

*Intramolecular Interaction between γ -Tertiary Amino- and Cyano-
groups.*

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[Reprint Order No. 6162.]

γ -Benzylmethylamino- and γ -dibenzylamino- $\alpha\alpha$ -diphenylalkyl cyanides readily lose one benzyl group (as benzyl chloride) in hot hydrochloric acid, yielding 2-iminopyrrolidines. Analogous cyanides having one or two α -hydrogen atoms are hydrolysed normally under similar conditions, with only slight debenzylation. γ -*tert.*-Benzylamino-acid hydrochlorides are readily cyclised in hot acetic anhydride to pyrrolid-2-ones, benzyl chloride and acetate being formed simultaneously. Benzylamine and 3-chloropropyl cyanide react rapidly, to give ammonia and 1-benzyl-2-benzyliminopyrrolidine. Alkaline hydrolysis of the latter affords *N*-benzyl- γ -benzylaminobutyramide, which is synthesised by an independent method.

2-IMINOPYRROLIDINES are readily obtained, along with benzyl chloride, by the action of boiling aqueous hydrochloric acid on γ -benzylmethylamino- $\alpha\alpha$ -diphenylalkyl cyanides, *e.g.*, (I; R = R' = Ph, R'' = Me) (Wilson, *J.*, 1952, 3524). This reaction probably involves an initial direct intramolecular interaction between the *tert.*-amino- and the cyano-group: $\geq N \curvearrowright C \equiv N \curvearrowright H^+$ (cf. Wilson, *Chem. and Ind.*, 1955, 200).

It has now been found that 3-dibenzylamino-1:1-diphenylpropyl cyanide (I; R = R' = Ph, R'' = CH₂Ph) in boiling hydrochloric acid, or more quickly in acetic-hydrochloric acid, affords benzyl chloride and 1-benzyl-2-imino-3:3-diphenylpyrrolidine (II; R = R' = Ph, R'' = CH₂Ph), the second benzyl group being stable. The structure of the iminopyrrolidine was confirmed by the formation of a basic *N*-acetyl derivative, and of a rather insoluble nitrate (cf. amidines; Walker, *J.*, 1949, 2000); nitrous acid also converted it into 1-benzyl-3:3-diphenylpyrrolid-2-one (III; R = R' = Ph, R'' = CH₂Ph).

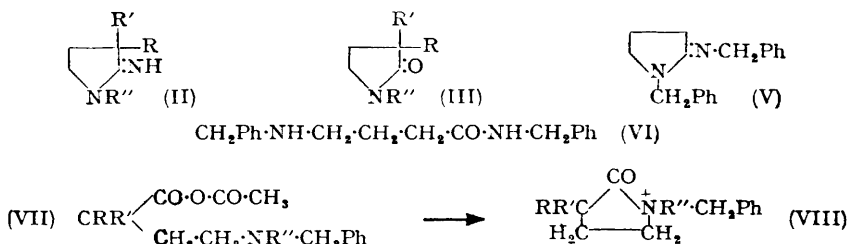


3-Benzylmethylamino- and 3-dibenzylamino-1-phenylpropyl cyanide were obtained by aminoalkylating benzyl cyanide. These basic cyanides did not afford much benzyl chloride in aqueous hydrochloric acid, being mainly hydrolysed to the corresponding γ -dialkylamino- α -phenylbutyric acids (IV; R = Ph). The dibenzylamino-cyanide gave also 1-benzyl-2-imino-3-phenylpyrrolidine (II; R = Ph, R' = H, R'' = CH₂Ph) as the hydrochloride (34%), which was identified by conversion into the corresponding pyrrolidone. In acetic-hydrochloric acid, more benzyl chloride was formed (16 and 27%) respectively, and the yields of *tert.*-amino-acids fell. With one exception, mentioned above, 2-iminopyrrolidines or their transformation products were not isolated from these reactions, or from melts of the benzylmethylamino-cyanide toluene-*p*-sulphonate. The γ -*tert.*-amino- α -phenyl acid hydrochlorides were esterified very rapidly in alcohols containing free hydrogen chloride; in hot acetic anhydride (also when heated alone at 225°) they were cyclised to the two pyrrolidones (III; R = Ph, R' = H, R'' = Me, and CH₂Ph). The second pyrrolidone was made also from α -phenyl- γ -butyrolactone and benzylamine.

