37. *Heterocyclic Imines and Amines. Part IX.* Glutarimidine and the Imidine from α-Phenylglutaronitrile.*

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Addition of ammonia to glutaronitrile gives the 6-membered ring compound, glutarimidine (II). This, like succinimidine, has two reactive imino-groups which undergo displacement reactions with water, hydroxylamine, and aniline.

There are apparently errors in early work by Biedermann on products from glutaronitrile and hydroxylamine.

α-Phenylglutaronitrile with ammonia yields the analogous α-phenylglutarimidine (XII), which condenses with aniline and hydroxylamine, the latter yielding the dioxime (XIII). This was degraded to α-phenylglutarimide, in turn synthesised from α-phenylglutaric acid.

Light absorptions are given (and revised for some succinimidine derivatives) and fine structures are discussed. The glutarimidines show no great readiness to undergo dehydrogenation, and are regarded as di-imino- or amino-imino-piperidines, not as diaminodihydropyridines.

The imidines described in previous papers [1-4] were 5-membered-ring compounds, prepared by addition of ammonia to 1 : 2-dinitriles. We have now obtained imidines with 6-membered rings, as readily, from the 1 : 3-dinitriles glutaronitrile and α-phenylglutaronitrile.

Glutarimidine.—Glutaronitrile (I) with methanolic ammonia at 100° afforded crystalline glutarimidine † (II), $C_5H_9N_3$, characterised as the picrate. The cyclic imidine structure (II) for the new base was indicated by its reactions and confirmed by infrared spectroscopy which showed the absence of a nitrile group (see Table 1, p. 210). Neither the base nor

* Part VIII, *J.*, 1957, 709.
† Concerning nomenclature, see *J.*, 1954, 442.

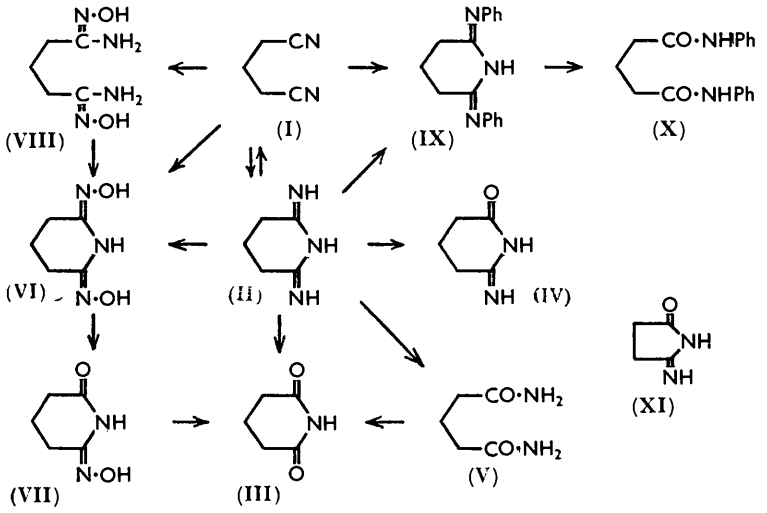
[1] Elvidge and Linstead, *J.*, 1952, 5000.
[2] *Idem*, *J.*, 1954, 442.
[3] Ficken and Linstead, *J.*, 1955, 3525.
[4] Linstead and Whalley, *ibid.*, p. 3530.

a salt has been described before, although Pinner [5] apparently obtained a molecular compound of the hydrochloride with glutardiamidine dihydrochloride from the reaction of di*iso*butyl glutardi-imidate with ammonia.

Glutarimidine was unstable to heat, and in boiling butanol dissociated into glutaronitrile (I) and ammonia. Analogous reversal of imidine formation occurred [6] on strong heating of di-imino*iso*indoline, which gave phthalonitrile and ammonia.

Glutarimidine resembled succinimidine [2] in being readily hydrolysed but there was a difference in that stepwise control of the hydrolysis was not easily achieved. On exposure of glutarimidine to moist air, ammonia and a mixture of solids were formed. Treatment of glutarimidine with cold water also gave a mixture, from which we isolated glutarimide (III). An intermediate hydrolysis product, the imino-imide (IV), was obtained when an ethanolic-toluene solution of the imidine was, by chance, exposed to the atmosphere for some days. The cyclic structure (IV) which is isomeric with glutaric cyano-amide [7] was confirmed by the infrared absorption (Table 1) which showed no nitrile stretching and a general similarity to that of iminosuccinimide (XI). After treatment of glutarimidine with boiling water, sparingly-soluble glutaramide (V) was isolated, the hydrolysis under these conditions having taken a different course, as discussed below.

