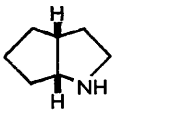
215. *Synthetic and Stereochemical Investigations of Reduced Cyclic Bases. Part VII.* The Synthesis of* cis- *and* trans-2 : 3-cyclo-*Pentanopyrrolidine.*

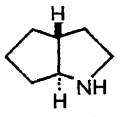
By H. Booth, F. E. King, K. G. Mason, J. Parrick, and R. L. St. D. Whitehead.

Both *cis*- and *trans*-2 : 3-*cyclo*pentanopyrrolidine have been synthesised [1] and the identity of the base hitherto tentatively regarded as the *trans*-isomer [2] has been confirmed.

cis- and *trans*-2 : 3-*cyclo*-Pentanopyrrolidine (I and II respectively) are of stereochemical interest in view of the strain in the *trans*-fused five-membered rings. The only recorded preparative work in the *cyclo*pentanopyrrolidine series was by Prelog and Szpilfogel,[2] who reduced the oxime (III; R = Ph) with sodium and ethanol or catalytically with platinum oxide in ethanol to an amine (IV; R = Ph) to which they assigned the *trans*-configuration. Attempts to prepare its stereoisomer by reduction of the oxime in acid solution were unsuccessful. When the amine (IV; R = Ph) was heated with hydrobromic acid, a bromo-amine hydrobromide (V) was produced, and cyclisation with alkali then yielded the presumed *trans*-2 : 3-*cyclo*-pentanopyrrolidine (II).



(I)



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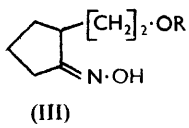

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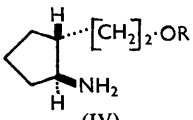

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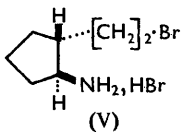

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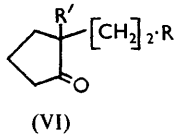


(VI)

cis- and *trans*-2 : 3-*cyclo*Pentanopyrrolidine have now been synthesised as follows.

First, 2-iodoethyl acetate was condensed with the sodium derivative of ethyl 2-oxo-*cyclo*pentanecarboxylate in benzene. The resulting keto-ester (VI; R = OAc, R′ = CO_2Et) was hydrolysed smoothly with dilute sulphuric acid to the hydroxy-ketone (VI; R = OH, R′ = H). When concentrated hydrochloric or hydrobromic acid was used as the hydrolytic agent, the product was the chloro- or bromo-ketone (VI; R = Cl or Br, R′ = H). The hydroxy-ketone was converted into the oxime (III; R = H) which was reduced with sodium in boiling ethanol to the crystalline *trans*-2-2′-hydroxyethyl*cyclo*-pentylamine (IV; R = H), the configuration appearing to follow from its production under alkaline conditions. Treatment of the base with hydrobromic acid afforded the bromo-amine hydrobromide (V), which was cyclised with aqueous alkali to a 2 : 3-*cyclo*-pentanopyrrolidine identical with that prepared by Prelog and Szpilfogel.[2]

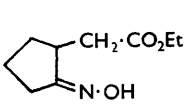
Attempts to prepare the geometrical isomer of (IV; R = H) by reduction of the oxime (III; R = H) in acetic acid with sodium amalgam, or in acetic anhydride with zinc dust, were unsuccessful. Application of the Leuckardt reaction, which usually gives a preponderance of the *cis*-isomer, to the ketone (VI; R = OH, R′ = H) resulted in a mixture containing at least 70% of the amine (IV) already prepared. However, when the oxime-ester (VII) was hydrogenated over Raney nickel the product consisted of ethyl *trans*-2-amino*cyclo*pentylacetate (VIII), *cis*-2 : 3-*cyclo*pentanopyrrolid-5-one (IX), and the secondary amine (X), which were separated by distillation.

* Part VI, Booth and King, *J.*, 1958, 2688.

