$: C, 68·5; H, 8·6%; equiv., 140]. Buchner and Jacobi (*Ber.*, 1898, **31**, 399) give m. p. 51—53°. (ii) 1-*Hydroxy*cyclo*heptanecarboxyanilide*, plates (from benzene), m. p. 171—172° (Found: C, 72·4; H, 8·1; N, 6·3. $C_{14}H_{19}O_2N$ requires C, 72·1; H, 8·2; N, 6·0%). Its identity was confirmed by hydrolysis (as above) to aniline hydrochloride and 1-hydroxy*cyclo*heptanecarboxylic acid, plates (from benzene), m. p. 78—79° (Buchner, *Ber.*, 1897, **30**, 1949, give m. p. 79—80°), and by mixed m. p. with synthetic anilide. (iii) The lactone-lactam 1-(1-*hydroxy*cyclo*heptanecarboxyanilido*)cyclo*heptanecarboxylic lactone*, prisms, m. p. 132—133° (from benzene–light petroleum), less readily soluble than compound (IX) in warm dilute alkali (Found: C, 74·2; H, 7·9; N, 4·3. $C_{22}H_{29}O_3N$ requires C, 74·3; H, 8·2; N, 3·9%).

Pyrolysis of 1-*Anilino*cyclo*hexanecarboxylic Acid* (II) *at* 500° (*Macro-method: Flow Reaction Vessel*).—The acid (89 g., 0·407 mole) was fed steadily in pellet form into the vessel during 3 hr. The gaseous pyrolysate (10·2 l. at N.T.P.) consisted of carbon monoxide (42·7, 44·0%), carbon dioxide (39·9, 39·9%), and hydrogen (17·4, 16·1%). The liquid pyrolysate (70·2 g.) yielded (i) (12·1 g.) b. p. 68—82°/760 mm., (ii) (0·9 g.) b. p. 45—86°/28 mm., (iii) (26·8 g.) b. p. 86—92°/28 mm., and (iv) a tarry residue. Fraction (i) was a mixture of *cyclo*hexene and benzene (*ca.* 2 : 1 molar), characterised by conversion into adipic acid and *m*-dinitrobenzene respectively and by infrared spectra. Fraction (iii) contained aniline (25·7 g.). Fractions (ii) and (iii) and residue (iv) contained no *cyclo*hexanone or *cyclo*hexylideneaniline (tested by 2 : 4-dinitrophenylhydrazine in dilute hydrochloric acid–ethanol); residue (iv), treated with benzene, gave no hydroxy-anilide. The yields were as in Table 3.

TABLE 3.

	CO	CO_2	H_2	C_6H_{10}	C_6H_6	NH_2Ph
Wt. (g.)	3·4	5·0	0·1	8·1	4·0	25·7
Mole	0·133	0·123	0·052	0·099	0·051	0·277
% of theory	33	30	6·4 *	24	12·5	68

* On assumption that 1 mole of acid (II) leads *via cyclo*hexene to 2 moles of hydrogen.

Prolonged Acidic Hydrolysis of 1-*Anilino*cyclo*pentanecarboxylic Acid* (I).—The acid (0·60 g.) was refluxed for 50 hr. with 4N-sulphuric acid (25 ml.); when made alkaline and extracted with ether, the hydrolysate yielded *N*-*cyclo*pentylaniline (XIII) (0·13 g.), identified as its acetate, m. p. and mixed m. p. 95—96°. Loevenich, Utsch, Moldrickx, and Schaefer, *Ber.*, 1929, **62**, 3094, give m. p. 96°.

Attempted Catalytic Rearrangement of 1-*Anilino*cyclo*hexanecarboxylic Acid* (II).—Concentrated phosphoric acid (6 ml.) was added to a solution of the anilino-acid (0·2 g.) in ether

(20 ml.); in a control experiment, the anilino-acid (0·18 g.) contained 1-hydroxy*cyclo*hexanecarboxyanilide (0·02 g.). After 15 days at room temperature, the former solution (homogeneous) yielded no hydroxy-anilide; the latter yielded 0·019 g. of the added hydroxy-anilide, m. p. and mixed m. p. 174—175°. Hence, there was no appreciable rearrangement of acid (II) in the first experiment.

*Thermal Stability of 1-Hydroxy*cyclo*hexanecarboxyanilide.*—The anilide, heated to 250° for 1 hr., remained unaltered in weight, m. p., and mixed m. p. (contrast pyrolysis at 540°: see Table 2).