Glutarimidine (II) condensed with 2 molecular proportions of hydroxylamine hydrochloride in boiling ethanol, as expected: [2] the cyclic dioxime structure (VI) for the product was confirmed by successive conversion with nitrous acid into the monoxime [8] (VII), and thence into glutarimide (III). The cyclic dioxime (VI) was also formed from glutaronitrile and 2 mols. of hydroxylamine at 90°. From glutaronitrile and hydroxylamine at 60—70°, the acyclic bisamidoxime (VIII) was obtained in low yield. This product showed a double melting point which suggested that it cyclised on heating: indeed, sublimation converted it smoothly into the cyclic dioxime (VI).



These inter-relations make the structures (VI), (VII), and (VIII) certain. We believe therefore that there are errors in a paper by Biedermann,[9] describing products from glutaronitrile and hydroxylamine. The melting points that he gave for compounds assigned structures (VIII) and (VI) are very different from ours. Moreover, he obtained his bisamidoxime (VIII) as a hydrate whereas, without precautions, our product (VIII) was

[5] Pinner, *Ber.*, 1890, **23**, 2942.
[6] Elvidge and Linstead, *J.*, 1955, 3536.
[7] Beilstein, " Handbuch der Organischen Chemie," 4th edn., H **2**, 634.
[8] Garny, *Ber.*, 1891, **24**, 3426.
[9] Biedermann, *Ber.*, 1889, **22**, 2967.

obtained anhydrous. That his " bisamidoxime " had perhaps been nadvertently converted into the cyclic dioxime (VI), as the melting point suggests, is supported by Garny's conversion [8] of it with 1 mol. of nitrous acid into the cyclic monoxime (VII).

Attempts to condense glutarimidine with 2-aminopyridine, 2 : 6-diaminopyridine, and di-imino*iso*indoline were abortive. However, condensation with aniline readily gave the diphenylimino-derivative (IX). The same compound (IX) was also obtained in good yield by basification of a hydrochloride produced by melting aniline hydrochloride with glutaronitrile. This last route to an *NN'*-diphenyl-imidine derivative had earlier been successful with succino- and phthalo-nitrile,[2] but had failed with αα'-dimethylsuccinonitrile.[4]

Hydrolysis of the diphenylimino-compound (IX) with boiling water yielded glutardianilide (X), a result analogous to the production of succindianilide from 2 : 5-diphenyliminopyrrolidine.[2] The hydrolysis also recalls that of glutarimidine to glutaramide, mentioned above. It is conceivable that the hydrolysis of an imidine [and derivatives such as (IX)] proceeds by ring opening to an amidino-amide and reclosure: there is, then, the possibility at 100°, that hydrolysis of the transient intermediate amidine will be faster than reclosure of the ring. In that event, diamide is formed, rather than imino-imide (and thence imide).

α-*Phenylglutarimidine* (2 : 6-*Di-imino*-3-*phenylpiperidine*).—α-Phenylglutaronitrile, readily available from benzyl cyanide and acrylonitrile,[10] reacted smoothly with ammonia in methanol at 80° to provide the new imidine (XII). Its infrared absorption, apart from phenyl vibrations, was similar to that of glutarimidine (see Table 1).

TABLE 1. *Infrared absorption* (*Nujol mulls*).

Compound	Principal max. (cm.$^{-1}$)
Glutarimidine (II)	Broad NH absorption; 1688, 1603, 1559, 1414, 1332, 1310, 1217, 1186, 1145, 1087, 1057(w), 966, 918, 910, 885, 758(w), 724(w).
α-Phenylglutarimidine (XII)	Broad NH absorption; 1674, 1600, 1534, 1335, 1292(w), 1284, 1258, 1220, 1100, 1070(w), 1039(w), 991, 930, 908, 876, 769, 750, 724(w), 699.
Iminoglutarimide (IV)	3145, 3072, 1816(w), 1697, 1661, 1531(w), 1332, 1266, 1255, 1176, 1143, 1052, 918, 813, 759, 723(w), 670.
Iminosuccinimide (XI)	3175, 3106, 1767(w), 1681, 1621, 1520, 1339(w), 1290, 1247, 1215, 1152, 1005, 926, 825, 762, 722(w), 676.

