

Heterocyclic Imines and Amines. Part III. Succinimidine.†*

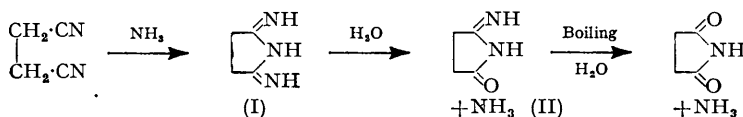
By J. A. ELVIDGE and R. P. LINSTAED.

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Addition of ammonia to succinonitrile yields succinimidine (I) (2 : 5-di-iminopyrrolidine), which has two reactive imino-groups. This pyrrolic derivative is compared with 1 : 3-di-iminoisoindoline; and its reactions with water, hydroxylamine, and aniline have been studied. The products (some of which are described in the earlier literature) have been degraded, and their structures are discussed. Blochmann's formulation of diphenylsuccinimidine is amended. Light-absorption data are given.

THE two previous papers in this Series * have dealt with aspects of the chemistry of 1 : 3-di-iminoisoindoline. Its potentialities for synthesis (Parts I and II; Elvidge and Linstead, *J.*, 1952, 5008; and forthcoming publications), resulting from the high reactivity of the imino-substituents, led us to examine analogous derivatives in the pyrrole series. The first of these prepared was succinimidine † (I).

This compound, hitherto unknown in the form of the free base, was readily obtained by heating succinonitrile (from acrylonitrile and hydrogen cyanide) with methanolic ammonia under pressure. This is similar to the preparation of di-iminoisoindoline from phthalonitrile (see Part I), though the conditions of the new reaction required more careful control to ensure a clean product. A satisfactory alternative (cf. Bayer Farbenfabr., Indian P. 43,679) was the treatment of succinonitrile at ordinary temperature with sodamide (communication from Imperial Chemical Industries Limited, Dyestuffs Division). The hydrochloride of succinimidine was described, but not investigated, by Pinner (*Ber.*, 1883, **16**, 352), who prepared it from diethyl succinimidoate dihydrochloride *via* succinamidine dihydrochloride, crystallisation of which from water effected ring-closure with elimination of the elements of ammonium chloride. This preparation was confirmed at Imperial Chemical Industries Limited (personal communication), and the derived picrate identified with that from the succinonitrile-ammonia reaction.



Neither succinimidine (I) nor its hydrochloride has a characteristic melting point. The salt is stable to cold water (Pinner, *loc. cit.*) but the base is remarkably sensitive to moisture and is best kept sealed at 0°. The base dissolved easily in water, and within a few minutes the solution smelled strongly of ammonia : 1 mol. was produced, and the monoimine, 5-imino-2-pyrrolidone (II), subsequently crystallised out almost quantitatively. This product with boiling water yielded succinimide with evolution of ammonia. 5-Imino-2-pyrrolidone (II) has been obtained (communication from Imperial Chemical Industries Limited) from Pinner's succinimidine hydrochloride and aqueous sodium hydroxide; also (though in a crude state) by Protiva, Řeřicha, and Jílek (*Chem. Listy*, 1950, **44**, 231) from the action of ammonia on ethyl β-ethoxycarbonylpropionimidoate hydrochloride, a preparation which confirms the structure.

For comparison with the above hydrolyses, 1 : 3-di-iminoisoindoline has been further

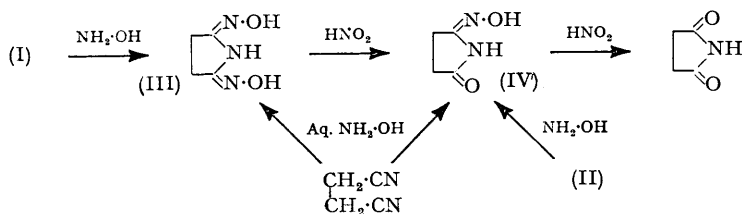
* Part I, *J.*, 1952, 5000; Part II, *J.*, 1953, 3593.

