[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN, ANN ARBOR, MICH., AND THE NEW MEXICO HIGHLANDS UNIVERSITY, LAS VEGAS, NEW MEX.]

# 1,5-Diaryl-2,3-pyrrolidinediones. XII. Enamines and the Pseudo-pyrrolidinediones[1,2]

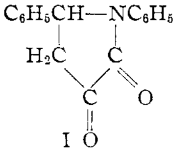
BY WYMAN R. VAUGHAN AND ROBERT C. TRIPP[3]

RECEIVED JANUARY 2, 1960

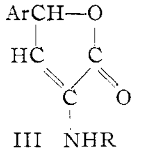
The reaction between pseudo-1,5-diaryl-2,3-pyrrolidinediones (3-arylamino-5-aryl-2(5H)-furanones) and aromatic amines may involve simple amine exchange or transformation to the enamine of a true 1,5-diaryl-2,3-pyrrolidinedione. The product of the reaction between *o*-phenylenediamine and either 3-phenylamino-5-phenyl-2(5H)-furanone or benzylidenepyruvic acid is 2-phenyl-2,3-dihydrofuro[2.3-b]quinoxaline. An alternative route to the enamines of 1,5-diaryl-2,3-pyrrolidinediones is also described: reaction of 4-carbalkoxy-1,5-diaryl-2,3-pyrrolidinediones with amines.

The reaction between 1,5-diphenyl-2,3-pyrrolidinedione (I) and primary aromatic amines and the reaction between the enamine IIa (anil) derived from I and aniline have been reported to afford the same product, IIb,[4] but this was not explicitly demonstrated.[4] Thus, while β-naphthylamine was used for both reactions, a melting point was recorded only for the product from I, and an analysis was reported only for the product from IIa. The only additional information was data for the reaction of I with *p*-toluidine and of IIa with *p*-nitroaniline.[4]

Since it has been shown that the compound assumed to be I was in fact 3-phenylamino-5-phenyl-2(5H)-furanone[5] (IIIa), it is necessary to reexamine both reactions. It has been suggested[6] that the reactions of IIa with phenylhydrazine and with aromatic amines should be the same, but an incorrect structure was assigned to the reaction products. With the correct structures now available[7] (IIc and IIb, respectively) the suggestion is still valid but requires confirmation. The purpose of the present investigation is clarification of the nature of the reaction of amines with compounds of type III and of type II. In addition, the reaction of 4-substituted-1,5-diaryl-2,3-pyrrolidinediones (IV), which are extensively enolized,[1] is included, for in two instances the expected enamine (Va[8] and Vb[1]) has been reported as the chief product of the reaction of benzaldehyde, aromatic amine and substituted pyruvic acid or ester, which otherwise affords IV.

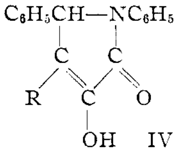


I

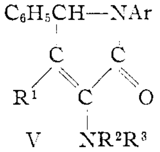


III

| | Ar | R |
|---|---|---|
| a, | $C_6H_5$ | $C_6H_5$ |
| b, | $C_6H_5$ | *p*-$C_6H_4CH_3$ |
| c, | $C_6H_5$ | β-$C_{10}H_7$ |
| d, | $C_6H_5$ | *p*-$C_6H_4OCH_3$ |
| e, | *p*-$C_6H_4OCH_3$ | *p*-$C_6H_4OCH_3$ |
| f, | *p*-$C_6H_4OCH_3$ | $C_6H_5$ |
| g, | $C_6H_5$ | *o*-$C_6H_4NH_2$ |
| h, | $C_6H_5$ | *o*-$C_6H_4NO_2$ |
| i, | *p*-$C_6H_4OCH_3$ | *o*-$C_6H_4NO_2$ |
| j, | *p*-$C_6H_4OCH_3$ | *o*-$C_6H_4NH_2$ |