Benzylmethylamine or dibenzylamine with 3-chloropropyl cyanide readily afforded the 3-dialkylaminopropyl cyanides (I; R = R' = H, R'' = Me and CH₂Ph). These cyanides were hydrolysed rapidly in hot hydrochloric acid, yielding the *tert.*-amino-acids (IV; R = H). In acetic-hydrochloric acid, 1-3% of benzyl chloride was formed in each case; in aqueous media, there was no trace of benzyl chloride. The benzylmethylamino- and dibenzylamino-acid (IV; R = H) were synthesised independently from diethyl malonate and the 2-dialkylaminoethyl chlorides. These amino-acid hydrochlorides were readily converted by hot acetic anhydride into 1-methyl- and 1-benzyl-pyrrolid-2-ones (III; R = R' = H, R'' = Me and CH₂Ph), benzyl chloride, and acetate. The infrared absorption of 1-benzylpyrrolid-2-one was identical with that of an authentic sample made from

γ -butyrolactone and benzylamine. These two pyrrolidones formed water-soluble salts with hydrochloric acid; so did *N*-benzyl-*N*-methylacetamide, which has a similar structure.

Ammonia was unexpectedly and rapidly evolved on treating benzylamine with 3-chloropropyl cyanide in alcohols, and 1-benzyl-2-benzyliminopyrrolidine (V) was obtained. This reaction could not be stopped at the evident intermediate stage (cf. the similar reaction described by King, Latham, and Partridge, *J.*, 1952, 4271). The pyrrolidine was stable to nitrous acid, and was not hydrolysed by acid. However, in hot alkali ring-scission occurred, and *N*-benzyl- γ -benzylaminobutyramide (VI) (56%) and a little benzylamine (22%) were formed. The structure of the amide follows from its synthesis from *N*-benzyl- γ -chlorobutyramide and benzylamine. Alkaline hydrolysis of the pyrrolidine evidently occurs by rupture of the $>N-C\leftarrow$ bond; the ring fission on hydrolysis of 2-alkyl-4:5-dihydroglyoxalines (cf., e.g., Aspinall, *J. Org. Chem.*, 1941, 6, 895) is probably similar.



Discussion.—The experimental results indicate that the debenzoylation by hydrochloric acid competes with ordinary hydrolysis of the cyano-group. The effect of acetic acid in promoting debenzoylation may be due to the lowered dielectric constant of the media, which would assist an intramolecular interaction. It is well known that $\alpha\alpha$ -diphenylalkyl cyanides resist hydrolysis, probably because of steric hindrance, and in this series, debenzoylation and iminopyrrolidine formation are virtually complete. The other basic cyanides studied have a single α -phenyl substituent, or none; they are mainly hydrolysed by hydrochloric acid to the *tert.*-amino-acids, although under favourable conditions (e.g., in acetic acid) a little benzyl chloride is also formed. The probable mechanism by which a cyano-group activates a suitably placed benzyl-nitrogen bond (Wilson, *loc. cit.*) suggests that carbonyl and carboxyl groups would not have the same effect. In accordance with this, 4-dibenzylaminopentan-2-one and γ -*tert.*-benzylamino-acids are stable in boiling hydrochloric acid; benzyltriethylammonium chloride is also stable under these conditions.

During the present work, several γ -*tert.*-benzylamino-acid hydrochlorides were cyclised to pyrrolidones by hot acetic anhydride. This debenzoylation (benzyl chloride and acetate are formed) possibly proceeds *via* a mixed anhydride (VII), and the ion (VIII), which should decompose into a pyrrolidone and a benzyl cation (cf. *J.*, 1952, 3526).