† Pinner's apt name for the compound (*Ber.*, 1883 **16**, 352), which is employed in Beilstein, 4th Edn., together with that of glutarimidine for the next higher homologue (Pinner, *Ber.*, 1890, **23**, 2942), will be used in our papers. On this system, 1 : 3-di-iminoisoindoline becomes phthalimidine, but unfortunately *Chem. Abstracts* has continued the use of this name in another, and illogical sense, *viz.* for 1-oxoisoindoline.

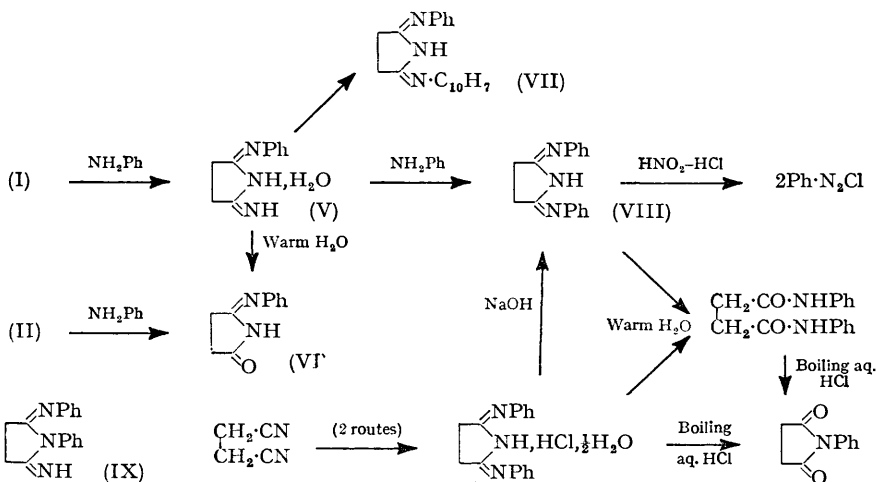
Compounds of the present class are capable of tautomerism, so that the generic term "imidine," which ignores the questions of fine structure, is a particularly good one. The strictly systematic names, such as 1 : 3-di-iminoisoindoline, are disadvantageous because they refer to definite bond structures.

examined. It is more stable to cold water, but during 3 days ammonia was evolved and 3-imino-1-oxoisindoline was then isolated in 70% yield. Boiling water hydrolysed the imino-oxoisindoline to phthalimide and ammonia.

With hydroxylamine hydrochloride in boiling ethanol, succinimidine afforded a dioxime (III). 1:3-Di-iminoisindoline similarly gave a dioxime, whilst 3-imino-1-oxoisindoline



yields a monoxime (Part I). The dioxime from succinimidine was identical with the product of interaction of succinonitrile and 2 mols. of hydroxylamine in aqueous alcohol (Sembritzki, *Ber.*, 1889, **22**, 2958; Garry, *Ber.*, 1891, **24**, 3426). Garry stated (without details) that the dioxime was decomposed by 1 mol. of nitrous acid to a monoxime, m. p. 197°, identical with a product from succinonitrile and 1 mol. of aqueous-alcoholic hydroxylamine. We confirmed Garry's experiments but found that repeated crystallisation of the monoxime (IV) raised its m. p. to 219°, which might perhaps be a result of *syn-anti*-isomerisation. An identical monoxime was formed by heating 5-imino-2-pyrrolidone (II) with hydroxylamine hydrochloride. Treatment of this monoxime (IV) with nitrous acid gave succinimide in high yield. The structures of the oximes (III) and (IV) are thus certain.



Succinimidine reacted stepwise with aniline, like 1:3-di-iminoisindoline (Part II).

In boiling methanol, the monophenylimine was produced, which crystallised as the monohydrate (V). It resisted complete dehydration under a high vacuum. The cyclic structure (V) followed from the absorption spectrum (see Table) and the formation of 5-phenylimino-2-pyrrolidone (VI) with warm water. The latter compound (VI) had been prepared by Comstock and Wheeler (*Amer. Chem. J.*, 1891, **13**, 520; also Wheeler and Barnes, *ibid.*, 1900, **23**, 135) from *O*-ethylsuccinimide and aniline in the cold, a route which indicates the gross structure. We prepared the phenyliminopyrrolidone (VI) by heating 5-imino-2-pyrrolidone (II) with aniline.