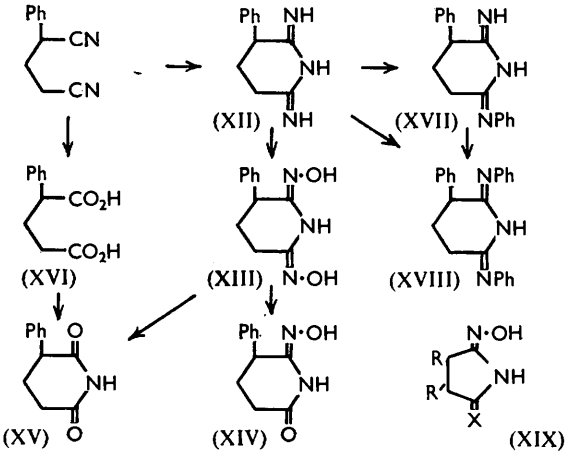
α-Phenylglutarimidine (XII) with hydroxylamine hydrochloride in boiling methanol yielded the dioxime (XIII), which was obtained both as a methanol solvate and solvent-free. Mild degradation of the dioxime with nitrous acid afforded a monoxime, presumably the " hindered " isomer (XIV), whilst hot dilute nitric acid smoothly gave the imide (XV). An authentic specimen of the imide was prepared by distillation of the ammonium salt of α-phenylglutaric acid (XVI), in turn derived by hydrolysis of α-phenylglutaronitrile. With aniline in boiling methanol, the imidine gave a monophenylimine, assigned the " unhindered " structure (XVII). At a higher temperature, with an excess of boiling aniline, the second imino-group was replaced, 3-phenyl-2 : 6-diphenyliminopiperidine (XVIII) being obtained.

Structure and Light Absorption.—The di-iminopiperidine structures (XX), (XXa) given to the foregoing compounds accounted satisfactorily for their reactions. Nevertheless, as for succinimidine,[2] the possibility of tautomerism to the amino-imino- (XXI) and diamino-forms (XXII) warranted consideration.

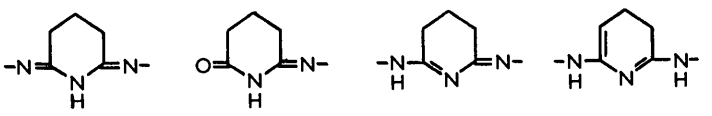
Tautomerism to the diamino-structure (XXII) could be rejected for the present system. This structure is formally a dihydropyridine, so that if tautomerism to this were real the compounds would be expected to be unstable and to undergo dehydrogenation to 2 : 6-diaminopyridine derivatives easily. But the compounds [even the favourable derivative (XVIII)] were rather stable. Moreover, α-phenylglutarimidine and its derivatives and the corresponding glutaric compounds have similar light absorptions (Table 2). This

[10] Koelsch, *J. Amer. Chem. Soc.*, 1943, **65**, 437.

shows that the α-phenyl group is not conjugated with the nitrogenous chromophore, and therefore that the form (XXII) makes no contribution to the structure of these compounds.



It was argued previously [2] that the diene system (XXI) would be expected to absorb light strongly in the 300 mμ region. Consequently it is concluded that the *N*-phenylglutarimidine and -α-phenylglutarimidine derivatives (IX), (XVII), and (XVIII), which



have maxima at approximately 290 mμ (Table 2), like the corresponding succinimidine derivatives,[2,3,4] probably exist in the di-imino-form (XX), but more evidence is being sought on this point.

TABLE 2. *Light absorptions (in ethanol, except as indicated).*

Compound	$\lambda_{max.}$ (mμ)	$10^{-3}\varepsilon$	Compound	$\lambda_{max.}$ (mμ)	$10^{-3}\varepsilon$
Glutarimidine (II)	252	17·2	Monoxime (XIX; R = R′ = H, X = O) [e]	220	13·0
Imino-imide (IV)	239	9·6	Dioxime (XIX; R = R′ = H, X = N·OH) [e]	228	13·3
Glutarimide (III) [a]	198	13·3 [12]	Monoxime (XIX; orientation probably [11] R = Me, R′ = H, X = O) [d]	221	10·0
Dioxime (VI)	234	18·8	Dioxime (XIX; R = Me, R′ = H, X = N·OH)	228	18·1
Monoxime (VII)	226	11·0	Monoxime (XIX; R = R′ = Me, X = O) [e]	221·5	10·5
Diphenylimine (IX)	228, 291	15·8, 11·8	Monoxime (XIX; R = R′ = ·[CH$_2$]$_4$·, X = O) [f]	221·5	10·4
α-Phenylglutarimidine (XII)	256	18·0			
α-Phenylglutarimide (XV) [b]	188, 201 *	51·2, 23·0			
Dioxime (XIII)	238	19·0			
Monoxime (XIV)	217,* 229	11·2, 9·4			
Phenylimine (XVII)	258, 290	15·8, 9·2			
Diphenylimine (XVIII)	227, 288	32·8, 9·75			
Succinimide [a]	191	15·4 [12]			