EXPERIMENTAL

3-Dibenzylamino-1:1-diphenylpropyl Cyanide.—The hydrochloride (m. p. 188°; 53% yield) and the base (m. p. 60—61°) were made following Dupré, Elks, Hems, Speyer, and Evans (*J.*, 1949, 504). The intermediate 2-dibenzylaminoethyl chloride formed a *picrate*, m. p. 123° (Found: N, 11.2. $C_{16}H_{18}NCl_2 \cdot C_6H_5O_7N_3$ requires N, 11.45%).

Debenzoylation of 3-Dibenzylamino-1:1-diphenylpropyl Cyanide.—(a) The hydrochloride (3 g.) and concentrated hydrochloric acid (40 c.c.) were refluxed for 48 hr., more acid (50 c.c.) being added during this period. The hydrochloride slowly dissolved, and a volatile oil separated. Steam-distillation gave benzyl chloride (0.4 g., 48%; characterised as *S*-benzylthiuronium picrate). The residual solution was concentrated, and concentrated hydrochloric acid added to precipitate crystals (1.2 g.; m. p. 273°). Recrystallisation from 15% hydrochloric acid gave 1-benzyl-2-imino-3:3-diphenylpyrrolidine hydrochloride (1.1 g., 47%) as needles, m. p. 292—293° (Found: C, 76.35; H, 6.25. $C_{23}H_{22}N_2 \cdot HCl$ requires C, 76.15; H, 6.4%).

(b) A mixture of glacial acetic acid (30 c.c.), concentrated hydrochloric acid (50 c.c.), and

the dibenzylamino-compound hydrochloride (3 g.) was refluxed for 7 hr., evaporated to small bulk, and treated with 15% hydrochloric acid (100 c.c.), yielding the iminopyrrolidine hydrochloride (2.0 g., 84%), m. p. 292—293°. This with aqueous potassium nitrate gave the *iminopyrrolidine nitrate*, m. p. 221—222° (Found: N, 10.65. $C_{23}H_{22}N_2 \cdot HNO_3$ requires N, 10.8%), only slightly soluble in cold water. The nitrate was also obtained from the iminopyrrolidine hydrochloride, aqueous acetic acid, sodium nitrite, and hydrochloric acid at 60°. However, boiling the hydrochloride for 2 min. with sodium nitrite in aqueous acetic acid gave 1-benzyl-3 : 3-diphenylpyrrolid-2-one, m. p. 93—94° (from aqueous methanol) (Found: N, 3.9. $C_{25}H_{21}ON$ requires N, 4.25%), which was insoluble in dilute hydrochloric acid. The iminopyrrolidine hydrochloride (420 mg.) was boiled with acetic anhydride (4 c.c.) for 5 min., then water was added. Crystallisation of the product from aqueous ethanol gave 2-acetimido-1-benzyl-3 : 3-diphenylpyrrolidine (0.4 g., 92%) as plates, m. p. 121° (Found: C, 81.45; H, 6.9. $C_{25}H_{24}ON_2$ requires C, 81.5; H, 6.6%), which dissolved in 2N-hydrochloric acid.

3-Dibenzylamino-1-phenylpropyl Cyanide.—2-Dibenzylaminoethyl chloride (36.4 g.) was treated with benzyl cyanide (14.4 g.) in dry benzene (180 c.c.) in the presence of sodamide (4.9 g.) at 40°, the reaction being completed at 80° for 2 hr. After washing with water, distillation gave 3-dibenzylamino-1-phenylpropyl cyanide (32 g., 67%), b. p. 164—168°/10⁻⁴ mm. (Found, on material regenerated from the oxalate: N, 8.2. $C_{24}H_{24}N_2$ requires N, 8.25%). The *hydrogen oxalate*, recrystallised from acetone-ether, had m. p. 134—135° (Found: C, 72.2; H, 6.0. $C_{24}H_{24}N_2 \cdot H_2C_2O_4$ requires C, 72.5; H, 6.1%). The cyanide (2.8 g.), concentrated hydrochloric acid (30 c.c.), and acetic acid (10 c.c.) were refluxed for 1 hr. The solution was evaporated to dryness and the product washed with a little chloroform. Recrystallisation from 15% hydrochloric acid gave γ -dibenzylamino- α -phenylbutyric acid hydrochloride (1.4 g., 60%), m. p. 202—204° (Found: N, 3.35. $C_{24}H_{25}O_2N \cdot HCl$ requires N, 3.55%). The original distillate gave benzyl chloride (280 mg., 27%) on neutralisation with sodium hydrogen carbonate and ether-extraction.

