Heterocyclic Imines and Amines. Part V. The Imidine of αα′-Dimethylsuccinic Acid.*

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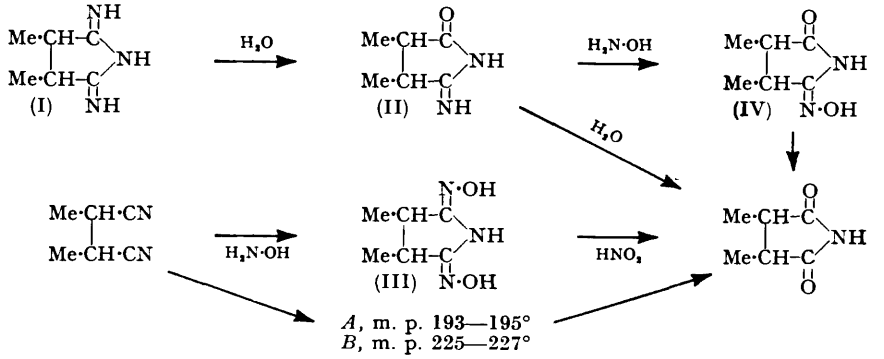
DL-αα′-Dimethylsuccinonitrile reacts with ammonia in methanol at 150° to give *DL*-2 : 5-di-imino-3 : 4-dimethylpyrrolidine (dimethylsuccinimidine) (I). The degradation of (I) with water is described. It reacts normally with hydroxylamine hydrochloride to give a dihydroxyiminopyrrolidine, a stereoisomeride of which is one of the products from the reaction of hydroxylamine hydrochloride and dimethylsuccinonitrile. Dimethylsuccinimidine reacts abnormally with other primary amines. With aniline, dehydrogenation to the dimethylmaleic derivative (V) occurs; aniline hydrochloride gives the phenyliminoanilide (VIII); benzylamine and *cyclo*hexylamine give substituted imino-imides (X). Light-absorption data are given.

IT has been shown that imidines are formed by adding ammonia to succinonitrile (Elvidge and Linstead, Part III, *J.*, 1954, 442) and hexahydrophthalonitrile (Ficken and Linstead *). This paper describes the symmetrically substituted *DL*-2 : 5-di-imino-3 : 4-dimethylpyrrolidine (dimethylsuccinimidine) (I) which is intermediate in structural type between these known imidines and is a valuable intermediate for the preparation of macrocyclic pigments.

DL-αα′-Dimethylsuccinonitrile (Linstead and Whalley, *J.*, 1954, 3722; the method described by Beech and Piggott, *J.*, 1955, 423, gives a mixture of *meso*- and *DL*-nitrile) reacts readily with methanolic ammonia to give good yields of dimethylsuccinimidine. This method resembles that used for succinimidine (Elvidge and Linstead, *loc. cit.*) and for 1 : 3-di-imino*iso*indoline (Elvidge and Linstead, Part I, *J.*, 1952, 5000). The temperature required



(150°) is higher than that previously used and careful control is essential: below 145° the yield of imidine is small whilst above 160° the product becomes increasingly difficult to work up. No dimethylsuccinimidine could be isolated after treatment of *DL*-αα′-dimethylsuccinonitrile with sodamide in formamide at room temperature or at 0° (cf. Part III), or by bubbling ammonia through a solution of the nitrile containing a trace of sodium (Part IV). No attempt was made to prepare the imidine from the less stable and less accessible *meso*-αα′-dimethylsuccinonitrile (Linstead and Whalley, *loc. cit.*) as the high temperature required for imidine formation would undoubtedly have caused inversion of configuration.

Dimethylsuccinimidine has no well-defined melting point, becomes blue at about 130°, and sinters at 140°. Hydrochloric acid hydrolyses it to *DL*-αα′-dimethylsuccinic acid. It therefore has the *DL*-configuration, which is known to be stable for cyclic derivatives of αα′-dimethylsuccinic acid (Linstead and Whalley, *loc. cit.*). Although fairly stable to atmospheric moisture, the imidine loses ammonia when its solution in cold water is allowed

* Part IV, preceding paper.

to stand. Evaporation of the water at room temperature then gives 5-imino-3 : 4-dimethylpyrrolid-2-one (II) which on further hydrolysis with boiling water gives *DL*-αα′-dimethylsuccinimide.