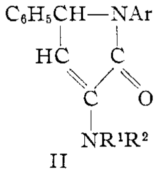


IV



V

| | R | Ar | $R^1$ | $R^2$ | $R^3$ |
|---|---|---|---|---|---|
| a, | $C_2H_5O\overset{O}{\overset{\parallel}{C}}$ | *p*-$C_6H_4CH_3$ | $C_2H_5O\overset{O}{\overset{\parallel}{C}}$ | *p*-$C_6H_4CH_3$ | H |
| b, | $CH_3$ | $C_6H_5$ | $CH_3$ | $C_6H_5$ | H |
| c, | $C_6H_5NH\overset{O}{\overset{\parallel}{C}}$ | $C_6H_5$ | $C_6H_5NH\overset{O}{\overset{\parallel}{C}}$ | $C_6H_5$ | H |
| d, | $C_5H_{10}N\overset{O}{\overset{\parallel}{C}}$ | $C_6H_5$ | $C_5H_{10}N\overset{O}{\overset{\parallel}{C}}$ | $-(CH_2)_5-$ | |
| e, | | $C_6H_5$ | $C_5H_{10}N\overset{O}{\overset{\parallel}{C}}$ | $C_6H_5$ | H |



II

| | Ar | $R^1$ | $R^2$ |
|---|---|---|---|
| a, | $C_6H_5$ | $C_6H_5$ | H |
| b, | $C_6H_5$ | Ar | H |
| c, | $C_6H_5$ | $NHC_6H_5$ | H |
| d, | $C_6H_5$ | *p*-$C_6H_4CH_3$ | H |
| e, | $C_6H_5$ | β-$C_{10}H_7$ | H |
| f, | $C_6H_5$ | *p*-$C_6H_4CH_3$ | H |
| g, | β-$C_{10}H_7$ | β-$C_{10}H_7$ | H |
| h, | $C_6H_5$ | $-(CH_2)_4-$ | |
| i, | $C_6H_5$ | $C_6H_5$ | $CH_3$ |
| j, | $C_6H_5$ | *p*-$C_6H_4NO_2$ | H |
| k, | *p*-$C_6H_4NO_2$ | *p*-$C_6H_4NO_2$ | H |
| l, | *p*-$C_6H_4OCH_3$ | *p*-$C_6H_4OCH_3$ | H |
| m, | $C_6H_5$ | *p*-$C_6H_4OCH_3$ | H |
| n, | *p*-$C_6H_4CH_3$ | $C_6H_5$ | H |
| o, | *p*-$C_6H_4NO_2$ | $C_6H_5$ | H |
| p, | *p*-$C_6H_4OCH_3$ | $C_6H_5$ | H |

The reactions of IIIa with *p*-toluidine and β-naphthylamine which were reported to yield IId and IIe, respectively,[4] were repeated, and in neither case was the expected product obtained. Instead *p*-toluidine afforded IIf under the original conditions (*i.e.*, the same product as from benzaldehyde, pyruvic acid and *p*-toluidine) and under milder conditions afforded only IIIb (*i.e.*, the same product obtained from benzylidenepyruvic acid and *p*-toluidine and described as I with *p*-tolyl in place of phenyl on nitrogen[4]). Likewise β-naphthylamine afforded IIIc (*i.e.*, the same compound obtained from the reaction of benzylidenepyruvic acid with β-naphthylamine). And more drastic conditions for the reaction of IIIa with β-naphthylamine af-

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[1] Previous paper in this series. W. R. Vaughan and I. S. Covey, THIS JOURNAL, **80**, 2197 (1958).

[2] Abstracted from the Ph.D. Dissertation of Robert C. Tripp, University of Michigan, 1959.

[3] Union Carbide Chemicals Co. Summer Fellow, 1957.

[4] S. Bodforss, *Ann.*, **455**, 41 (1927).

[5] W. L. Meyer and W. R. Vaughan, *J. Org. Chem.*, **22**, 98, 1560 (1957).

[6] W. R. Vaughan, *ibid.*, **20**, 1619 (1955).

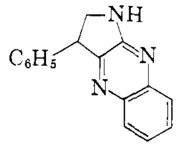
[7] W. L. Meyer and W. R. Vaughan, *ibid.*, **22**, 1565 (1957).

[8] L. J. Simon and A. Conduché, *Ann. chim. phys.*, [8] **12**, 5 (1907).

forded the cinchoninic acid, 2-phenyl-5,6-benzo[f]-quinoline-4-carboxylic acid, which is invariably the reaction product of benzaldehyde, pyruvic acid and $\beta$-naphthylamine.[9,10] Indeed all attempts to prepare IIg have led to the cinchoninic acid, frequently the result of prolonged heating of compounds of type III with the amine ($RNH_2$) and aldehyde (ArCHO).[11,12] Thus the principal reaction of III with primary aromatic amines appears to be simple exchange, with more drastic conditions leading either to II in which both Ar and R are the same, or to a cinchoninic acid.