1-Benzyl-2-imino-3-phenylpyrrolidine Hydrochloride.—3-Dibenzylamino-1-phenylpropyl cyanide (1 g.) was refluxed with concentrated hydrochloric acid (20 c.c.) for 6 hr. Benzyl chloride (54 mg., 15%) was isolated; the aqueous solution was evaporated to 10 c.c. and water (10 c.c.) added. The crystals of γ -dibenzylamino- α -phenylbutyric acid hydrochloride (0.64 g., 55%), m. p. 202—204°, were filtered off. Evaporation of the filtrate and recrystallisation from ethanol-ether gave 1-benzyl-2-imino-3-phenylpyrrolidine hydrochloride (0.28 g., 34%), m. p. 206—208° (Found: N, 9.75. $C_{17}H_{15}N_2 \cdot HCl$ requires N, 9.75%). The m. p. was depressed to 185° on admixture with the amino-acid hydrochloride. The pyrrolidine hydrochloride was dissolved in acetic acid, aqueous sodium nitrite added, and the mixture boiled for 2 min., to give 1-benzyl-3-phenylpyrrolid-2-one, m. p. and mixed m. p. 99° (cf. below).

1-Benzyl-3-phenylpyrrolid-2-one.—(a) γ -Dibenzylamino- α -phenylbutyric acid hydrochloride was heated at 220—230° for 1 hr. The dark product, recrystallised from ethanol (charcoal), gave the *pyrrolidone* (5%), m. p. 101—102° (Found: C, 81.2; H, 6.9. $C_{17}H_{17}ON$ requires C, 81.25; H, 6.8%). (b) The same hydrochloride (420 mg.) was boiled with acetic anhydride (10 c.c.) for 5 min. The anhydride was removed at 20 mm. and the residue recrystallised from aqueous ethanol, yielding the pyrrolidone (200 mg., 100%), m. p. 101—102°. (c) 3-Hydroxy-1-phenylpropyl cyanide (35%), b. p. 137—141°/0.01 mm., was made by a method similar to that employed by King, Latham, and Partridge (*J.*, 1952, 4269), except that benzene was the sole solvent used. This cyanide (9.8 g.), concentrated hydrochloric acid (60 c.c.), and water (10 c.c.) were refluxed for 12 hr.; ether-extraction gave α -phenyl- γ -butyrolactone (6.1 g., 62%), b. p. 118—129°/0.01 mm. (Rothstein, *Bull. Soc. chim. France*, 1935, 80, gives b. p. 178°/13.5 mm.; McElvain and Loughton, *J. Amer. Chem. Soc.*, 1951, 73, 451, give b. p. 131—134°/0.3 mm.). The lactone (1.5 g.), benzylamine (10 c.c.) and concentrated hydrochloric acid (0.5 c.c.) were heated at 180° for 12 hr. The residue, after extraction with dilute acetic acid, recrystallised from aqueous ethanol, yielding the pyrrolidone (1.9 g., 78%), m. p. 101—102°.

3-Benzylmethylamino-1-phenylpropyl Cyanide.—This cyanide (b. p. 141—144°/0.01 mm.; 62% yield; Bergel, Hindley, Morrison, and Rinderknecht, U.S.P. 2,405,555; *Chem. Abs.*, 1947, 41, 159; Kägi and Miescher, *Helv. Chim. Acta*, 1949, 32, 2498) gave a *hydrochloride*, m. p. 140—142° (Found: N, 9.25. $C_{18}H_{20}N_2 \cdot HCl$ requires N, 9.3%). The *hydrogen oxalate*, m. p. 121—123°, was recrystallised from acetone-ether (Found: C, 67.7; H, 6.1. $C_{18}H_{20}N_2 \cdot H_2C_2O_4$ requires C, 67.8; H, 6.25%). The *toluene-p-sulphonate* had m. p. 144—146° (from ethanol-ether) (Found: N, 6.25. $C_{18}H_{20}N_2 \cdot C_7H_7O_2S$ requires N, 6.4%).