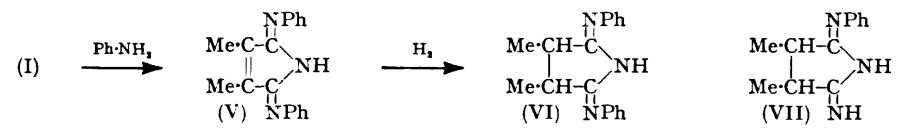
Dimethylsuccinimidine reacted in the expected manner with hydroxylamine hydrochloride in ethanol to give a dioxime (III*A*), m. p. 193—195°, identical with the product from the reaction of *DL*-αα′-dimethylsuccinonitrile with 2 mols. of hydroxylamine hydrochloride in boiling aqueous ethanol. Treatment of the dioxime (III*A*) at 0° with 2 mols. of sodium nitrite in dilute hydrochloric acid readily yielded *DL*-αα′-dimethylsuccinimide. Attempts at stepwise degradation of (III*A*) to the monoxime (IV) by reducing the proportion of sodium nitrite to less than 1 mol. led to *DL*-αα′-dimethylsuccinimide and hydroxylamine hydrochloride only. This suggested that the presumed intermediate monoxime (IV) was readily hydrolysed. The monoxime (IV) was prepared from the imino-imide (II) and hydroxylamine hydrochloride in boiling ethanol, and its rapid hydrolysis with dilute hydrochloric acid was confirmed.

A second dioxime (III*B*), m. p. 225—227°, was obtained from *DL*-αα′-dimethylsuccinonitrile and hydroxylamine hydrochloride in aqueous ethanol at 70°. This compound (III*B*) yielded *DL*-αα′-dimethylsuccinimide when treated with nitrous acid, whilst on irradiation in ethanol with ultraviolet light it gave the stable isomer (III*A*), m. p. 193—195°. These two dioximes are probably geometrical isomers of (III) for which three forms can be written (*syn-syn*, *syn-anti*, *anti-anti*). Tautomeric forms are also possible but seem to be excluded as the light absorptions of the two oximes are nearly identical. Indications of the existence of similar isomers have already been obtained in the succinic, 3 : 4 : 5 : 6-tetrahydrophthalic and hexahydrophthalic series (*locc. cit.*).

The reactions of dimethylsuccinimidine with water and with hydroxylamine conformed to those established for succinic and phthalic imidines. In its reaction with primary amines, however, dimethylsuccinimidine proved anomalous, and the symmetrically disubstituted product was not obtained. Three types of reaction occurred.

(a) *With aniline.* Dimethylsuccinimidine reacted with 2 mols. of aniline, very slowly at room temperature or in boiling ethanol, more rapidly in boiling propanol, or best at 90° with no solvent. The product was the unsaturated diphenylimine (V) which is a derivative of dimethylmaleic acid. The reaction is analogous to the dehydrogenation observed under similar conditions with *cis*-hexahydrophthalimidine (Ficken and Linstead, *loc. cit.*). The presence of the double bond is established by the light absorption and by the degradation to dimethylmaleimide. There was no evidence of the stepwise reaction with aniline, to give the monophenyl derivative, observed with 1 : 3-di-imino*iso*indoline (Clark, Elvidge, and Linstead, Part II, *J.*, 1953, 3593) and with succinimidine (Part III). An attempt to prepare the monophenyl derivative (VII) by using 1 mol. of aniline gave the di-imine (V) alone.

Hydrogenation of the diphenylimine (V) over palladium–charcoal in ethanol gave the saturated diphenylimine (VI) which on hydrolysis yielded *DL*-αα′-dimethylsuccinimide.



Catalytic hydrogenation would be expected to give *cis*-addition of hydrogen to the ethylenic double bond as in the case of dimethylmaleimide which yields *meso*-αα′-dimethylsuccinimide (Linstead and Whalley, *loc. cit.*). It seems probable in the present case either that inversion of the labile *meso*-form occurs during the hydrolysis or that hydrogenation goes by an indirect process involving the nitrogen atoms. Rearrangement of the primary *N*-hydride would then yield the *C*-hydride in the stable *DL*-configuration.