In boiling butanol mono-*N*-phenylsuccinimidine (V) condensed with a further mol. of amine. β -Naphthylamine yielded the naphthylimino-phenyliminopyrrolidine (VII), and aniline the 2:5-diphenyliminopyrrolidine (VIII).

Blochmann (*Ber.*, 1887, 20, 1856) fused succinonitrile with aniline hydrochloride, and after crystallising the product from water obtained an infusible hydrochloride hemihydrate, which yielded a diphenylsuccinimidine with alkali. We repeated this preparation, and also obtained a similar salt from diethyl succindi-imidoate dihydrochloride and aniline in the cold, and showed that the derived base was identical with Blochmann's and with our diphenyl compound (VIII) from succinimidine. For comparison, we fused phthalonitrile with aniline hydrochloride and obtained 1:3-diphenyliminoisoindoline hydrochloride: this has previously been prepared by the imidic ester and by the imidine route (Parts I and II). Blochmann formulated his diphenylsuccinimidine as (IX) because with boiling water the hydrochloride gave *N*-phenylsuccinimide. We regard his structure as incorrect, though we confirmed the degradation, which recalls the (misleading) formation of *N*-phenylphthalimide from 1-oxo-3-phenyliminoisoindoline under certain conditions (Part II, *loc. cit.*). Our structure (VIII) is given by analogy with that of compound (III) and derivatives in the isoindoline series, and follows from the preparation from (V). When either the base (VIII) or its salt was warmed with water, succindianilide was formed—and not an oxo-derivative, which would have been expected from (IX) by analogy with the hydrolysis of (V) to (VI). Succindianilide was converted into *N*-phenylsuccinimide in boiling water containing a trace of acid, and thus a source of the imide degradation product emerges. The best evidence for structure (VIII) was the rapid formation of 2 mols. of phenyldiazonium chloride (converted into phenylazo-2-naphthol) when the compound was treated in dilute hydrochloric acid with sodium nitrite.

1:3-Diphenyliminoisoindoline was not degraded cleanly by nitrite and acid, affording <1 mol. of phenyldiazonium salt, and further differed from diphenylsuccinimidine in being stable to boiling water, whilst its hydrochloride was quickly hydrolysed to phthalimide and not to phthalic dianilide.

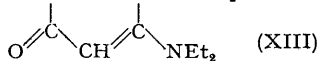
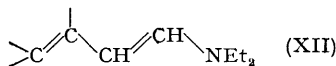
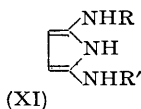
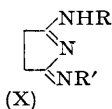
Light absorption characteristics in methanol.

| Compound (I) | $\lambda_{\max.}$ (Å) | ϵ | Compound (V) | $\lambda_{\max.}$ (Å) | ϵ |
|--------------|-----------------------|------------|---------------|-----------------------|------------|
| (I) | 2370 | 20,000 | (V) | 2400 | 19,600 |
| (II) * | 2270 | 22,000 | (V) | 2510 | 13,300 |
| (III) | 2270 | 14,700 | (V) | 2800 | 12,600 |
| (III) | 2330 † | 12,800 | (VI) | 2270 | 5,600 |
| (IV) | 2260 | 12,000 | (VIII) | 2650 | 10,600 |
| Succinimide | — | >200 | (VIII) | 2270 | 13,000 |
| | | | (VIII) | 2800 | 16,700 |
| | | | (VIII) | 2940 | 17,400 |
| | | | Hydrochloride | 2270 | 15,000 |
| | | | hemihydrate | 2511 | 7,700 |
| | | | of (VIII) | 2580 | } 8,500 |
| | | | | 2650 | |
| | | | | 3120 | |

* In water.

† Inflection.