* Inflexion.
[a] In MeCN. } These measurements were very kindly made by Dr. D. W. Turner of
[b] In 50 : 1 hexane–MeCN. } this Department.
[e] In MeOH; revised data, correcting that in ref. 1.
Correction to data in (*d*) ref. 11, (*e*) ref. 4, *f* (ref. 3).

The tautomeric structure (XXI) is formally a tetrahydropyridine, but it should be reasonably resistant to dehydrogenation because aromatisation to a diaminopyridine could occur only by rearrangement. In fact, dehydrogenation did not accompany the reactions

of the glutarimidines (II) and (XII) with aniline at its boiling point. This behaviour contrasts with that of the substituted succinimidines, *cis*-hexahydrophthalimidine [3] and αα'-dimethylsuccinimidine,[4] which both yield maleimidine derivatives when condensed with aniline under mild conditions, but the dehydrogenation here does not necessitate rearrangement.

A salient feature of glutarimidine and its hydrolysis and hydroxylamine reaction products is their absorption at longer wavelengths than the corresponding succinimidine derivatives,[2,3,4,11] (Table 2). (Initial apparent anomalies led to the redetermination of the spectra of the succinic compounds. Revised data, obtained with a Perkin-Elmer Spectracord 4000, are included in Table 2.) The bathochromic shift for glutarimidine was taken at first to signify a contribution to the structure from the amino-imino-tautomer (XXI). However, tautomerism could hardly be invoked to explain the shift between the oximes in the glutaric series (VI) and (VII) and those in the succinic series (XIX). None of these derivatives shows hydroxylamine character (*i.e.*, instability, ready oxidation) and they all are certainly best represented as having the fixed hydroxyimino-structures of types (XX) and (XIX). It appeared therefore that the shifts were related to the change in ring size between the glutaric and the succinic series. Indeed, this is the basis of Turner's explanation [12] for the longer-wavelength absorption of glutarimide over succinimide. With the expansion in ring size there is no longer coplanarity within the imide group because the carbonyl groups are now twisted about the CO–N linkages. This change in conformation both increases the energy of the ground state and decreases that of the excited state, thus reducing the excitation energy, for an $N \longrightarrow V$ transition of the –CO–NH– chromophore. If the absorption bands for the (structurally closely related) imines and derived oximes and imino-imides arise also from $N \longrightarrow V$ transitions of the analogous –C(:NR)–NH– chromophores (where R = H, OH), then there should be shifts to longer wavelengths on passing from the succinic compounds to the corresponding glutarimidine derivatives. This is observed, and moreover the various shifts are of roughly equal energies, as would be expected. Thus the 15 mμ shift for the imidines represents a decrease in excitation energy of 6·5 kcal./mole,[13] which is of the same order as the energy equivalent of the 7 mμ shift for the imides, namely 5·5 kcal./mole. It is concluded therefore that the glutarimidines (II) and (XII) and their transformation products (IV), (VI), (VII), (XIII), and (XIV) are probably best represented by the di-imino-piperidine structures (XX), (XXa).

The dioxime in the monomethylsuccinimidine series (XIX; R = Me, R' = H, X = N·OH), data for which are included in Table 2, was prepared from monomethylsuccinonitrile [11] and hydroxylamine.

Experimental

Analyses were by the staff of the Microanalytical Laboratory (Miss J. Cuckney), and measurements of infrared absorption by Mr. R. L. Erskine, B.Sc., and of near-ultraviolet light absorption by Mrs. A. I. Boston of this Department.

Glutarimidine (2 : 6-*Di-iminopiperidine*) (II).—Liquid ammonia (100 c.c.) was added cautiously to methanol (300 c.c.; dried by fractionation) and the solution heated with glutaronitrile [14] (50 c.c., 47·6 g.; $n_D^{18\cdot5}$ 1·4362) in an autoclave at 100° overnight. Evaporation of the solution afforded *glutarimidine* (25·1 g., 45%), which crystallised from dimethylformamide–benzene as prismatic needles, m. p. 157—158° (decomp.) (Found: C, 53·6; H, 8·2; N, 38·0. $C_5H_9N_3$ requires C, 54·0; H, 8·2; N, 37·8%).