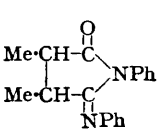
(b) *With aniline hydrochloride.* The reaction of aniline hydrochloride (2 mols.) with dimethylsuccinimidine was investigated as a possible route to the diphenylimine (VI), for it is known that 1 : 3-di-imino*iso*indoline with aniline hydrochloride gives 1 : 3-diphenylimino*iso*indoline hydrochloride. Reaction proceeded slowly at room temperature but

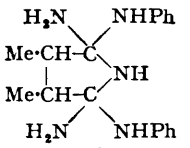
rapidly in boiling propanol, the only product isolated being the free base, 3 : 4-dimethyl-1-phenyl-5-phenyliminopyrrolid-2-one (VIII). The identity of the product was established by hydrolysis to *DL*-αα'-dimethyl-*N*-phenylsuccinimide. The light absorption was in agreement with structure (VIII). The formation of this compound, phenylated on the cyclic nitrogen atom, must involve a complex series of changes. Of possible courses for the reaction, the following seems the most likely : (*a*) formation from the imidine of the addition product (IX) ; (*b*) ring-opening and re-closing with elimination of ammonia ; (*c*) hydrolysis of the imino-group. This conclusion will be correlated with other results in a later paper.

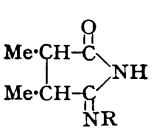
The *DL*-αα'-dimethyl-*N*-phenylsuccinimide required for comparison was prepared by the following route : mixed αα'-dimethylsuccinic acids ⟶ anhydrides ⟶ anilic acids ⟶ *N*-phenylimide. The product corresponded to that prepared by Bischoff and Voit (*Ber.*, 1890, **23**, 643). Hydrolysis of the *N*-phenylimide with concentrated hydrochloric acid yielded *DL*-αα'-dimethylsuccinic acid only, indicating that the phenylimide was the *DL*-form.

Attempts to prepare the saturated diphenylimine (VI) by fusion of *DL*-αα'-dimethylsuccinonitrile with aniline hydrochloride failed (cf. succinonitrile and phthalonitrile; Part II).

(c) *With benzylamine and* cyclo*hexylamine.* Dimethylsuccinimidine reacts slowly with *cyclo*hexylamine at room temperature or in ethanol, or rapidly at 100° in the absence of solvent, to give a low yield of the substituted dimethylsuccinic imino-imide (X ; R = C_6H_{11})


(VIII)


(IX)


(X)

which was isolated as the hydrochloride. Benzylamine reacts in the same way but more readily, even rapidly at room temperature, to give (X ; R = CH_2Ph), also isolated as the hydrochloride. Both products gave *DL*-αα'-dimethylsuccinimide on hydrolysis.

Although dimethylsuccinimidine gives anomalous products with primary amines, the imino-imide (II) reacts normally with aniline and *cyclo*hexylamine, to give (X ; R = Ph and C_6H_{11} respectively). These products are hydrolysed to *DL*-αα'-dimethylsuccinimide, indicating that dehydrogenation had not occurred.

The bases (V), (VI), (VIII), and (X ; R = Ph, CH_2Ph, or C_6H_{11}) were readily hydrolysed to the corresponding imides with ethanolic dilute hydrochloric acid, but (VI) was known to be stable to hot dilute alkali for long periods. This behaviour corresponded to that of 1 : 3-diphenylimino*iso*indoline and, to a smaller extent, 1-imino-3-phenylimino*iso*indoline, which are stable to water and dilute alkali but are rapidly hydrolysed to phthalimide in the presence of dilute acid. Hydrolysis of the diphenylimine (VI) to the imide contrasted with that of 2 : 5-diphenyliminopyrrolidine (Part III) which in warm water gave succindianilide.

Like the imidines described in previous papers, dimethylsuccinimidine could be converted into tetrazaporphins. Solutions of the imidine, on prolonged boiling in propanol or butanol, slowly deposited a blue pigment. This contained metal-free octamethyltetrazaporphin, spectroscopically identical with the pigment prepared from dimethylfumaronitrile (Baguley, France, Linstead, and Whalley, *J.*, 1955, 3521), together with a hydrogenation product of octamethyltetrazaporphin (main bands at 687 and 525 mμ). In boiling chlorobenzene–nitrobenzene, conversion of dimethylsuccinimidine into octamethyltetrazaporphin proceeded rapidly and in good yield. Dimethylsuccinimidine thus formed tetrazaporphins less readily than *cis*-hexahydrophthalimidine (Part IV) but much more easily than succinimidine (Elvidge and Linstead, following paper) from which metal-free tetrazaporphin could not be obtained directly. In one preparation of dimethylsuccinimidine during which the temperature exceeded 170° a good yield of macrocrystalline (unhydrogenated) octamethyltetrazaporphin was obtained.