The 2:5-di-iminopyrrolidine structures account satisfactorily for the chemistry which we have outlined of succinimidine and its derivatives. By analogy with the isoindoline series (Part II) the incompletely substituted compounds should be capable of tautomerism, so that they might equally well be represented as amino-imino-pyrrolines (X).



The systems (XII) and (XIII) show high-intensity absorption in the 2800—3000 Å region (Braude, *Ann. Reports*, 1945, 42, 105), and the substitution of N for C within 1:3-dienes has little effect on the position of maximal light absorption (Barany, Braude, and Pianka, *J.*, 1949, 1898). Arguing by analogy it would be expected that compounds of type (X) would absorb strongly at or above 3000 Å. The absence of such absorption suggests that the form (X) makes no appreciable contribution to the structures of com-

pounds (I), (II), (III), (IV), and (VI) in solution. The fine structures of (V) and (VIII) are less certain; in these compounds the form (X) may contribute.

An additional general possibility is the diaminopyrrole type of structure (XI). There is no chemical evidence in favour of this from the reactions so far studied, and the spectroscopic evidence is inconclusive because the effect of substituents on light absorption among pyrroles is considerable (Cookson, *J.*, 1953, 2789; Gore and Linstead, unpublished work) but has not yet been placed on a sufficiently firm footing for useful predictions to be made. The fine structure and tautomerism of succinimidine and related substances are being studied further.

EXPERIMENTAL

Succinimidine (2 : 5-Di-iminopyrrolidine).—(a) A solution of succinonitrile (40 g.) (Kurtz, G.P. 707,852; *Org. Reactions*, 5, 111) in dry methanol (150 c.c.) was treated cautiously with liquid ammonia (70 c.c.), then heated in a stout glass vessel at 70° for 18 hr., and cooled. The faintly buff-coloured crystalline mass (33.6 g.) was washed with ethyl acetate and dry ether; evaporation of the mother-liquors under reduced pressure gave a second crop (7 g.) (total yield, 85%). From dimethylformamide, 2 : 5-di-iminopyrrolidine crystallised as colourless prisms, which decomposed above 200° without melting (Found: C, 49.65, 49.0; H, 7.45, 7.3; N, 42.3, 42.5. $C_4H_7N_3$ requires C, 49.4; H, 7.3; N, 43.3%).

(b) Succinonitrile (8 g.) was dissolved in a cold solution of sodamide (5 g.) in formamide (30 c.c.) (cf. Bayer, *loc. cit.*), and after 48 hr. the colourless crystalline product (4.5 g., 47%) was collected and washed with cold formamide, *n*-propanol, ethyl acetate, and ether (Found: N, 40.6%); a trace of a sodium compound was present. That the product was essentially succinimidine was confirmed by converting a portion (100 mg.) with cold water into 5-imino-2-pyrrolidone (90 mg.), m. p. 244—246° (decomp.) undepressed in admixture with authentic material.

Hydrolysis to 5-Imino-2-pyrrolidone.—A solution of succinimidine (1.50 g.) [from method (a)] in cold water (5 c.c.) had pH >10.5, and after 5 min. smelt of ammonia. Next day, 5-imino-2-pyrrolidone (1.50 g., 99%), m. p. 241—246° (decomp.), had separated: it crystallised readily from water, as large colourless prisms, m. p. 250° (decomp.) with darkening from ca. 240° (Found: C, 49.2; H, 6.4; N, 28.3. $C_4H_6ON_2$ requires C, 49.0; H, 6.2; N, 28.6%). Protiva and Jílek (*loc. cit.*) gave m. p. 190—195° raised to 227—230° (decomp.) by crystallisation from aqueous ethanol.

Succinimidine (35.5 mg.) was hydrolysed with cold water (3 c.c.) in a Conway unit, the liberated ammonia being absorbed by 0.941N-sulphuric acid (1.00 c.c.) contained in the second compartment. Next day, the acid required 1.24 c.c. of 0.520N-sodium hydroxide for neutralisation (Found: NH_3 , 0.92 mol.).