The *picrate*, prepared in ethanol, recrystallised from ethanol as yellow prisms, m. p. 210—211° (decomp.) (Found: C, 39·2; H, 4·0; N, 24·4. $C_{11}H_{12}O_7N_6$ requires C, 38·8; H, 3·6; N, 24·7%).

[11] Brown, Spiers, and Whalley, *J.*, 1957, 2882.
[12] Turner, *ibid.*, p. 4555.
[13] Bowen, "Chemical Aspects of Light," Oxford, 1942, p. 188.
[14] *Org. Synth.*, Coll. Vol. I, p. 536.

Action of Heat.—Glutarimidine (2 g.) evolved ammonia slowly when boiled in butanol (20 c.c.). After 18 hr., the solution was evaporated and the oily residue taken up in benzene and chromatographed on alumina. Elution of the yellow band, with benzene, evaporation of the eluate, and distillation of the residue under reduced pressure afforded glutaronitrile (1·16 g., 69%), b. p. 81°/0·15 mm., n_D^{19} 1·4368.

Hydrolyses.—(i) Glutarimidine was exposed to the atmosphere until ammonia evolution ceased. After being crystallised from ethanol–toluene, the solid (*A*) had m. p. 137—180°. Further fractionation from methanol–benzene, eventually gave a solid (*B*), m. p. 150—160°. These m. p. ranges were unaffected by admixture of *A* with the imino-imide (IV) described below, and of *B* with glutarimide. A mixture of the imino-imide (IV) and glutarimide had the depressed m. p. 137—150°.

(ii) A solution of glutarimidine in a minimum of cold water was kept at 0° for 24 hr. during which ammonia was evolved. Evaporation of a portion of the solution left a solid, m. p. *ca.* 160—200°, which was not separated into its constituents by crystallisation from ethanol and methanol–benzene. Ether-extraction of the remainder of the aqueous hydrolysate for 24 hr. and evaporation of the extract yielded crude glutarimide, m. p. 144—147° and mixed m. p. 145—150° with authentic glutarimide, m. p. 154—155°, prepared by distillation of glutaramide and crystallisation of the distillate from ethyl acetate–light petroleum (b. p. 40—60°).

(iii) Glutarimidine was dissolved in hot toluene by addition of ethanol. After several days, 6-*imino*-2-*piperidone* (IV) had crystallised as plates, m. p. 181—182° (decomp.) (Found: C, 53·9; H, 7·5; N, 24·8. $C_5H_8ON_2$ requires C, 53·6; H, 7·2; N, 25·0%).

(iv) Glutarimidine (2 g.) was boiled with water (2 c.c.) for 1·5 hr. and the solution then kept at 0° overnight. Glutaramide (V) (1·56 g., 42%) separated as leaflets, m. p. 180—181° raised on recrystallisation from water (charcoal) to 182—183° (Found: C, 46·2; H, 7·9; N, 21·1. Calc. for $C_5H_{10}O_2N_2$: C, 46·1; H, 7·8; N, 21·5%). Authentic glutaramide (mixed m. p. undepressed), obtained from dimethyl glutarate and concentrated aqueous methanolic ammonia, crystallised from ethanol as shining plates, m. p. 181—182°. Earlier workers [7] gave m. p.s 175, 176°.

2 : 6-*Dihydroxyiminopiperidine* (VI).—(a) *Preparation.* (i) Glutarimidine (2 g.) and hydroxylamine hydrochloride (2·6 g., 2 mols.) were boiled together in methanol (30 c.c.) for 1·5 hr. Cooling of the solution gave 2 : 6-*dihydroxyiminopiperidine* (1·2 g., 47%), m. p. 231—232° (decomp.), which after crystallisation (3 times) from water, formed prisms, m. p. 240—241° (decomp.) (Found: C, 42·0; H, 6·5; N, 29·5. $C_5H_9O_2N_3$ requires C, 42·0; H, 6·3; N, 29·4%). The compound in aqueous ethanol gave a red-violet colour with ferric chloride and a yellow-green with cupric acetate. (ii) Glutaronitrile (5 g.), hydroxylamine hydrochloride (9·4 g., 2 mols.), and sodium carbonate (7·2 g.) were kept in 50% aqueous ethanol (20 c.c.) at 90° overnight. The clarified solution was evaporated to dryness and the residue extracted with boiling water. Cooling of the extract afforded the dioxime (4·6 g.), m. p. 233—234° and mixed m. p. 234—235°.