Attempted Debenzylation of 3-Benzylmethylamino-1-phenylpropyl Cyanide.—(a) The cyanide (5.3 g.) and concentrated hydrochloric acid (50 c.c.) were refluxed for 3 hr. Only traces of

benzyl chloride were formed. The solution was evaporated to dryness and the residue recrystallised from aqueous hydrochloric acid, giving γ -benzylmethylamino- α -phenylbutyric acid hydrochloride (6.2 g., 97%), m. p. 202—204° (Found: N, 4.4. $C_{18}H_{21}O_2N \cdot HCl$ requires N, 4.4%).

(b) The cyanide hydrochloride (3.35 g.), concentrated hydrochloric acid (25 c.c.), and acetic acid (25 c.c.) were refluxed for 7 hr. (liquid temp. 107°), to give γ -benzylmethylamino- α -phenylbutyric acid hydrochloride (2.3 g., 65%), m. p. 202°, and benzyl chloride (250 mg., 18%). In a similar hydrolysis, the crude product from 3.3 g. of cyanide was dissolved in methanol (25 c.c.), and a little ether was added; ammonium chloride (0.5 g., 72%) was filtered off. The methanol was evaporated and the residue dissolved in cold water and basified, liberating as an oil methyl γ -benzylmethylamino- α -phenylbutyrate (1.6 g., 43%), b. p. 118—120°/0.01 mm. (Found: N, 4.65. $C_{18}H_{23}O_2N$ requires N, 4.7%). The ester (800 mg.) and 15% hydrochloric acid (25 c.c.), refluxed for 8 hr., gave γ -benzylmethylamino- α -phenylbutyric acid hydrochloride (600 mg., 70%), m. p. 201°.

(c) The cyanide toluene-*p*-sulphonate was heated at 200° for 4 hr.; trituration with acetone gave unchanged toluene-*p*-sulphonate (90%). A similar fusion in the presence of free toluene-*p*-sulphonic acid gave a resin.

1-Methyl-3-phenylpyrrolid-2-one.— γ -Benzylmethylamino- α -phenylbutyric acid hydrochloride (2 g.) and acetic anhydride (20 c.c.) were refluxed for 30 min., the anhydride distilled off, and the residue recrystallised from light petroleum (b. p. 40—60°)—benzene. The pyrrolidone (220 mg., 20%) had m. p. 58—59° (Found: N, 7.8. $C_{11}H_{13}ON$ requires N, 8.0%). Benzyl chloride was identified in the distillate.

3-Dibenzylaminopropyl Cyanide.—3-Chloropropyl cyanide (yield 61%; b. p. 71—74°/8 mm.; Whitmore *et al.*, *J. Amer. Chem. Soc.*, 1944, **66**, 730) (5.1 g.), dibenzylamine (20 g.), sodium iodide (50 mg.), and anisole (25 c.c.) were refluxed for 3 hr., then light petroleum (b. p. 60—80°) (50 c.c.) was added. Dibenzylammonium chloride (10.4 g.) was filtered off, and the solution distilled, yielding 3-dibenzylaminopropyl cyanide (8.1 g., 63%), b. p. 152—155°/0.01 mm., m. p. 45—46° (from light petroleum, b. p. 40—60°) (Found: N, 10.3. $C_{18}H_{20}N_2$ requires N, 10.6%). The hydrochloride and picrate were syrups; the hydrogen oxalate formed rosettes, m. p. 142—144° from acetone (Found: N, 7.7. $C_{18}H_{20}N_2 \cdot H_2C_2O_4$ requires N, 7.9%).