Hydrolysis of 5-Imino-2-pyrrolidone.—The imine (500 mg.) was boiled with water (5 c.c.) for 2 hr., during which ammonia was evolved. A trace of insoluble matter was filtered off, and the filtrate evaporated, yielding succinimide (426 mg., 84%), m. p. 118—120°. After being crystallised from ethanol, the latter had m. p. 121—123° alone and in admixture with an authentic sample.

Hydrolysis of 1 : 3-Di-iminoisindoline.—A solution of the di-imine (0.5 g.) in water (25 c.c.) deposited during 2 days 3-imino-1-oxoisindoline (0.15 g.), m. p. and mixed m. p. 201—203°. Concentration of the filtrate to 5 c.c. in a vacuum-desiccator, during a third day, afforded another crop (0.2 g.) (total yield, 70%), m. p. 194—198° and mixed m. p. 198—203°.

3-Imino-1-oxoisindoline (500 mg.) was boiled with water (25 c.c.) for 1 hr., during which ammonia was evolved. The solution was evaporated under reduced pressure, and the residue taken up in ethanol. On concentration of the extract, phthalimide (418 mg., 83%) separated, m. p. and mixed m. p. 230—231°.

2 : 5-Dihydroxyiminopyrrolidine.—(a) *Preparation.* (i) Succinimidine (0.5 g.) and hydroxylamine hydrochloride (1 g.) were boiled together in ethanol (30 c.c.) for 2.5 hr. Ammonium chloride was filtered off, and the filtrate evaporated to 15 c.c. 2 : 5-Dihydroxyiminopyrrolidine (0.5 g.) separated as needles with m. p. 170—180° (decomp.), raised to 211° (decomp.) by repeated crystallisation from ethanol (charcoal) (Found: C, 37.2; H, 5.6; N, 32.5. Calc. for $C_4H_7O_2N_3$: C, 37.2; H, 5.5; N, 32.55%).

(ii) Interaction of succinonitrile (2 g.) in ethanol (10 c.c.) with hydroxylamine (from 3.46 g. of the hydrochloride) in water (15 c.c.) at 65—70° (Garny, *loc. cit.*) afforded a product with

m. p. ca. 165° (decomp.), raised by crystallisation from water to 193° (decomp.) (yield then 1.25 g.). After being dried at 90° under reduced pressure, and recrystallised from ethanol, the dioxime had m. p. 205—206° alone and when mixed with that from succinimidine. Garny recorded m. p. 207°. A Sembritzki's colour reactions (*loc. cit.*) were confirmed.

(b) *Degradation.* A solution of the dioxime (295 mg.) in warm water (15 c.c.) was chilled in ice, and treated with sodium nitrite (160 mg.) in water, and then with 2*N*-hydrochloric acid (1.5 c.c.), added dropwise. Each drop produced a yellow colour, momentarily, and there was evolution of gas. After 5 min. at room temperature, the solution was evaporated under reduced pressure, and the colourless residue extracted with hot ethanol. Evaporation of the extract yielded the monoxime (140.5 mg.), m. p. 168—170° (decomp.), raised to 214—215° (decomp.) by crystallisation (twice) from ethanol (Found: N, 24.8%). The m. p. was not depressed by the authentic monoxime (IV), m. p. 219° (decomp.), described below.

1:3-Dihydroxyiminoisoindoline.—1:3-Di-iminoisoindoline (0.5 g.) and hydroxylamine hydrochloride (1 g.) were heated together in ethanol (40 c.c.) under reflux for 4 hr.; the solution was then concentrated under reduced pressure, and the crystalline product washed with water (yield, 0.53 g.). From isopropanol, 1:3-dihydroxyiminoisoindoline formed prisms, m. p. 261° (decomp.) (Found: C, 53.8; H, 3.85; N, 23.4. $C_8H_7O_2N_3$ requires C, 54.25; H, 4.0; N, 23.7%). It gave a dark yellow-brown colour with ethanolic cupric acetate, and was soluble in aqueous sodium hydroxide but not in cold concentrated hydrochloric acid. Light absorption in ethanol: max. at 2270, 2510, 2570 (inflection), 2650, 2970 Å ($\epsilon = 12,700, 9,000, 11,000, 12,700, 14,200$, respectively).