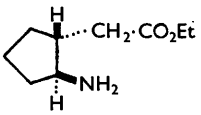
[1] Cf. Booth, King, Parrick, and Whitehead, *Chem. and Ind.*, 1956, 466.

[2] Prelog and Szpilfogel, *Helv. Chim. Acta*, 1945, **28**, 178.

The *trans*-configuration of the ester (VIII) was evident from its resistance to cyclisation, it being recovered unchanged after 24 hours' refluxing in benzene and polymerised when heated for 2 hr. at 140°. This behaviour contrasts with that of methyl *trans*-2-amino*cyclo*hexylacetate, from which the corresponding lactam, *trans*-octahydro-2-oxoindole [3] is obtained without difficulty.



(VII)



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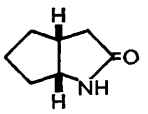

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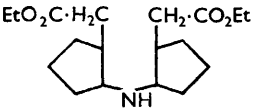

(X)

Hydrolysis of the amino-ester (VIII) and of the lactam (IX) with dilute hydrochloric acid gave two different amino-acids, and accordingly the lactam must have the *cis*-configuration. *cis*-2 : 3-*cyclo*Pentanopyrrolidine was then prepared by reducing the lactam (IX) with lithium aluminium hydride. When the *trans*-amino-ester (VIII) was treated with lithium aluminium hydride, an amino-alcohol identical with (IV; R = H) was isolated, thus confirming the configuration attributed to this amino-alcohol and of the *cyclo*pentanopyrrolidine prepared by ring-closure of the bromo-amine hydrobromide (V).

Measurements of the principal physical constants of the two *cyclo*pentanopyrrolidines show that the *trans*-base has the higher b. p. and refractive index, but the lower density. The qualitative effect of stereochemical differences on these constants, formerly stated in the Auwers–Skita rule, is now more accurately expressed by Allinger's generalisation [4] that the higher values are attributable to the less stable configuration. Since the *trans*-*cyclo*pentanopyrrolidine is the less stable owing to the greater strain inherent in the *trans*-configuration, the rule is confirmed in respect of b. p. and refractive index, but not of density. In the analogous 3-oxa- and 3-thia-*bicyclo*[3 : 3 : 0]octane series also it is the *trans*-isomers which have the higher b. p.s and refractive indexes.[5,6] The densities of the oxa*bicyclo*octanes have not been recorded, and those of the *cis*- and *trans*-thia*bicyclo*-octanes were measured at different temperatures, but the published figures (*cis*, d^{20} 1·0427, d^{25} 1·0386: *trans*, d^{30} 1·0294) suggest that under comparable conditions the value for the *cis*-thia*bicyclo*octane, as with the *cyclo*pentanopyrrolidines, may again be the greater.

Preliminary work was carried out on an alternative synthesis of *cis*-2 : 3-*cyclo*pentanopyrrolidine. It used 2-2′-nitroethyl*cyclo*pentanone which was hydrogenated in methanol over Raney nickel. The filtered solution, which presumably contained a *cyclo*pentenopyrrolidine (cf. King, Bovey, Mason, and Whitehead [7]), was treated with sodium and boiling ethanol: a poor yield of *cis*-2 : 3-*cyclo*pentanopyrrolidine was obtained.

Experimental

Ethyl 1-2′-*acetoxyethyl*-2-*oxo*cyclo*pentanecarboxylate* (VI; R = OAc, R′ = CO_2Et).—Ethyl 2-oxo*cyclo*pentanecarboxylate (150 g.) was added to a suspension of powdered sodium (23 g.) in benzene (1 l.), and the mixture was heated under reflux for 2 hr. The cooled mixture was treated with freshly distilled 2-iodoethyl acetate (230 g.), and refluxing was continued for 4 days. The resulting solution was poured into 2% hydrochloric acid, and the benzene layer was separated, dried, and evaporated. Distillation yielded the *keto-ester* (145 g., 62%), b. p. 175—177°/16 mm. (Found: C, 60·1; H, 7·4. $C_{12}H_{18}O_5$ requires C, 59·7; H, 7·4%). The *semicarbazone* had m. p. 110° (from light petroleum–ethyl acetate) (Found: C, 52·15; H, 6·9; N, 14·2. $C_{13}H_{21}O_5N_3$ requires C, 52·15; H, 7·0; N, 14·0%).