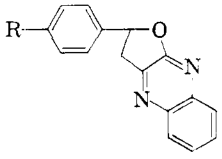
Unfortunately, it proved impossible to study the exchange reaction systematically or to any extent quantitatively, for conditions promoting complete equilibration (*e.g.*, higher temperature and/or longer reaction time) usually led either to extensive decomposition or the formation of other products (*e.g.*, cinchoninic acids). In addition to the cases cited above, aniline was found to replace *p*-toluidine in IIIb (giving IIIa) and to replace *p*-anisidine in IIIe, and to exchange with *p*-anisidine in IIId.

The reaction of IIIa with *o*-phenylenediamine or of benzylidenepyruvic acid with the same substance has been reported[4] to yield a substance with the molecular formula, $C_{15}H_{12}N_2O$, with the evolution of carbon dioxide. Stoichiometry requires the loss of $H_2$ as well, but this was disregarded, and a benzodiazepine structure was assigned without regard for the usual behavior of benzylidenepyruvic acid or type III (considered to be type I) compounds with aromatic amines. In contrast 4-phenyl-2,3-pyrrolidinedione has been reported to react with *o*-phenylenediamine to give a quinoxaline derivative[13]



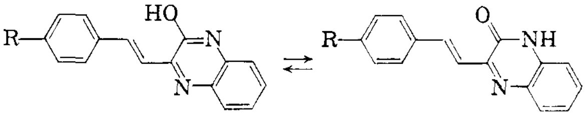
Upon repetition of the original procedures and upon reaction between IIIb and *o*-phenylenediamine the same product was obtained, and apparently it was that originally obtained, VIa. However, upon microanalysis the molecular formula was found to be $C_{16}H_{12}N_2O$; thus one molecule each of *o*-phenylenediamine and benzylidenepyruvic acid react with elimination of two molecules of water; or IIIa reacts with the diamine with the loss of water and aniline, while IIIb reacts similarly with the loss of water and *p*-toluidine. It thus seems reasonable to ascribe to the initial reaction product (not isolated) of *o*-phenylenediamine with each of the three other reactants the structure IIIg: that is, with benzylidenepyruvic acid the normal product of reaction with an aromatic amine (III) is obtained, and with IIIa and IIIb exchange of the amine already present occurs. An attempt to isolate the methoxy derivatives of IIIj by catalytic reduction of IIIi, its nitro analog, failed, the product appearing from its infrared spectrum to be impure VIb, a pure sample of which was prepared from *p*-anisylidenepyruvic acid and *o*-phenylenediamine. However, attempts to effect purification failed.

The most obvious course of reaction open to the insolable IIIg is loss of water to yield VIa, which on this basis should be assigned the structure VI.



VIa, R = H
b, R = $OCH_3$

A similar substance was prepared from *p*-anisylidenepyruvic acid and *o*-phenylenediamine (VIb). An alternative structure of either derivative of



VII

VI would be VII, in which the furane ring is open. However, either form of VII contains a styrene type group, and the ultraviolet absorption spectra of VIa and VIb lack absorption in the 280–295 mu region usually associated with stilbene and stilbene-like compounds.[14] Similarly the infrared spectra of VIa and VIb exhibit no hydroxyl or NH bands, nor do the compounds produce a color with alcoholic ferric chloride. Thus it seems reasonable to formulate them as quinoxalines.

The behavior of compounds of type II with amines was found to proceed with amine exchange essentially as originally described,[4] and the reaction with the amine was shown to occur at the enamine group rather than in the ring by reaction of I with *p*-toluidine to give the same product as the reaction of IIa with *p*-toluidine. The only amines tried with type II compounds which did not react were benzylamine, *o*-nitroaniline and N-methylaniline.

This type of exchange of the 3-amino function with another amine is characteristic of type II compounds in general: for example, the reaction of IIa with phenylhydrazine[6] or with hydroxylamine,[15] and several of the type II compounds prepared in the course of the present work were converted to the corresponding oximes.

Substances similar to type II, but derived from secondary amines, are available from I and various secondary amines, *e.g.*, pyrrolidine and N-methylaniline, but not piperidine, which afforded an uncharacterizable product. These enamines (IIh and IIi) possess infrared spectra very similar to those of other type II compounds, though of course lacking the NH absorptions. Like other type II compounds they also resist hydrolysis.

In the course of preparing and studying the enamines derived from I, it became desirable to improve the synthesis of I which involves the thermal hydrolytic decarbalkoxylation of IVa originally dis-

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[9] O. Döbner and P. Kuntze, *Ann.*, **249**, 109 (1888).