Kampschmidt and Wibaut (*Rec. Trav. chim.*, 1952, **71**, 601) appear to have obtained the dioxime, m. p. 264°, from phthalaldehyde and hydroxylamine.

3-Hydroxyimino-1-oxoisoindoline (Part I) in ethanol has max. at 2510, 2570, 2650, 3050 Å ($\epsilon = 9,400, 11,700, 14,000, 5,000$, respectively).

5-Hydroxyimino-2-pyrrolidone.—(a) *Preparation.* (i) 5-Imino-2-pyrrolidone (1 g.), hydroxylamine hydrochloride (1 g.), ethanol (40 c.c.), and 2-methoxyethanol (15 c.c.) were heated together under reflux for 6 hr. The solution was concentrated to small bulk under reduced pressure, and the solid extracted with boiling ethanol. Recrystallisation of the extracted material (0.8 g.) from ethanol (several times) afforded prisms of 5-hydroxyimino-2-pyrrolidone, m. p. 219° (decomp.) (Found: C, 42.4; H, 5.6; N, 24.7. Calc. for $C_4H_6O_2N_2$: C, 42.1; H, 5.3; N, 24.6%).

(ii) Succinonitrile (2 g.) in ethanol (10 c.c.), and hydroxylamine (from 1.73 g. of the hydrochloride) in water (10 c.c.), were kept together at 65° overnight. The solution was evaporated, and the product, m. p. ca. 185° (decomp.), isolated by extracting the residue with boiling ethanol (Garny, *loc. cit.*). After two crystallisations from ethanol the 5-hydroxyimino-2-pyrrolidone had m. p. 211—212° (decomp.) undepressed in admixture with the preceding preparation. Garny recorded m. p. 197° (decomp.). The colours given with ferric chloride and copper acetate described by him were confirmed, but no blue colour was obtained with sodium hydroxide.

(b) *Degradation.* A solution of 5-hydroxyimino-2-pyrrolidone [300 mg.; m. p. 219° (decomp.)] in warm water (15 c.c.) was chilled in ice, and treated with sodium nitrite (200 mg.) in water, and then dropwise with 2*N*-hydrochloric acid (2 c.c.). After 5 min., the solution was evaporated under reduced pressure, and the residue dried by distilling chloroform from it. By extraction of the residue with hot acetone, succinimide (260 mg., 1.99 mols.) was isolated, m. p. 122—123° and mixed m. p. 122—124°.

2-Imino-5-phenyliminopyrrolidine.—A solution of succinimidine (2 g.) and aniline (4 c.c.) in methanol (35 c.c.) was boiled under reflux for 4 hr. Evaporation of the solution left a gum which slowly crystallised; the solid (3 g.) was washed with ether. From dimethylformamide-benzene, 2-imino-5-phenyliminopyrrolidine crystallised as colourless needle-clusters of the hydrate, m. p. 169° (decomp.) with darkening from ca. 160° (Found: C, 62.95; H, 7.05; N, 21.7. $C_{10}H_{11}N_3 \cdot H_2O$ requires C, 62.8; H, 6.85; N, 22.0%). This was partially dehydrated (i) at 50°/10⁻⁵ mm., or (ii) by several crystallisations from dry acetone; the m. p. was unchanged [Found: (i) C, 67.45; H, 6.7. (ii) C, 64.9; H, 6.8. $C_{10}H_{11}N_3 \cdot \frac{1}{2}H_2O$ requires C, 67.6; H, 6.5. $C_{10}H_{11}N_3 \cdot \frac{2}{3}H_2O$ requires C, 64.8; H, 6.7%].