2-2′-*Bromoethyl*cyclo*pentanone*.—The foregoing keto-ester (29·2 g.) was heated under reflux

[3] Booth and King, *J.*, 1958, 2688.
[4] Allinger, *Experientia*, 1954, **10**, 328.
[5] Owen and Peto, *J.*, 1955, 2383.
[6] Birch, Dean, Hunter, and Whitehead, *J. Org. Chem.*, 1955, **20**, 1178.
[7] King, Bovey, Mason, and Whitehead, *J.*, 1953, 250.

for 5 hr. with 30% hydrobromic acid (120 c.c.). The mixture was neutralised with sodium carbonate solution and extracted with ether. Evaporation of the dried ethereal extracts yielded an oil which was distilled. After a small forerun (1·2 g.), b. p. 56°/14 mm., the bromo-ketone (9·1 g., 40%) distilled at 116°/14 mm. The *semicarbazone* crystallised from ethanol–acetic acid in needles, m. p. 158° (decomp.) (Found: C, 38·4; H, 5·7; N, 16·8. $C_8H_{14}ON_3Br$ requires C, 38·7; H, 5·7; N, 16·9%). The 2 : 4-*dinitrophenylhydrazone* crystallised from acetic acid in yellow prisms, m. p. 156° (Found: C, 42·2; H, 4·1; N, 15·0. $C_{13}H_{15}O_4N_4Br$ requires C, 42·1; H, 4·0; N, 15·1%).

2-2′-*Chloroethyl*cyclo*pentanone*.—Hydrolysis of the keto-ester (6 g.) with (32%) hydrochloric acid (25 c.c.) for 7 hr. and working up as described above for the bromo-compound gave the chloro-ketone (1·8 g., 50%), b. p. 98—100°/10 mm. This yielded a *semicarbazone*, needles (from ethanol), m. p. 180° (decomp.) (Found: C, 47·6; H, 7·2; N, 20·4; Cl, 17·6. $C_8H_{14}ON_3Cl$ requires C, 47·3; H, 6·9; N, 20·6; Cl, 17·4%), and a 2 : 4-*dinitrophenylhydrazone*, plates (from acetic acid), m. p. 158° (Found: C, 47·7; H, 5·0; N, 17·5. $C_{13}H_{15}O_4N_4Cl$ requires C, 47·8; H, 4·6; N, 17·1%).

2-2′-*Hydroxyethyl*cyclo*pentanone*.—Ethyl 1-2′-acetoxyethyl-2-oxo*cyclo*pentanecarboxylate (63·5 g.) was treated with 10% sulphuric acid (250 c.c.), and the mixture was refluxed for 1½ hr. The cooled solution was neutralised with concentrated aqueous ammonia and evaporated under reduced pressure until solid separated. Extraction with ether then afforded the hydroxy-ketone (20 g., 59%), b. p. 127—130°/14 mm. The *semicarbazone* crystallised from ethyl acetate in needles, m. p. 157° (Found: C, 52·0; H, 8·0; N, 22·4. $C_8H_{15}O_2N_3$ requires C, 51·9; H, 8·1; N, 22·7%), and the 2 : 4-*dinitrophenylhydrazone* from ethanol in orange needles, m. p. 174—176° (Found: C, 50·6; H, 5·5; N, 18·2. $C_{13}H_{16}O_5N_4$ requires C, 50·6; H, 5·2; N, 18·2%).