[10] R. Ciusa and G. Zerbini, *Gazz. chim. ital.*, **50**, II, 317 (1920).

[11] R. Ciusa and L. Musago, *ibid.*, **59**, 796 (1929).

[12] G. Carrara, *ibid.*, **58**, 309 (1928); **61**, 623 (1931).

[13] H. Rupe and B. Pieper, *Helv. Chim. Acta*, **12**, 637 (1929).

[14] E. A. Braude, *Ann. Repts. Prog. Chem.* (*Chem. Soc., London*), **42**, 105 (1945).

[15] W. L. Meyer and W. R. Vaughan, *J. Org. Chem.*, **22**, 1554 (1957).

covered by Covey[16] and reported by Meyer and Vaughan.[6] The chief difficulty with the synthesis is the fact that much of the I produced undergoes extensive aldolization. Consequently, a solvent was sought which minimized this shortcoming, and the most successful solvent tried proved to be methyl benzoate. Surprisingly, *cis*-decalin appeared to be most effective in promoting aldolization, and if the heating was continued, a new compound was formed (VIII), which appears to be a dehydration product of the aldol. Its infrared spectrum corresponds closely to those reported by Southwick and co-workers[17] for two similarly dehydrated 2,3-pyrrolidinedione aldol-dimers. Thus for VIII the principal absorptions occur at 1693, 1654 and 1632 cm.$^{-1}$, while those for Southwick's compounds occur at 1683, 1690; 1662, 1672; and 1628, 1636.[17] Likewise a greenish color is produced from VIII with alcoholic ferric chloride, as with Southwick's 3,3′-bipyrrolidylidenes. Unfortunately VIII proved exceedingly difficult to purify and a satisfactory microanalysis could not be obtained, nor could it be converted into a suitable derivative.

In view of the difficulty of obtaining adequate supplies of I for conversion to enamines, attention was turned to the possibility of carrying out the thermal hydrolytic decarbalkoxylation in the presence of the amine to be used for enamine formation. Accordingly IVa was heated in methyl benzoate with aniline, and a good yield of IIa was obtained.

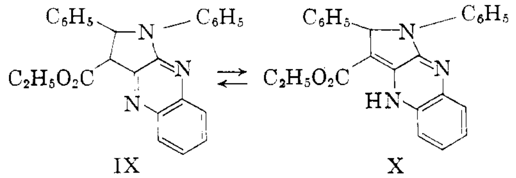
However, when IVa was heated with aniline in *cis*-decalin, the anilide of IVa was formed (IVc), and it was subsequently discovered that amide formation occurs at temperatures far below that required for decarbalkoxylation. Treatment of IVc with aniline in glacial acetic acid led to the formation of the enamine Vc, which would appear not to be formed in decalin simply because IVc precipitates immediately on being produced. The possibility that either IVc or Vc are intermediates in the production of I from IVa was ruled out by the failure of either substance to be converted to I under the conditions suitable for conversion of IVa to I.

Thus IVa can react with aniline in two different ways, and the nature of the solvent determines the course of the reaction. Apparently the decomposition of IVa in methyl benzoate proceeds in essentially the same manner whether aniline is present or not, and the initial product is I, and in the presence of aniline IIa is formed from it. Why aniline should form an anilide more readily in *cis*-decalin than in methyl benzoate is not entirely clear. Possibly in the latter solvent the nitrogen is more or less intimately associated with the carbonyl carbon of the solvent, whereas in decalin it is free to attack the carbonyl carbon of IVa.

It was noted above that Compound I did not afford a characteristic derivative with piperidine. However, IVa reacted readily with this amine in *cis*-decalin to produce a mixture consisting of the piperidide IVd and the derived enamine Vd. Both IVd and Vd reacted with aniline to produce the phenylenamine Ve. Neither IVc or IVd afforded O-acyl derivatives in spite of strong characteristic hydroxyl absorption in their infrared spectra But IVc did form an oxime on being treated with hydroxylamine hydrochloride in pyridine.