(b) *Degradation.* (i) The dioxime (VI) (2 g.) was dissolved in a mixture of 50% aqueous ethanol (10 c.c.) and dioxan (10 c.c.), and 10% sodium nitrite solution (4·83 c.c.) was added. To the stirred solution, 10% hydrochloric acid (2·2 c.c.) was added during 1 hr. Next day, the solution was evaporated to dryness and the residue extracted with boiling ethanol. Concentration of the extract afforded 6-hydroxyimino-2-piperidone (VII) (0·24 g., 28%), m. p. 199—201°, which crystallised from ethanol as prisms, m. p. 201—202° (Found: C, 47·3; H, 6·6; N, 21·6. Calc. for $C_5H_8O_2N_2$: C, 46·9; H, 6·3; N, 21·9%). Garny [8] reported m. p. 196°. The compound in aqueous ethanol gave a faint purple-red colour with ferric chloride and a bright green with cupric acetate. (ii) To this monoxime (VII) (0·2 g.), dissolved in acetic acid (10 c.c.), concentrated hydrochloric acid (0·31 c.c.) was added, followed by 10% aqueous sodium nitrite (1·08 c.c.) in drops. Next day the solution was evaporated, the residue extracted with ethanol, and the extract evaporated. Crystallisation of the solid, m. p. 150—152°, from a minimum of water gave glutarimide as plates, m. p. 153—154° (Found: N, 12·75. Calc. for $C_5H_7O_2N$: N, 12·4%), which did not depress the m. p. of the authentic specimen (above).

Glutardiamidoxime (VIII).—(a) *Preparation.* A solution of glutaronitrile (5 g.), hydroxylamine hydrochloride (4·7 g.), and sodium carbonate (3·6 g.) in 50% aqueous ethanol (20 c.c.) was kept at 60° for 16 hr. The solution was evaporated under reduced pressure and the residue extracted with ethanol. Cooling of the extract gave *glutardiamidoxime* (2·3 g., 27%) which crystallised from ethanol as tiny plates, m. p. 164—165° (with evolution of gas, resolidification, and decomp. at *ca.* 220°) (Found: C, 37·7; H, 7·6; N, 34·7. $C_5H_{12}O_2N_4$ requires C, 37·5;

H, 7·6; N, 35·0%). The compound in water gave an orange colour with ferric chloride and a dull yellow with cupric acetate.

(b) *Cyclisation.* Sublimation of the preceding diamidoxime at 150°/10 mm. and crystallisation of the sublimate from water afforded the cyclic dioxime (VI), m. p. 228—230° undepressed by that prepared from glutarimidine and hydroxylamine, above.

2 : 6-*Diphenyliminopiperidine* (IX).—(a) *Preparation.* (i) A solution of glutarimidine (2 g.) and aniline (3·4 g.) in ethanol (20 c.c.) was boiled for 18 hr. (ammonia evolved), and then evaporated under reduced pressure. The residue was chromatographed in benzene on a column (14 × 1 cm.) of alumina (Spence type H), the eluate was evaporated, and the gummy product covered with light petroleum (b. p. 40—60°) and kept at 0°. By next day crystallisation had occurred. From ethyl acetate (charcoal), the 2 : 6-*diphenyliminopiperidine* (3·6 g., 76%) formed colourless prisms, m. p. 153° (Found: C, 77·4; H, 6·7; N, 16·0. $C_{17}H_{17}N_3$ requires C, 77·5; H, 6·5; N, 16·0%).

(ii) Glutaronitrile (5·1 g.) and aniline hydrochloride (14 g.) were mixed together and heated in an oil-bath at 230°. At *ca.* 200° (internal temperature) an exothermic reaction set in, with a rise in temperature to 280°. When the melt had partly solidified, the oil-bath was removed, and subsequently the orange solid was triturated with water, collected, and dried (yield, 11·3 g.; m. p. 255—265°). Crystallisation from ethanol (charcoal) afforded 2 : 6-*diphenyliminopiperidine hydrochloride*, m. p. 274—275° (decomp.) (Found: C, 68·2; H, 6·2; N, 13·9; Cl, 12·0. $C_{17}H_{18}N_3Cl$ requires C, 68·1; H, 6·0; N, 14·0; Cl, 11·8%). The hydrochloride (7 g.) was stirred with 50% aqueous ethanol (80 c.c.) whilst N-sodium hydroxide (23·4 c.c.) was added, followed by water (200 c.c.). Extraction of the solution with chloroform, evaporation of the extract, and treatment of the residue with dry ether gave 2 : 6-diphenyliminopiperidine (6 g.), m. p. and mixed m. p. 152—153°.