Hydrolysis to 5-Phenylimino-2-pyrrolidone.—The preceding imine hydrate (500 mg.) was kept in a mixture of methanol (5 c.c.) and water (1 c.c.) at 45° overnight. Ammonia was evolved. Evaporation of the solution to small bulk afforded a solid (352 mg.) with m. p. 204—206°, raised to 215—217° after crystallisation from ethanol. The m. p. was not depressed by the phenylimino-pyrrolidone next described.

5-Phenylimino-2-pyrrolidone.—5-Imino-2-pyrrolidone (0.33 g.) and aniline (0.5 c.c.) were boiled together in 2-methoxyethanol (5 c.c.) for 3 hr., during which ammonia was evolved. Next day, 5-phenylimino-2-pyrrolidone had separated as leaflets (0.5 g.), m. p. 216° (with darkening from ca. 205°), raised to 219° by crystallisation from *n*-propanol (Found: C, 68.7; H, 6.1; N, 15.9. Calc. for C₁₀H₁₀ON₂: C, 69.0; H, 5.8; N, 16.1%). Comstock and Wheeler (*loc. cit.*) recorded m. p. 216°.

2-2'-Naphthylimino-5-phenyliminopyrrolidine.—2-Imino-5-phenyliminopyrrolidine (1 g.), 2-naphthylamine (0.85 g.), and *n*-butanol (15 c.c.) were heated together under reflux for 3 hr., ammonia being evolved. The solution was evaporated, and the residue triturated with ether, and then taken up in boiling methanol (charcoal). After several crystallisations from methanol-water, 2-2'-naphthylimino-5-phenyliminopyrrolidine was obtained as a colourless crystalline powder, m. p. 191° (decomp.) (Found: C, 80.5; H, 5.5; N, 13.6. C₂₀H₁₇N₃ requires C, 80.2; H, 5.7; N, 14.1%).

2:5-Diphenyliminopyrrolidine.—(a) Preparation. (i) 2-Imino-5-phenyliminopyrrolidine (1 g.), aniline (1 c.c.), and *n*-butanol (15 c.c.) were heated under reflux for 4 hr. The solution was evaporated, and the solid (1.2 g.) washed with ether. Several crystallisations from methanol-water yielded the 2:5-diphenyliminopyrrolidine as colourless needles, m. p. 204° (decomp.) (Found: C, 77.2; H, 6.35; N, 17.0. C₁₆H₁₅N₃ requires C, 77.1; H, 6.05; N, 16.85%).

(ii) Powdered diethyl succindi-imidoate dihydrochloride (1 g.) (Pinner, *Ber.*, 1883, 16, 352) and aniline (2 c.c.) were mixed in dry methanol. Next day, the solid was washed with ethanol and dried. From water, the 2:5-diphenyliminopyrrolidine hydrochloride hemihydrate (1.3 g.) crystallised as long needles, which darkened, without melting, above 230° (Found: C, 65.4; H, 6.0; N, 14.5. C₁₆H₁₅N₃.HCl. $\frac{1}{2}$ H₂O requires C, 65.2; H, 5.8; N, 14.3%).

Treatment of this salt, suspended in ethanol, with the calculated quantity of aqueous sodium hydroxide yielded 2:5-diphenyliminopyrrolidine, which crystallised from methanol-water as needles, m. p. and mixed m. p. 204° (decomp.) (Found: N, 16.9%).

(iii) Fusion of succinonitrile (0.62 g.) with powdered aniline hydrochloride (2 g.) at 165° for 15 min. (Blochmann, *loc. cit.*), and crystallisation of the product from water, gave the hydrochloride hemihydrate (1.3 g.) (Found: C, 64.95; H, 5.8%). With ethanolic aqueous sodium hydroxide, this was converted into 2:5-diphenyliminopyrrolidine, which crystallised from methanol as needles, m. p. and mixed m. p. 203—204° (decomp.).

(b) Degradation. (i) A solution of 2:5-diphenyliminopyrrolidine hydrochloride hemihydrate (0.2 g.) in a mixture of water (7 c.c.) and methanol (2 c.c.) was kept at 60—70° for 6 hr., and then at room temperature overnight. Leaflets (neutral, insoluble in hot water) had then separated, m. p. 225—226° undepressed by succindianilide (m. p. 230°), prepared from succinoyl chloride (Morrell, *J.*, 1914, 105, 1733).