2-2′-*Acetoxyethyl*cyclo*pentanone*.—The hydroxy-ketone (6 g.) was heated under reflux with acetic anhydride (30 c.c.) and fused sodium acetate (8 g.). After the usual working-up, the acetoxy-ketone (6 g., 75%) was obtained as an oil, b. p. 128°/15 mm. [*semicarbazone*, needles (from ethanol), m. p. 151° (Found: C, 53·1; H, 7·4; N, 18·2. $C_{10}H_{17}O_3N_3$ requires C, 53·1; H, 7·5; N, 18·4%)]. The acetoxy-ketone with 2 : 4-dinitrophenylhydrazine sulphate in methanol (" Brady's reagent ") gave the derivative of the hydroxy-ketone; this had m. p. and mixed m. p. 175° (Found: 17·7. Calc. for $C_{13}H_{16}O_5N_4$: N, 18·2%).

2-2′-*Hydroxyethyl*cyclo*pentanone Oxime*.—The hydroxy-ketone (12·8 g.) was dissolved in moist ether (50 c.c.), and an intimate mixture of hydroxylamine hydrochloride (14 g.) and sodium hydrogen carbonate (20 g.) was added. After the mixture had been warmed on the water-bath for 3 hr., the ether was separated, dried, and evaporated. Distillation of the residue afforded the *oxime* (12·6 g., 88%), b. p. 183—185°/20 mm. Crystallisation from ethyl acetate gave octahedra, m. p. 84° (Found: C, 59·1; H, 9·0; N, 10·1. $C_7H_{13}O_2N$ requires C, 58·75; H, 9·1; N, 9·8%).

trans-2-2′-*Hydroxyethyl*cyclo*pentylamine*.—The foregoing oxime (6·5 g.) was dissolved in hot dry ethanol (140 c.c.) and treated with sodium (12 g.) added in portions during 30 min. The mixture was refluxed for 30 min., cooled, and acidified with 15% hydrochloric acid. After removal of ethanol under suction, the residual acid solution was washed with ether and basified, the liberated amine being recovered by ether-extraction. trans-2-2′-*Hydroxyethyl*cyclo*pentyl-amine* (3·4 g., 58%) distilled at 128—130°/13 mm. Crystallisation from light petroleum (b. p. 40—60°) gave prisms, m. p. 73—75° (Found: C, 65·2; H, 11·5; N, 10·7. $C_7H_{15}ON$ requires C, 65·1; H, 11·6; N, 10·9%). The *dibenzoyl derivative* (Schotten–Baumann) crystallised from light petroleum (b. p. 60—80°) in feathery needles, m. p. 109° (Found: C, 74·6; H, 6·7; N, 4·3. $C_{21}H_{23}O_3N$ requires C, 74·8; H, 6·8; N, 4·2%), and *picrolonate* from ethanol in orange prisms, m. p. 203—204° (Found: C, 51·8; H, 6·2. $C_{17}H_{23}O_6N_5$ requires C, 51·9; H, 5·9%).

trans-2-2′-*Bromoethyl*cyclo*pentylamine Hydrobromide*.—The foregoing hydroxy-amine (17 g.) was heated under reflux with 48% hydrobromic acid (800 c.c.) for 5 hr. The solution was evaporated to dryness under reduced pressure and the residue crystallised from ethyl acetate. The *bromo-amine hydrobromide* (20 g., 56%) was thus obtained as colourless plates, m. p. 148—149° (Found: C, 31·0; H, 5·5. Calc. for $C_7H_{15}NBr_2$: C, 30·8; H, 5·5%) (Prelog and Szpilfogel [2] record m. p. 140·5°). The *bromo-amine picrate*, prepared from the hydrobromide and aqueous picric acid, crystallised from water in yellow needles, m. p. 155° (Found: C, 36·8; H, 3·8. $C_{13}H_{17}O_7N_4Br$ requires C, 37·1; H, 4·0%).

trans-2 : 3-cyclo*Pentanopyrrolidine*.—A solution of the *trans*-bromo-amine hydrobromide (3·1 g.) in water (100 c.c.) was added during 5 hr. to a stirred solution of potassium hydroxide