The ultraviolet absorption data for dimethylsuccinimidine and its derivatives are

summarised in the Table. The spectra of compounds (I), (II), (III), (IV), (VI), and (X; R = Ph) closely resemble those of the corresponding derivatives of *cis*-hexahydrophthalimidine (Ficken and Linstead, *loc. cit.*) and of succinimidine (Elvidge and Linstead, Part III); that of the unsaturated diphenylimine (V) corresponds to that of the diphenyl derivative of 3 : 4 : 5 : 6-tetrahydrophthalimidine.

Light absorption of DL-αα′-*dimethylsuccinimidine and its derivatives in* EtOH.

Compound	Formula	$\lambda_{max.}$ (mμ)	$10^{-3}\varepsilon$
Imidine	(I)	237	17·8
Dioxime from imidine	(III*A*)	228	17·6
Dioxime from nitrile	(III*B*)	228	16·4
Diphenylimidine	(VI)	228	14·2
		282	16·8
Unsaturated diphenylimidine	(V)	228	15·3
		258, 266	15·3
		328	7·4
		348	7·4
Imino-imide	(II)	227	27·0
Imino-imide oxime	(IV)	226	10·5
Phenylimino-imide	(X; R = Ph)	227	9·2
		269	11·5
*cyclo*Hexylimino-imide hydrochloride	(X; R = C_6H_{11}),HCl	250	6·5
Benzylimino-imide hydrochloride	(X; R = CH_2Ph),HCl	247	6·6
Phenylimino-anil	(VIII)	227	23·4
		265	5·0
N-Phenylimide	—	244	10·3

Experimental

DL-2 : 5-*Di-imino*-3 : 4-*dimethylpyrrolidine* (*Dimethylsuccinimidine*).—A solution of *DL*-αα′-dimethylsuccinonitrile (2·0 g.) in methanol (12 c.c.) was treated with liquid ammonia (8 c.c.), and the mixture heated in a sealed tube at 148° for 18 hr. The methanolic solution was filtered through charcoal and the residual oil triturated with ethyl acetate. After several hours a crystalline mass was obtained. Crystallisation from dimethylformamide–benzene gave pale yellow prisms of DL-2 : 5-*di-imino*-3 : 4 *dimethylpyrrolidine* (1·58 g., 69%), sinters at 140° after becoming blue at 130° (Found : C, 57·5; H, 8·8; N, 33·0. $C_6H_{11}N_3$ requires C, 57·6; H, 8·9; N, 33·6%). The *picrate* crystallised in yellow needles, m. p. 193—195° (decomp.), from ethanol (Found : C, 40·9; H, 4·1; N, 23·7. $C_{12}H_{14}O_7N_6$ requires C, 40·7; H, 4·0; N, 23·7%).

Hydrolysis. (*a*) Dimethylsuccinimidine (147 mg.) in water (1 c.c.) was refluxed for 1 hr. and the water evaporated under reduced pressure, giving *DL*-αα′-dimethylsuccinimide (123 mg., 82%), m. p. and mixed m. p. 104—106°.

(*b*) Dimethylsuccinimidine (300 mg.) was dissolved in cold water (3 c.c.). Ammonia evolution commenced after about 5 min. After 24 hr. the water was removed under reduced pressure. The sticky residue was crystallised from ethanol, giving colourless prisms of 5-*imino*-3 : 4-*dimethylpyrrolid*-2-*one* (178 mg., 59%), m. p. 173—176° (decomp.; darkening from 150°) (Found : C, 57·2; H, 8·1; N, 21·5. $C_6H_{10}ON_2$ requires C, 57·1; H, 8·0; N, 22·2%). The *picrate*, m. p. 208—210°, crystallised from ethanol (Found : C, 40·7; H, 4·0; N, 19·9. $C_{12}H_{13}O_8N_5$ requires C, 40·6; H, 3·7; N, 19·6%).