(b) *Hydrolysis.* The diphenylimine (0·5 g.), dissolved in dioxan (15 c.c.), was boiled with water (25 c.c.) overnight. On cooling of the solution, glutardianilide separated (0·5 g.), which crystallised from dioxan as needles, m. p. 224° (Found: N, 10·1. Calc. for $C_{17}H_{18}O_2N_2$: N, 9·9%). Barnicoat [15] gives m. p. 223°.

α-*Phenylglutarimidine* (2 : 6-*Di-imino*-3-*phenylpiperidine*) (XII).—α-Phenylglutaronitrile [10] (48·3 g.) and a solution of liquid ammonia (100 c.c.) in methanol (300 c.c.) were heated in an autoclave at 80° for 18 hr. The solid product (27·9 g.) was crystallised from ethanol to yield α-*phenylglutarimidine* as plates, m. p. 201—202° (decomp.) (Found: C, 70·3; H, 7·1; N, 22·3. $C_{11}H_{13}N_3$ requires C, 70·6; H, 7·0; N, 22·4%).

2 : 6-*Dihydroxyimino*-3-*phenylpiperidine* (XIII).—(a) *Preparation.* α-Phenylglutarimidine (2 g.) and hydroxylamine hydrochloride (1·5 g.) were boiled together in ethanol (20 c.c.) for 2·5 hr. during which ammonium chloride separated. The solvent was evaporated under reduced pressure, and the residue was triturated with water. From methanol the product (1·9 g.) crystallised as the *methanol solvate*, m. p. 226—227° (decomp.) (Found: C, 57·2; H, 6·9; N, 16·9. $C_{11}H_{13}O_2N_3,CH_3{\cdot}OH$ requires C, 57·4; H, 6·8; N, 16·7%), which was dried at 120°/18 mm. for 1·5 hr. to yield the solvent-free 2 : 6-*dihydroxyimino*-3-*phenylpiperidine*, m. p. unchanged (Found: C, 60·3; H, 6·2; N, 19·05. $C_{11}H_{13}O_2N_3$ requires C, 60·3; H, 6·0; N, 19·2%). The compound in methanol gave a dark red colour with ferric chloride.

(b) *Degradation.* (i) To the preceding dioxime (0·3 g.) in dioxan (10 c.c.), water (10 c.c.) was added, followed by sodium nitrite (0·2 g.) and then, with ice-cooling, 2N-hydrochloric acid (2 c.c.) in drops. After 15 min., the solution was evaporated under reduced pressure and the residue extracted with ethanol (2 × 20 c.c.). Evaporation of the extract left an oil, which solidified on being triturated with water [yield, 0·19 g.; m. p. *ca.* 200° (decomp.)]. Several crystallisations from ethanol–water (charcoal) yielded 2-*hydroxyimino*-3-*phenyl*-6-*piperidone* (XIV) as prisms, m. p. 225—226° (decomp.) (Found: C, 64·6; H, 6·2; N, 13·6. $C_{11}H_{12}O_2N_2$ requires C, 64·7; H, 5·9; N, 13·7%). The compound gave a pale orange colour with ferric chloride.

(ii) The dioxime (XIII) (0·5 g.) was warmed on the steam-bath with 2N-nitric acid (10 c.c.). Initially, there was effervescence. After 50 min., ethanol was added, and the solution was evaporated under reduced pressure, and again after addition of ethanol and benzene. The resulting viscous syrup was dissolved in a little ethanol. At 0°, needle-shaped crystals separated (147 mg.), m. p. 138—140°, followed by a further crop (84 mg.), m. p. 135—160°, from the mother-liquors. From benzene, with rejection of insoluble matter and by addition of ether,

[15] Barnicoat, *J.*, 1927, 2926.

α-phenylglutarimide (167 mg.) was obtained as needles, m. p. 143° undepressed by the authentic material, next described.