(11 g.) in water (150 c.c.). Stirring was continued for a further 1 hr. and the mixture then extracted with ether. The ethereal extracts were shaken with dilute hydrochloric acid and the base was recovered from the acid extracts in the usual way. *trans*-2 : 3-*cyclo*Pentanopyrrolidine (0·75 g., 60%) was thus obtained as an oil, b. p. 173—176° (bath-temp.)/756 mm. A redistilled sample had b. p. (Siwoloboff) 167—168°/764 mm., n_D^{18} 1·4845, d^{18} 0·930, $[M]_R$ 34·1 (Calc. 33·7) (Prelog and Szpilfogel record b. p. 151—155°/731 mm., n_D^{21} 1·4867, d^{21} 0·9478). The base afforded the following derivatives: picrate, yellow rods (from water), m. p. 87—90° (varies with rate of heating), undepressed when mixed with a specimen, m. p. 87—90°, kindly provided by Professor Prelog (Found: C, 45·6; H, 4·4; N, 16·8. Calc. for $C_{13}H_{16}O_7N_4$: C, 45·9; H, 4·7; N, 16·5%); orange-yellow picrolonate (from ethanol), m. p. 239—240° (Found: N, 18·5. Calc. for $C_{17}H_{21}O_5N_5$: N, 18·7%); 3 : 5-*dinitrobenzoate* needles (from ethyl acetate), m. p. 157° (Found: C, 52·1; H, 5·1; N, 13·3. $C_{14}H_{17}O_6N_3$ requires C, 52·0; H, 5·3; N, 13·0%) (Prelog and Szpilfogel record the m. p. of picrate and picrolonate as 103—104° and 239·5° respectively).

trans-1-*Methyl*-2 : 3-cyclo*pentanopyrrolidine*.—*trans*-2 : 3-*cyclo*Pentanopyrrolidine (3·7 g.) was refluxed for 4 hr. with 40% aqueous formaldehyde (5 c.c.) and 90% formic acid (9 c.c.). Extraction of the basified solution with ether gave the tertiary amine (2·7 g., 59%), b. p. 51°/14 mm. The *picrate* crystallised from ethanol as yellow plates, m. p. 197—198° (Found: C, 47·8; H, 5·3; N, 15·7. $C_{14}H_{18}O_7N_4$ requires C, 47·5; H, 5·1; N, 15·8%); the *methiodide* crystallised from acetone–ethyl acetate in needles, m. p. 243° (decomp.) (Found: C, 40·8; H, 6·5; N, 5·1; I, 47·0. $C_9H_{18}NI$ requires C, 40·5; H, 6·7; N, 5·2; I, 47·5%).

Leuckardt Reaction with 2-2′-*Hydroxyethyl*cyclo*pentanone* (cf. Ingersoll [8]).—The hydroxy-ketone (13·9 g.) was added slowly to ammonium formate (35 g.), previously heated to 165° in an oil-bath. The temperature was then raised gradually to 180° and was kept there for 4 hr., an aqueous distillate being removed meanwhile. The product was then heated under reflux with aqueous sodium hydroxide (50 g. in 280 c.c.) for 3 hr. to hydrolyse the amides produced. The oily layer produced was worked-up by ether-extraction. Distillation gave the mixed amines (5·8 g., 41%), b. p. 135°/18 mm. The mixture partly solidified and the solid was removed. Crystallisation from light petroleum (b. p. 40—60°) gave colourless prisms of *trans*-2-2′-hydroxyethyl*cyclo*pentylamine (4·2 g.), m. p. and mixed m. p. 73—75°. The filtrate probably contained a mixture of *cis*- and *trans*-hydroxy-amines but separation of the *cis*-amine was not attempted.