Hydrolysis of 3-Dibenzylaminopropyl Cyanide.—(a) The cyanide (1 g.) and concentrated hydrochloric acid (30 c.c.) were boiled for 3 hr. No benzyl chloride was detected; the mixture was evaporated to dryness under reduced pressure, concentrated aqueous ammonia (10 c.c.) added, and the mixture again evaporated. The solid was extracted with hot chloroform, the ammonium chloride being filtered off. Evaporation of the chloroform gave the crude amino-acid as a syrup; treatment with ethereal hydrogen chloride and recrystallisation from acetone-ethanol gave γ -dibenzylaminobutyric acid hydrochloride (1 g., 83%), m. p. 122—126° (Found: N, 4.4. $C_{18}H_{21}O_2N \cdot HCl$ requires N, 4.4%).

(b) The cyanide (3.7 g.), acetic acid (10 c.c.), and hydrochloric acid (30 c.c.) were refluxed for 2 hr., affording benzyl chloride (53 mg., 3%) and γ -dibenzylaminobutyric acid hydrochloride (3.4 g., 76%), m. p. 122—124° after recrystallisation from ethanol-ether.

Independent Synthesis of γ -Dibenzylaminobutyric Acid Hydrochloride.—Diethyl sodiomalonate was treated with 2-dibenzylaminoethyl chloride, as described below for the benzylmethylamino-analogue. The crude diethyl 2-dibenzylaminoethylmalonate decomposed on attempted distillation at 10^{-4} mm. (The ester has been made by Eisleb and Ehrhart, *G.P.*, 550,762; *Chem. Zentr.*, 1932, II, 615.) The crude ester (3.3 g.), glacial acetic acid (10 c.c.), and concentrated hydrochloric acid (20 c.c.) were refluxed for 12½ hr., and gave γ -dibenzylaminobutyric acid hydrochloride (1.6 g., 57%), m. p. 124—126°.

3-Benzylmethylaminopropyl Cyanide.—A mixture of benzylmethylamine (15.8 g.), 3-chloropropyl cyanide (6.75 g.), sodium iodide (50 mg.), and toluene (50 c.c.) was refluxed for 4 hr., washed with water and distilled, yielding 3-benzylmethylaminopropyl cyanide (8 g., 65%), b. p. 150—151°/1 mm. (Found: N, 14.5. $C_{12}H_{16}N_2$ requires N, 14.9%). The hydrochloride was a syrup, and the hydrogen oxalate formed rosettes m. p. 136—137°, from acetone-ethanol (Found: N, 10.4. $C_{12}H_{16}N_2 \cdot H_2C_2O_4$ requires N, 10.1%).

Hydrolysis of 3-Benzylmethylaminopropyl Cyanide.—(a) The cyanide (2 g.) and concentrated hydrochloric acid (30 c.c.) were refluxed for 3 hr. No benzyl chloride was formed. The solution was evaporated almost to dryness at 15 mm., concentrated ammonia solution (10 c.c.) added, and the whole again evaporated. The free amino-acid was extracted into chloroform and treated with ethereal hydrogen chloride, to yield γ -benzylmethylaminobutyric acid hydrochloride (2.3 g., 89%), m. p. 168—169° (Found: N, 5.55. $C_{12}H_{17}O_2N \cdot HCl$ requires N, 5.75%). The m. p. was not depressed on admixture with a specimen prepared from malonic ester (see below).

(b) The cyanide (3 g.), acetic acid (10 c.c.), and concentrated hydrochloric acid (30 c.c.) were refluxed for 2 hr., and yielded benzyl chloride (30 mg., 1½%).