α-Phenylglutarimide (XV).—α-Phenylglutaronitrile (10 g.) was hydrolysed with a boiling solution of sodium hydroxide (10 g.) in water (30 c.c.) and ethanol (15 c.c.) for 1·5 hr., the mixture (sodium salt had separated) was then acidified with hydrochloric acid and extracted with ether, and the ether was evaporated. Exposure of the syrup as a thin layer to the air gave crude acid, m. p. 65—67°, which was pressed between porous tiles for several days. The α-phenylglutaric acid then had m. p. 80° (Equiv. by titration, 109. Calc. for $C_{11}H_{12}O_4$: equiv., 104). Fichter and Merckens [16] give m. p. 82—83°. The acid in ether (200 c.c.) was converted with ethereal ammonia into ammonium α-phenylglutarate (10·2 g.), distillation of which at atmospheric pressure gave the crude imide, m. p. 130—133° raised to 138—139° on crystallisation from methanol (yield 2·2 g.). From ethyl acetate–ether, *α-phenylglutarimide* formed needles, m. p. 142—143° (Found: C, 70·0; H, 6·2; N, 7·5. $C_{11}H_{11}O_2N$ requires C, 69·8; H, 5·9; N, 7·4%).

2-Imino-3-phenyl-6-phenyliminopiperidine (XVII).—α-Phenylglutarimidine (1 g.) and aniline (1 c.c.; 1 mol.) were boiled in ethanol (20 c.c.) for 24 hr. Evaporation of the solution and trituration of the residue with ether and then ethyl acetate yielded *2-imino-3-phenyl-6-phenyliminopiperidine* (1·3 g., 92%) which crystallised from ethanol–water as plates, m. p. 169—170° (decomp.) (Found: C, 77·4; H, 6·7; N, 15·8. $C_{17}H_{17}N_3$ requires C, 77·5; H, 6·5; N, 16·0%).

3-Phenyl-2 : 6-diphenyliminopiperidine (XVIII).—(i) α-Phenylglutarimidine (2 g.) was boiled in aniline (20 c.c., freshly distilled) overnight and the aniline was then removed at 100°/0·2 mm. The residue crystallised from ethanol, to give pale orange-yellow laths of *3-phenyl-2 : 6-diphenyliminopiperidine* (2·2 g.), m. p. 163° (Found: C, 81·6; H, 6·2; N, 12·4. $C_{23}H_{21}N_3$ requires C, 81·4; H, 6·2; N, 12·4%), whilst from aqueous ethanol the yellow *hemihydrate* separated as very small plates, m. p. 163° (with softening at 149—150°) (Found: C, 79·0; H, 6·25; N, 11·7. $C_{23}H_{21}N_3,\frac{1}{2}H_2O$ requires C, 79·2; H, 6·4; N, 12·0%).

(ii) The diphenylimino-compound (0·1 g.), mixed m. p. undepressed, was isolated similarly after interaction of the monophenylimine (XVII) (0·2 g.) with boiling aniline (1 c.c.) overnight.

Attempts at Dehydrogenation.—No evidence for the formation of substituted diaminopyridines was obtained in preliminary attempts to dehydrogenate 2 : 6-diphenyliminopiperidine (IX), α-phenylglutarimidine (XII) and 3-phenyl-2 : 6-diphenyliminopiperidine (XVIII) by distillation, by heating them in solvents with palladised charcoal and by treatment with chloranil or tetrachloro-*o*-benzoquinone.

2 : 5-Dihydroxyimino-3-methylpyrrolidine (XIX; R = Me, R′ = H, X = N·OH).—Hydroxylamine hydrochloride (1·6 g.) was dissolved in hot ethanol (50 c.c.) containing methylsuccinonitrile [11] (1 g.), sodium carbonate (1·2 g.) was added cautiously, and the mixture boiled for 3 hr. and then filtered hot. The filtrate was evaporated to dryness under reduced pressure and the residue extracted with boiling ethyl acetate (3 × 25 c.c.). Evaporation of the filtered extract afforded *2 : 5-dihydroxyimino-3-methylpyrrolidine* (1·2 g.), m. p. 157—158°, which crystallised from ethyl acetate as prisms, m. p. 161° (Found: C, 41·9; H, 6·1; N, 29·1. $C_5H_9O_2N_3$ requires C, 41·95; H, 6·3; N, 29·4%). It gave a dull violet colour with aqueous ferric chloride and a yellow-green with cupric acetate.

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[16] Fichter and Merckens, *Ber.*, 1901, **34**, 4174.