Hydrolysis of Lactone-lactam (IX).—(a) *With sodium hydroxide.* The lactone-lactam dissolved readily in warm dilute sodium hydroxide; addition of dilute mineral acid then precipitated a sticky paste which gradually solidified. The solid product was regenerated lactone-lactam, m. p. and mixed m. p. 143—144° (95% recovery).

(b) *With sulphuric acid.* The lactone-lactam (2·8 g.) was refluxed (20 hr.) with 4N-sulphuric acid. Unchanged material (1·06 g.) was filtered off; the filtrate, brought to pH *ca.* 5 by dilute sodium hydroxide, afforded *1-carboxy*cyclo*pentyl 1-anilino*cyclo*pentanecarboxylate* (X), recrystallising from benzene as diamond-shaped prisms, m. p. 148—155° (decomp.) [Found: C, 68·5; H, 7·1; N, 4·5%; equiv. (titration), 316. $C_{18}H_{23}O_4N$ requires C, 68·1; H, 7·3; N, 4·4%; equiv., 317]. A trace (*ca.* 2 mg.) of 1-hydroxy*cyclo*pentanecarboxylic acid (XIV) was also formed (m. p. and mixed m. p. 103—104°). Compound (X) was readily soluble in dilute sodium hydroxide, soluble with difficulty in dilute sulphuric acid [less soluble than acid (I)], gave a light yellow oil on treatment with nitrous acid, and when heated for 5 min. at 250° evolved water and regenerated the original lactam-lactone, m. p. and mixed m. p. 143—144° (identity confirmed by infrared spectrum). In a further hydrolysis of the lactone-lactam (5·47 g.), the acid hydrolysate was made alkaline; ether-extraction then yielded N-*cyclo*pentylaniline (XIII) (0·15 g.), identified as its acetate, m. p. and mixed m. p. 95—96°.

Attempted Ring-opening of Lactone-lactam (IX) *with Aniline and Water.*—The lactone-lactam (1·08 g.) was heated for 1 hr. under reflux (bath, 250°) with aniline (0·98 g.) and water (0·3 g.) (approx. molar ratio of reagents, 1 : 3 : 5). The residue was dissolved in benzene (15 ml.) and extracted with hydrochloric acid to remove aniline; no hydroxy-anilide was obtained.

Attempted Combination of cyclo*Hex-1-enecarboxylic Acid with 1-Hydroxy*cyclo*hexanecarboxyanilide.*—The acid (1·23 g.) was heated for 1 hr. under reflux (bath, 260°) with the anilide (2·14 g.). The only detectable products were unchanged acid (0·96 g.), m. p. and mixed m. p. 29—31°, and unchanged anilide (1·86 g.), m. p. and mixed m. p. 174—175°.

New Infrared Data.—The following are the principal infrared absorption bands of the compounds studied.

Anilino-acid (I): 1715(s), 1615(ms), 1514(m), 1335(m), 1297, 1276 (doublet; m), 1210(m), 1193(w), 962(m) cm.$^{-1}$.

Anilino-acid (II): 1635(s), 1508(w), 1388(s), 1316(w), 1274(w) cm.$^{-1}$.

Anilino-acid (III): 1715(m), 1615, 1576 (doublet; s), 1520(ms), 1355(m), 1340(ms), 1296(m), 1258(m), 1205(m) cm.$^{-1}$.

Hydroxy-anilide from (I): *ca.* 3430(s), 1669(s), 1622(s), 1570(s), 1349(m), 1185(m), 1048(m), 1018(m) cm.$^{-1}$.

Hydroxy-anilide from (II): *ca.* 3450(s), 1670(s), 1625(ms), 1570(s), 1175(ms), 1155(m), 1048(w), 996(ms) cm.$^{-1}$.

Hydroxy-anilide from (III): *ca.* 3490(ms), 1686(s), 1620(m), 1570(ms), 1465(s), 1070(m), 1050(w) cm.$^{-1}$.

Lactone-lactam from (I): 1760(s), 1680(s), 1512(m), 1405(s), 1342(s), 1282(s), 1244(ms), 1175(s), 1126(m), 1028(m) cm.$^{-1}$.

Lactone-lactam from (II): 1750(ms), 1685(ms), 1354(s), 1318(ms), 1271(m), 1231(s), 1131(ms), 1010(m) cm.$^{-1}$.

Lactone-lactam from (III): 1750(s), 1680(s), 1416(m), 1309(ms), 1261, 1242 (doublet; m), 1184(m), 1050(m) cm.$^{-1}$.

Anilino-acid (X): 1740(s), 1630(m), 1526(m), 1340(s), 1282(m), 1190(ms) cm.$^{-1}$.

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