Independent Synthesis of γ -Benzylmethylaminobutyric Acid Hydrochloride.—Diethyl malonate (23.5 g.), then a solution of 2-benzylmethylaminoethyl chloride (22.5 g.) in ethanol (50 c.c.), were added in quick succession to a solution of sodium (3.0 g.) in anhydrous ethanol (100 c.c.) at 20°. The mixture was refluxed for 3 hr., evaporated, diluted with water, and extracted with ether-benzene, to give *diethyl 2-benzylmethylaminoethylmalonate* (17 g., 46%), b. p. 135–136°/0.01 mm. (Found: N, 4.65. $C_{17}H_{25}O_4N$ requires N, 4.55%). The ester (6.2 g.), acetic acid (15 c.c.), and concentrated hydrochloric acid (30 c.c.) were refluxed for 18 hr.; evaporation and recrystallisation from ethanol-ether gave γ -benzylmethylaminobutyric acid hydrochloride (4.7 g.), m. p. 170–172°.

1-Methylpyrrolid-2-one.—The foregoing hydrochloride (4.7 g.) and acetic anhydride (30 c.c.) were boiled for 3½ hr. The anhydride was distilled off, and dilute hydrochloric acid added; benzyl chloride and acetate were removed by ether-extraction. The aqueous solution was basified and extracted with ether, yielding 1-methylpyrrolid-2-one (1 g., 52%), b. p. 71–72°/12 mm. (Prill and McElvain, *J. Amer. Chem. Soc.*, 1933, **55**, 1241, give b. p. 84–85°/14 mm.; Craig, *ibid.*, p. 297, b. p. 94–96°/20 mm.). Etheral hydrogen chloride gave the hydrochloride, which formed needles, m. p. 85–87°, from acetone-ether (McElvain and Vozza, *ibid.*, 1949, **71**, 897, give m. p. 86–88°). Similarly *N*-benzyl-*N*-methylacetamide formed a *hydrochloride*, m. p. 129° (Found: N, 7.25. $C_{16}H_{13}ON, HCl$ requires N, 7.0%).

1-Benzylpyrrolid-2-one.—(a) The following is a modification of the method described by Späth and Lintner (*Ber.*, 1936, **69**, 2730). γ -Butyrolactone (12.9 g.), benzylamine (80 c.c.), and benzylammonium chloride (2.5 g.) were refluxed for 16 hr., cooled, and made strongly alkaline with 10*N*-sodium hydroxide. Ether-extraction and distillation afforded benzylamine and a residue of *N*-benzyl- γ -hydroxybutyramide (14.6 g., 47%), m. p. 74° (Späth and Lintner, *loc. cit.*, give m. p. 74–75°). The benzylamide (10 g.) and benzylammonium chloride (0.5 g.) were heated at 280° (dimethyl phthalate vapour bath) for 1 hr. The product was dissolved in ether, washed with aqueous sodium hydroxide, and distilled, yielding 1-benzylpyrrolid-2-one (8.3 g., 92%), b. p. 112–115°/0.08 mm., n_D^{20} 1.5550 (Späth and Lintner, *loc. cit.*, give b. p. 130–140°/1 mm.; Iselin and Hofmann, *Helv. Chim. Acta*, 1954, **37**, 178, b. p. 112–113°/0.08 mm.). The pyrrolidone gave a syrupy, water-soluble hydrochloride.

(b) γ -Dibenzylaminobutyric acid hydrochloride (3.7 g.) and acetic anhydride (30 c.c.) were heated at 100° for 1 hr., then refluxed for ½ hr. Acetic anhydride was distilled off at 15 mm. and the residue stirred with 2*N*-hydrochloric acid (20 c.c.) and extracted with ether. The pyrrolidone was liberated by adding potassium carbonate to the aqueous layer; it had b. p. 112–113°/0.08 mm., n_D^{20} 1.5478 (yield, 1.4 g., 78%). The infrared absorption over the range 1800–750 cm^{-1} of the pyrrolidone samples prepared by methods (a) and (b) were almost identical; there was a broad, strong CO stretching band at 1690 cm^{-1} (cf. the 1700- cm^{-1} band in pyrrolidone, quoted by Bellamy, "The Infrared Spectra of Complex Molecules," Methuen, London, 1954, p. 183).