3 : 4-*Dimethyl*-5-*phenyliminopyrrolid*-2-*one*.—5-Imino-3 : 4-dimethylpyrrolid-2-one (274 mg.) and aniline (210 mg.) in propanol (2 c.c.) were refluxed for 6 hr. The propanol was removed and the sticky residue was crystallised from aqueous methanol and then from ethanol–light petroleum (b. p. 60—80°). It gave colourless prisms of 3 : 4-*dimethyl*-5-*phenyliminopyrrolid*-2-*one* (170 mg., 43%), m. p. 130—132° (Found : C, 71·6; H, 7·3; N, 14·5. $C_{12}H_{14}ON_2$ requires C, 71·3; H, 7·0; N, 13·9%).

The phenylimino-compound (49 mg.) was refluxed with 2N-hydrochloric acid (1 c.c.) and ethanol (1 c.c.), and the solvents were removed. The residue was sublimed under reduced pressure, giving *DL*-αα′-dimethylsuccinimide (26 mg., 84%), m. p. 103—105°.

5-cyclo*Hexylimino*-3 : 4-*dimethylpyrrolid*-2-*one Hydrochloride*.—5-Imino-3 : 4-dimethylpyrrolid-2-one (600 mg.) and *cyclo*hexylamine (1 g.) in propanol (10 c.c.) were refluxed for 6 hr. The propanol was removed under reduced pressure. The residue was dissolved in ether, and the ether solution dried (Na_2SO_4) and saturated with hydrogen chloride. The ether was removed and the solid crystallised from ethanol–light petroleum (b. p. 60—80°), giving

5-*cyclo*hexylimino-3 : 4-dimethylpyrrolid-2-one hydrochloride (27 mg., 3%), m. p. 248—250° alone or in admixture with the product from dimethylsuccinimidine.

5 - *Hydroxyimino* - 3 : 4 - *dimethylpyrrolid* - 2 - *one*.—5 - Imino-3 : 4 - dimethylpyrrolid - 2 - one (572 mg.), hydroxylamine hydrochloride (350 mg.), and anhydrous sodium carbonate (266 mg.) in absolute ethanol (8 c.c.) were refluxed for 24 hr. and the ethanol was removed. The residue was extracted with ethyl acetate, giving colourless prisms of 5-*hydroxyimino*-3 : 4-*dimethylpyrrolid*-2-*one* (146 mg., 23%), m. p. 182—183° (Found : C, 51·1; H, 7·1; N, 19·3. $C_6H_{10}O_2N_2$ requires C, 50·7; H, 7·1; N, 19·7%). *DL*-αα′-Dimethylsuccinimide (10 mg.), m. p. 104—106°, was obtained from the mother-liquors.

The hydroxyimino-compound (27 mg.) was warmed at 65° for 15 min. with 0·01N-hydrochloric acid (0·5 c.c.). On cooling and evaporation, *DL*-αα′-dimethylsuccinimide (15 mg., 62%) separated.

2 : 5-*Dihydroxyimino*-3 : 4-*dimethylpyrrolidines*.—(*a*) A solution of *DL*-αα′-dimethylsuccinonitrile (2·0 g.), hydroxylamine hydrochloride (2·8 g., 2 mols.), and sodium carbonate (1·4 g.) in ethanol (16 c.c.) and water (16 c.c.) was refluxed for 16 hr. Traces of metal-free octamethyltetrazaporphin were formed during the early stages of the reaction. The ethanol and water were removed under reduced pressure and the dried solid extracted with ethyl acetate.

2 : 5-*Dihydroxyimino*-3 : 4-*dimethylpyrrolidine* (III*A*) (1·6 g., 56%), m. p. 193—196° (decomp.), was obtained as colourless prisms from ethyl acetate (Found : C, 46·0; H, 7·1; N, 26·2. $C_6H_{11}O_2N_3$ requires C, 45·9; H, 7·1; N, 26·7%).

(*b*) Dimethylsuccinimidine (100 mg.), hydroxylamine hydrochloride (112 mg.), and sodium carbonate (86 mg.) in absolute ethanol (6 c.c.) were refluxed for 24 hr. and the solvent was then removed. The residue crystallised from ethyl acetate, giving 2 : 5-dihydroxyimino-3 : 4-dimethylpyrrolidine (89 mg., 71%), m. p. 193—196° (decomp.) alone and in admixture with the above product from *DL*-αα′-dimethylsuccinonitrile (Found : C, 45·8; H, 7·1%).