2-*Dimethylaminomethyl*cyclo*pentanone* (cf. Mannich and Schaller [9]).—A mixture of *cyclo*pentanone (33·6 g.), dimethylamine hydrochloride (16·2 g.), methanol (10 c.c.), and 40% aqueous formaldehyde (15 g.) was heated under reflux on a steam-bath for 30 min. The cooled mixture was treated with water (50 c.c.) and extracted with ether to remove *cyclo*pentanone. The aqueous residue was cooled thoroughly in ice, basified, and extracted with ether. After removal of ether from the dried extracts, distillation afforded the Mannich base (8·6 g., 31%), b. p. 89—94°/18 mm. (Mannich and Schaller record b. p. 88—90°/15 mm. and do not quote a yield.)

2-2′-*Nitroethyl*cyclo*pentanone*.—A mixture of 2-dimethylaminomethyl*cyclo*pentanone (18·3 g.) and nitromethane (12·4 g.) was heated on a steam-bath and sodium methoxide (3·65 g.) in methanol (36·5 g.) was added gradually, with stirring. The semi-solid mass was then removed from the steam-bath, and methanol (24 c.c.) was added. The solution was set aside for an hour and then poured slowly into an ice-cold solution of acetic acid (16 g.) in water (150 c.c.). Extraction with ether gave the nitro-ketone (3·4 g., 17%), b. p. 135—138°/3 mm. The *semi-carbazone* crystallised from ethanol in colourless plates, m. p. 203° (decomp.) (Found: C, 45·1; H, 6·6; N, 26·0. $C_8H_{14}O_3N_4$ requires C, 44·9; H, 6·55; N, 26·2%).

Ethyl 2-*Hydroxyimino*cyclo*pentylacetate*.—A mixture of hydroxylamine hydrochloride (54 g.) and sodium hydrogen carbonate (61·5 g.) was added to a solution of ethyl 2-oxo*cyclo*pentyl-acetate (Linstead and Meade [10]) (90 g.) in moist ether (250 c.c.), and the mixture was heated under reflux for 12 hr. The ethereal solution was filtered, dried (Na_2SO_4), and evaporated. Distillation of the residue yielded the *hydroxyimino-ester* (90 g., 92%), b. p. 130—132°/0·5 mm., n_D^{21} 1·4813 (Found: C, 58·2; H, 8·2; N, 7·8. $C_9H_{15}O_3N$ requires C, 58·3; H, 8·2; N, 7·6%).

Hydrogenation of Ethyl 2-*Hydroxyimino*cyclo*pentylacetate over Raney Nickel*.—The hydroxy-imino-ester (30 g.), in dry ethanol (30 c.c.), was reduced over Raney nickel with hydrogen at an initial pressure of 70 atm. and at room temperature. After 4 hr., the mixture was filtered and

[8] Ingersoll, *J. Amer. Chem. Soc.*, 1936, **58**, 1808.
[9] Mannich and Schaller, *Arch. Pharm.*, 1938, **276**, 575.
[10] Linstead and Meade, *J.*, 1934, 935.

ethanol was removed by evaporation. The residue was separated by distillation into three fractions:

(i) *Ethyl* trans-2-*amino*cyclo*pentylacetate* (4·5 g.), b. p. 60—65°/0·5 mm., n_D^{19} 1·4616 (Found: C, 63·4; H, 9·8. $C_9H_{17}O_2N$ requires C, 63·2; H, 10·0%). The *benzoyl derivative* (Schotten–Baumann in sodium hydrogen carbonate solution) crystallised from benzene–light petroleum (b. p. 40—60°) in needles, m. p. 91—92° (Found: C, 70·0; H, 7·5. $C_{16}H_{21}O_3N$ requires C, 69·8; H, 7·7%). Reduction of the amino-ester (3 g.) in ether (70 c.c.) with lithium aluminium hydride (1 g.) gave *trans*-2-2′-hydroxyethyl*cyclo*pentylamine (1·2 g., 57%), m. p. and mixed m. p. 73—75° (picrolonate, m. p. and mixed m. p. 203—204°).

(ii) An oil (4·2 g.), b. p. 102—108°/0·5 mm., which crystallised on standing. Recrystallisation from light petroleum (b. p. 40—60°) gave cis-2 : 3-cyclo*pentanopyrrolid*-5-*one* as hygroscopic prisms, m. p. 51—53° (evacuated tube) (Found: C, 66·9; H, 8·9. $C_7H_{11}ON$ requires C, 67·2; H, 8·8%).