(ii) 2:5-Diphenyliminopyrrolidine (0.2 g.) was similarly hydrolysed, in methanol (10 c.c.), with water (4 c.c.) at 60—70° for 6 hr., to succindianilide, m. p. 228—229° and mixed m. p. 229—230°.

The diphenyliminopyrrolidine was recovered in 65% yield after being kept in a mixture of methanol (10 c.c.) and water (3 c.c.) at 40—45° for 6 hr.

(iii) 2:5-Diphenyliminopyrrolidine hydrochloride hemihydrate (0.5 g.) was boiled with water (20 c.c.) for 1 hr., and the solution then cooled in ice. *N*-Phenylsuccinimide (0.25 g.) separated as prismatic needles, m. p. 152—153° raised to 154° by recrystallisation from water (Found: C, 68.25; H, 5.2; N, 8.0. Calc. for C₁₀H₉O₂N: C, 68.6; H, 5.2; N, 8.0%).

When succindianilide (50 mg.), m. p. 230°, was heated under reflux for 6 hr. with ethanol (3 c.c.), water (20 c.c.), and concentrated hydrochloric acid (0.1 c.c.), and the solution then concentrated under reduced pressure, needles separated, m. p. 150—152° undepressed by *N*-phenylsuccinimide.

(iv) 2:5-Diphenyliminopyrrolidine hydrochloride hemihydrate (500 mg.) was dissolved in hot 0.5*N*-hydrochloric acid (15 c.c.). The solution was chilled in ice, and treated dropwise with sodium nitrite (0.3 g.) in water. After 5 min., 2-naphthol (0.5 g.) in *N*-sodium hydroxide (16 c.c.) was added, and the orange-red precipitate was subsequently collected, washed well with water, and dried (yield: 812.5 mg., 1.93 mols.). It had m. p. 128—129°, and mixed m. p. 129—130° with authentic phenylazo-2-naphthol.

Reaction of Phthalonitrile with Aniline Hydrochloride.—An intimate mixture of the nitrile (1.7 g.) and the salt (3.4 g.) was heated at 235—240° for 30 min. The dark product was triturated with water, yielding a yellow powder (1.2 g.), m. p. 245—250°, which crystallised from acetic acid as yellow prisms, m. p. 275—278° undepressed by 1:3-diphenyliminoisindoline hydrochloride, m. p. 278°.

Degradation of 1 : 3-Diphenyliminoisoindoline with Nitrous Acid.—Sodium nitrite (250 mg.) in water (3 c.c.) was added dropwise to an ice-cooled solution of the base (400 mg.) in a mixture of dioxan (30 c.c.) and 50% aqueous acetic acid (10 c.c.). The mixture was kept at room temperature : pale yellow needles separated and later redissolved. After 45 min. the solution was poured into alkaline 2-naphthol (0.4 g. in an excess of N-sodium hydroxide) at 0°, and the crude reddish precipitate was collected and washed (382 mg., 0.95 mol.). This crystallised from ethanol-water, giving orange-red needles of phenylazo-2-naphthol but in only 30% yield.

An even cruder product resulted when the reaction time, or the quantity of nitrite, was increased.

Stability of 1 : 3-Diphenyliminoisoindoline to Water.—The base (0.2 g.) was recovered, m. p. 124—126° and mixed m. p. 125—127°, after being heated under reflux with water (3 c.c.) and ethanol (7 c.c.) for 6 hr.

1 : 3-Diphenyliminoisoindoline hydrochloride was boiled in aqueous ethanol for 30 min., and the then almost colourless solution cooled in ice. Phthalimide separated, m. p. and mixed m. p. 230—231°; it crystallised from benzene as laths, m. p. 231° (Found : C, 65.1; H, 3.5. Calc. for $C_8H_5O_2N$: C, 65.3; H, 3.5%).

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