(*c*) *DL*-αα′-Dimethylsuccinonitrile (1·0 g.), hydroxylamine hydrochloride (0·71 g., 1 mol.), anhydrous sodium carbonate (0·4 g.), ethanol (8 c.c.), and water (8 c.c.) were heated at 70° overnight, and the ethanol and some of the water removed. The remaining solid crystallised from ethyl acetate, giving 2 : 5-*dihydroxyimino*-3 : 4-*dimethylpyrrolidine* (III*B*), m. p. 225—227° (decomp.) (Found : C, 46·2; H, 7·2; N, 27·1%).

Irradiation of an ethanolic solution of this dioxime with ultraviolet light for 6 hr. gave the isomer (III*A*), m. p. 193—196°.

Degradation of 2 : 5-*Dihydroxyiminopyrrolidines*.—(a) *The isomer* (III*A*). (i) The dioxime (248 mg.) was dissolved in warm water (20 c.c.), and the solution cooled in ice. Sodium nitrite (218 mg.) was added, followed by 2N-hydrochloric acid (2·1 c.c.) in portions. After 5 min. the water was removed under reduced pressure and the residue sublimed (156 mg., 88%); it had m. p. 101—104° alone and when mixed with *DL*-αα′-dimethylsuccinimide.

(ii) The dioxime (200 mg.) was treated with sodium nitrite (34 mg.) and 2N-hydrochloric acid as above. The solid obtained on evaporation of the solution was extracted with ethanol, giving hydroxylamine hydrochloride (14 mg., 17%), m. p. and mixed m. p. 150—151°, and *DL*-αα′-dimethylsuccinimide (87 mg., 54%), m. p. 104—106°.

(iii) The compound (100 mg.) was hydrolysed with concentrated hydrochloric acid, giving *DL*-αα′-dimethylsuccinic acid (75 mg., 92%), m. p. 123—127°.

(b) *The isomer* (III*B*). This form (100 mg.) was treated with sodium nitrite (88 mg.) and 2N-hydrochloric acid (1 c.c.) as above, giving *DL*-αα′-dimethylsuccinimide (74 mg., 93%), m. p. and mixed m. p. 105—107°.

3 : 4-*Dimethyl*-2 : 5-*diphenylimino*-Δ^3-*pyrroline*.—(*a*) A solution of dimethylsuccinimidine (610 mg.) and aniline (910 mg.) in propanol was refluxed for 20 hr. The propanol was removed under reduced pressure, the residue chromatographed (alumina–benzene), and the eluate evaporated. The sticky residue was crystallised several times from 50% aqueous ethanol, giving yellow needles of 3 : 4-*dimethyl*-2 : 5-*diphenylimino*-Δ^3-*pyrroline* (190 mg., 14%), m. p. 98—100° (Found : C, 78·5; H, 6·4; N, 15·6. $C_{18}H_{17}N_3$ requires C, 78·5; H, 6·2; N, 15·3%).

(*b*) Dimethylsuccinimidine (200 mg.) and aniline (300 mg.) were warmed at 90° overnight and the mixture was worked up as above, giving the same diphenylimine (50 mg., 12%).

The diphenylimine was recovered unchanged after refluxing for 4 hr. with 2N-sodium hydroxide.

The dimethyldiphenyliminopyrroline (100 mg.) was refluxed with 2N-hydrochloric acid (2 c.c.) and ethanol (1 c.c.) for 10 min., the solvents were removed, and the residue was crystallised from water, giving dimethylmaleimide (32 mg., 70%), m. p. and mixed m. p. 118—119°.

Hydrolysis of Phenyliminoisoindolines.—(*a*) 1-Imino-3-phenyliminoisoindoline was unchanged after being boiled for 5 min. with water or for 10 min. with 0·1N-sodium hydroxide (10 c.c.) and ethanol (10 c.c.). (*b*) 1 : 3-Diphenyliminoisoindoline (0·1 g.), 0·1N-sodium hydroxide (10 c.c.), and ethanol (10 c.c.) were refluxed for 10 hr. Addition of a few drops of concentrated hydrochloric acid gave a bright yellow solid, which, crystallised from glacial acetic acid, had m. p. 285° alone or in admixture with the authentic hydrochloride. (*c*) The base (0·1 g.) was unchanged after being refluxed overnight with 40% sodium hydroxide solution (10 c.c.).