(iii) A basic oil (10·3 g.), b. p. 142—144°/0·5 mm. This was probably *di*-(2-*ethoxycarbonylmethyl*cyclo*pentyl*)*amine* (Found: C, 66·7; H, 9·7; N, 4·3. $C_{18}H_{31}O_4N$ requires C, 66·4; H, 9·6; N, 4·3%).

trans-2-*Amino*cyclo*pentylacetic Acid Hydrochloride*. Ethyl *trans*-2-amino*cyclo*pentylacetate (0·5 g.) was refluxed for 15 hr. with 7% hydrochloric acid (15 c.c.). The solution was evaporated to dryness under reduced pressure and the residue was crystallised from ethanol–ether. The *acid hydrochloride* (0·4 g., 76%) was thus obtained in prisms, m. p. 158—160° (Found: C, 47·0; H, 7·8. $C_7H_{14}O_2NCl$ requires C, 46·8; H, 7·8%).

cis-2-*Amino*cyclo*pentylacetic Acid Hydrochloride*.—*cis*-2 : 3-*cyclo*Pentanopyrrolid-5-one (0·5 g.) was refluxed for 3 hr. with 7% hydrochloric acid (10 c.c.). Hydrochloric acid (2 c.c.; 30%) was then added and the mixture was refluxed for a further 2 hr., and then evaporated to dryness. Crystallisation of the residue from ethanol–ether gave colourless prisms (0·6 g., 84%) of the cis-*acid hydrochloride*, m. p. 173—175° (decomp.) (Found: C, 46·9; H, 7·6%).

cis-2 : 3-cyclo*Pentanopyrrolidine*.—(*a*) *cis*-2 : 3-*cyclo*Pentanopyrrolid-5-one (2·6 g.) in ether (40 c.c.) was added dropwise to a solution of lithium aluminium hydride (1·5 g.) in ether (40 c.c.). After being heated under reflux for 2 hr., the mixture was cooled and diluted with moist ether to decompose excess of lithium aluminium hydride. The ethereal layer was separated and shaken with dilute hydrochloric acid. The acid solution was made alkaline and the base was extracted into ether. cis-2 : 3-cyclo*Pentanopyrrolidine* (1·4 g., 61%) was thus obtained as a colourless oil, b. p. 160—165° (bath temp.)/764 mm. A twice redistilled sample had b. p. (Siwoloboff) 161°/764 mm., n_D^{18} 1·4795, d_4^{18} 0·944, $[M]_R$ 33·4 (Calc., 33·7), and afforded the following derivatives: *picrate*, m. p. 111° (from benzene) (Found: C, 45·8; H, 4·8%); *picrolonate*, prisms (from ethanol), m. p. 204—205° (Found: C, 54·2; H, 5·8%); 3 : 5-*dinitrobenzoate*, plates, m. p. 201—203° (from ethyl acetate) (Found: C, 52·3; H, 5·4; N, 13·2%).

(*b*) 2-2′-Nitroethyl*cyclo*pentanone (2 g.) in methanol (65 c.c.) was hydrogenated over Raney nickel at room temperature and pressure. An absorption of hydrogen equivalent to that required for reduction of the nitro-group alone took place in 1—2 hr. The filtered solution was diluted with ethanol (65 c.c.), heated to boiling, and treated with sodium (11 g.), in portions during 30 min. The cooled solution was acidified and evaporated under reduced pressure to remove ethanol. Basification and ether extraction afforded *cis*-2 : 3-*cyclo*pentanopyrrolidine (0·2 g., 14%), b. p. 55—60°/17 mm., identified as the 3 : 5-dinitrobenzoate, m. p. and mixed m. p. 203° (Found: C, 52·4; H, 5·2; N, 13·0%).

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[*Received, November 12th*, 1958.]