1-Benzyl-2-benzyliminopyrrolidine.—3-Chloropropyl cyanide (4.7 g.) propan-1-ol (20 c.c.), sodium iodide (50 mg.), and benzylamine (9.4 g.) were refluxed for 8 hr.; ammonia was copiously evolved. The basic product was separated and treated with ethereal hydrogen chloride, yielding 1-benzyl-2-benzyliminopyrrolidine hydrochloride (9.4 g., 68%), m. p. 187–188° (Found: N, 9.0. $C_{18}H_{20}N_2, HCl$ requires N, 9.3%). The *picrate* had m. p. 136° (Found: N, 14.15. $C_{18}H_{20}N_2, C_6H_5O_7N_3$ requires N, 14.2%); the *nitrate*, m. p. 147–148° (Found: N, 12.55. $C_{18}H_{20}N_2, HNO_3$ requires N, 12.85%), was almost insoluble in cold water. The hydrochloride was unchanged after 17 hours' refluxing with concentrated hydrochloric acid. A mixture of the hydrochloride (2 g.), ethanol (10 c.c.), and 5*N*-sodium hydroxide (10 c.c.) was refluxed for 10½ hr. The ethanol was distilled off and treated with hydrogen chloride, affording benzylammonium chloride (200 mg., 22%). The mixture was extracted with ether, and ethereal hydrogen chloride added. Recrystallisation of the product from ethanol or water afforded *N*-benzyl- γ -benzylaminobutyramide hydrochloride (1.2 g., 56%), m. p. 211–213° (Found: N, 9.0. $C_{18}H_{22}ON_2, HCl$ requires N, 8.8%).

Independent Synthesis of N-Benzyl- γ -benzylaminobutyramide.— γ -Butyrolactone (20 g.) and concentrated hydrochloric acid (100 c.c.) were refluxed for 16 hr., yielding γ -chlorobutyric acid (4.3 g., 15%), b. p. 67–70°/0.1 mm. (cf. Cloves, *Annalen*, 1901, **319**, 360). The chloro-acid was converted *via* the acid chloride into γ -chlorobutyrobenzylamide (63%), m. p. 67° (Hanford and Adams, *J. Amer. Chem. Soc.*, 1935, **57**, 924, give m. p. 68°). The chloro-amide (1.1 g.) benzylamine (0.58 g.), sodium iodide (10 mg.), and ethanol (20 c.c.) were refluxed for 8 hr., and

ether was added. *N*-Benzyl- γ -benzylaminobutyramide hydrochloride (0.4 g., 24%), separated as needles, m. p. 211—213°.

4-Dibenzylaminopentan-2-one.—Ethyl acetoacetate (10 g.) was added to a solution of sodium (1.95 g.) in ethanol (100 c.c.). 2-Dibenzylaminoethyl chloride (22 g.) was then added dropwise during 1 hr. to the boiling mixture. After 4 hours' further refluxing, the mixture was filtered and evaporated. The crude oxo-ester (15 g.) was stirred with a solution of potassium hydroxide (2.5 g.) in ethanol (30 c.c.) and water (100 c.c.) at 20° for 4 hr. A slight excess of 2*N*-hydrochloric acid was added and the solution heated at 70° to expel carbon dioxide. Excess of 10*N*-sodium hydroxide was added, and the basic ketone (7.4 g., 60%), b. p. 138—145°/0.01 mm., was isolated by ether-extraction (Eisleb and Ehrhart, *loc. cit.*, give b. p. 185—195°/3 mm., for this compound, made by a related procedure). *4*-Dibenzylaminopentan-2-one was refluxed with concentrated hydrochloric acid for 6 hr.; no benzyl chloride was formed. Benzyltriethylammonium chloride was recovered unchanged after being boiled for 3 hr. with concentrated hydrochloric acid; no benzyl chloride was formed.

The authors are grateful to Professor M. Stacey, F.R.S., for encouragement, Dr. D. H. Whiffen for the infrared absorption measurements, and Mr. D. Skidmore for the microanalyses. One of them (M. W. G.) thanks the University of Birmingham for a research scholarship.

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[Received, February 21st, 1955.]