3 : 4-*Dimethyl*-2 : 5-*diphenyliminopyrrolidine.*—3 : 4-Dimethyl-2 : 5-diphenylimino-Δ^3-pyrroline (281 mg.) was hydrogenated over 5% palladium–charcoal in ethanol, and the catalyst and the solvent were removed. The residue crystallised from aqueous ethanol, giving colourless prisms of 3 : 4-*dimethyl*-2 : 5-*diphenyliminopyrrolidine hemihydrate* (203 mg., 72%), m. p. 101—103° (Found : C, 75·8; H, 7·4; N, 15·1. $C_{18}H_{19}N_3,\frac{1}{2}H_2O$ requires C, 75·5; H, 7·1; N, 14·7%).

This diphenylimine (61 mg.) was refluxed with 2N-hydrochloric acid (1 c.c.) and ethanol (0·5 c.c.) for 10 min. Evaporation of the solvent and sublimation of the residue gave *DL*-αα′-dimethylsuccinimide (21 mg., 75%), m. p. and mixed m. p. 101—106°.

1 : 3-*Diphenyliminoisoindoline Hydrochloride.*—1 : 3-Di-iminoisoindoline (250 mg.) and aniline hydrochloride (450 mg.) were refluxed in propanol for 24 hr. and the propanol removed under reduced pressure. The remaining solid was crystallised several times from glacial acetic acid, giving 1 : 3-diphenyliminoisoindoline hydrochloride (320 mg., 56%), m. p. and mixed m. p. 275—278°.

3 : 4-*Dimethyl*-1-*phenyl*-5-*phenyliminopyrrolid*-2-*one.*—Dimethylsuccinimidine (250 mg.) and aniline hydrochloride (520 mg.) were refluxed in propanol for 6 hr. The precipitated ammonium chloride was removed and the solvent evaporated. The sticky residue was crystallised from aqueous ethanol, giving colourless needles of 3 : 4-*dimethyl*-1-*phenyl*-5-*phenyliminopyrrolid*-2-*one* (117 mg., 22%), m. p. 107—109° (Found : C, 77·7; H, 6·5; N, 10·3. $C_{18}H_{18}ON_2$ requires C, 77·7; H, 6·5; N, 10·1%).

Hydrolysis of the substance (63 mg.) in ethanol (1 c.c.) and 2N-hydrochloric acid (2 c.c.) yield *DL*-αα′-dimethyl-*N*-phenylsuccinimide (25 mg., 55%), m. p. and mixed m. p. 126—127°.

DL-αα′-*Dimethyl*-N-*phenylsuccinimide.*—A mixture of the stereoisomeric αα′-dimethylsuccinic acids (5 g.) was refluxed with acetyl chloride (20 c.c.) for 45 min. and the mixture cooled and filtered. The acetyl chloride and acetic acid were removed under reduced pressure, giving a mixture of *meso*- and *DL*-αα′-dimethylsuccinic anhydride (3·54 g., 81%), m. p. 60—75°. The mixture was refluxed with aniline (2·64 g.) and ethanol (25 c.c.) for 6 hr., the ethanol evaporated, and the residue crystallised several times from aqueous ethanol, giving *meso*- and *DL*-αα′-dimethylsuccinanilic acid (3·90 g., 64%), m. p. 151—154° (Bone and Sprankling, *J.*, 1899, **75**, 861, give m. p. 169—171° for the *meso*- and 135—136° for the *DL*-anilic acid) (Found : C, 65·9; H, 7·1; N, 6·6. Calc. for $C_{12}H_{15}O_3N$: C, 65·2; H, 6·8; N, 6·3%).

Hydrolysis of this mixture of anilic acids (200 mg.) with concentrated hydrochloric acid (2·5 c.c.) yielded a mixture of *meso*- and *DL*-αα′-dimethylsuccinic acid (127 mg., 96%), m. p. 145—150°.

The mixture of αα′-dimethylsuccinanilic acids (1·0 g.) was heated at 150° for 10 min., the residue sublimed under reduced pressure, and the sublimate crystallised from ethanol, giving *DL*-αα′-dimethyl-*N*-phenylsuccinimide (0·87 g., 96%), m. p. 126—127° (Bischoff and Voit, *Ber.*, 1890, **23**, 643, give m. p. 126—127°) (Found : C, 70·7; H, 6·4; N, 7·2. Calc. for $C_{12}H_{13}O_2N$: C, 70·9; H, 6·4; N, 6·9%).

Hydrolysis of *DL*-αα′-dimethyl-*N*-phenylsuccinimide (117 mg.) with concentrated hydrochloric acid (82 mg., 97%), m. p. 125—127° alone and in admixture with *DL*-αα′-dimethylsuccinic acid.

The anil was recovered unchanged after being refluxed for 10 min. with ethanol and 2N-hydrochloric acid (1 : 2).

5-cyclo*Hexylimino*-3 : 4-*dimethylpyrrolid*-2-*one Hydrochloride.*—Dimethylsuccinimidine (500 mg.) and *cyclo*hexylamine (800 mg.) were heated on the steam-bath overnight (evolution of ammonia occurred slowly at room temperature). The product was dissolved in ether, and the solution washed with water and dried (Na_2SO_4). The oil obtained after evaporation of the ether was dissolved in ethanol (1 c.c.) and dry ether (10 c.c.), and the solution saturated with hydrogen chloride. The *pyrrolidone hydrochloride* separated (47 mg., 9%), having m. p. 248—250° (decomp.) after crystallisation from ethanol–light petroleum (b. p. 60—80°) (Found : C, 59·0; H, 8·4; N, 11·5; Cl, 14·7. $C_{12}H_{21}ON_2Cl$ requires C, 58·8; H, 8·6; N, 11·5; Cl, 14·5%).

Hydrolysis of the hydrochloride (41 mg.) with boiling ethanol (0·5 c.c.) and 2N-hydrochloric acid (0·5 c.c.) gave *DL*-αα′-dimethylsuccinimide (11 mg., 52%), m. p. 103—105°.

5-Benzylimino-3 : 4-dimethylpyrrolid-2-one Hydrochloride.—Dimethylsuccinimidine (500 mg.) and benzylamine (1 g.) were heated on the steam-bath overnight (evolution of ammonia at room temperature was rapid) and the residue dissolved in ether. The ether solution was washed with water and dried (Na_2SO_4), and evaporated. The sticky residue was dissolved in ether (10 c.c.), the solution saturated at 0° with hydrogen chloride, and the ether removed. A colourless solid, m. p. 218—227°, separated and gave, on recrystallisation from ethanol, *5-benzylimino-3 : 4-dimethylpyrrolid-2-one hydrochloride* (173 mg., 17%), m. p. 236—238° (Found : C, 61·5; H, 6·6; N, 10·9; Cl, 13·9. $C_{13}H_{17}ON_2Cl$ requirss C, 61·8; H, 6·8; N, 11·1; Cl, 14·0%).

The hydrochloride (37 mg.) was refluxed for 15 min. with ethanol (0·5 c.c.) and 2N-hydrochloric acid (0·5 c.c.), and the solvents were removed under reduced pressure. Sublimation of the residue gave *DL*-αα′-dimethylsuccinimide (9 mg., 48%).

Octamethyltetra-azaphorphin.—Dimethylsuccinimidine (150 mg.) was refluxed with chlorobenzene (5·5 c.c.) and nitrobenzene (4·5 c.c.) for 5 hr. The mixture was diluted with methanol, and the solid was filtered off and crystallised from chlorobenzene, giving prisms of metal-free octamethyltetra-azaporphin (59 mg., 45%) (Found : C, 67·2; H, 6·1; N, 25·5. Calc. for $C_{24}H_{26}N_8$: C, 67·6; H, 6·2; N, 26·3%) ($\lambda_{max.}$ in chlorobenzene : 6270, 5560 Å; cf. Baguley, France, Linstead, and Whalley, *J.*, 1955, 3521).

Microanalyses and spectrographic determinations were made in the microanalytical (Mr. F. H. Oliver) and the spectrographic (Mrs. A. I. Boston) laboratories of this Department.

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