Perhaps the most striking characteristic of the enamines Vc and Vd is the ease with which they may be hydrolyzed to the parent enolic compounds IVc and IVd in contrast to enamines of type II, which are resistant to hydrolysis,[15,18,19] as are other carbonyl derivatives (*e.g.*, ethylene ketal, oxime[15]). In view of this apparently anomalous ease of hydrolysis, which would seem to be promoted by the 4-carbamido substituents, the enamine Vb was examined and found to hydrolyze equally readily. Since the electronic characteristics of the 4-substituents in these hydrolyzable enamines are different, it is not possible to account for the anomaly on other than steric grounds. Attention has been called to the effect of a 4-substituent in I on both the difficulty of formation of carbonyl derivatives and production of extensive enolization (which is absent in I itself).[1] In these situations, also, the effect is not related to the electronic character of the substituent. Bearing in mind the reversible nature of enolization and carbonyl derivative formation, one may presume that the 4-substituent promotes enolization as a means of relieving non-bonded interaction between itself and the 1- and 5-substituents and renders more difficult the formation of carbonyl derivatives as a consequence of non-bonded interaction between itself and the consequent 3-substituent. Thus the hydrolysis of an enamine (3- and 4-substituents coplanar) would relieve the latter strain. The fact that amines attack the 4-carbethoxy group to form an amide before they react with the 3-carbonyl system, contrary to usual behavior (*e.g.*, phenylhydrazine with β-keto-ester), emphasizes the extent of inhibition of enamine formation.

In only one case does an amine appear to show preference for the 3-carbonyl system over the ester in IVa: *o*-phenylenediamine reacts to form what must be considered 1,2-diphenyl-2,3-dihydro-3-carbethoxy-1-pyrrolo[2.3-*b*]quinoxaline (IX), or, judging from the infrared spectrum, its tautomer X



IX X

(*e.g.*, NH band at 3360 cm.$^{-1}$ (s), conjugated ester carbonyl band at 1675 cm.$^{-1}$ (s)).

## Experimental[20–22]

**3 - Arylamino - 5 - aryl - 2(5H) - furanones (III)** were prepared by condensing the appropriate arylidenepyruvic

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[16] I. S. Covey, Ph.D. Dissertation, University of Michigan, 1957.

[17] P. L. Southwick, E. R. Previc, J. Casanova, Jr., and E. H. Carlson, *J. Org. Chem.*, **21**, 1087 (1956).

[18] H. Bücherer and R. Russischwili, *J. prakt. Chem.*, **128**, 89 (1930).

[19] O. Döbner and M. Gieseke, *Ann.*, **244**, 290 (1887).

[20] Melting points, determined in open capillaries, are uncorrected.

[21] Infrared spectra obtained from Nujol mulls by means of a Perkin–Elmer model 21 spectrophotometer.

[22] Microanalyses for carbon and hydrogen are by Mrs. Anna Griffen, University of Michigan, except for those marked (S). The latter and all nitrogen analyses by Spang Microanalytical Laboratory, Ann Arbor, Mich.

acid with a primary aromatic amine as described by Vaughan and Peters[23] for the preparation of (pseudo)-1,5-diaryl-2,3-pyrrolidinediones. Melting points are recorded in Table I.

TABLE I

3-ARYLAMINO-5-ARYL-2(5*H*)-FURANONES

| Compound | M.p., °C. | Reported m.p., °C. | Ref. |
|---|---|---|---|
| IIIa | 159–160 d.[b] | 160.0–160.5 d.[b] | 23 |
| IIIb | 142.5–143.0 d.[b] | 143[b] | 4 |
| IIIc | 149.5–150.5 d.[b] | 150[b] | 4 |
| IIId | 118.5–119.5 d.[b] | 118–119 d.[b] | 23 |
| IIIe | 122.0–123.5 d.[b] | 124–125 d.[b] | 23 |
| IIIf | 153–154 d.[b] | 153–154 d.[b] | 23 |
| IIIh | 138–140[a] | 154 | 18 |
| IIIi | 161–162 d.[a,b] | | |

[a] See text of Experimental. [b] Gas.

**3 - (*o* - Nitrophenylamino) - 5 - phenyl - 2(5H) - furanone (IIIh)**, m.p. 138–140°.—The product did not precipitate until the reaction mixture had stood at room temperature for several days. The yield from 7.1 g. (0.05 mole) of *o*-nitroaniline and 8.8 g. (0.05 mole) of benzylidenepyruvic acid was 2.7 g. (20%).

*Anal.* Calcd. for $C_{16}H_{12}N_2O_4$: C, 64.86; H, 4.08; N, 9.46. Found: C, 64.92; H, 3.99; N, 9.51.

Bücherer and Russischwili[18] prepared this compound by the direct reaction of pyruvic acid, benzaldehyde and *o*-nitroaniline. They reported a melting point of 154°.

**3 - (*o* - Nitrophenylamino) - 5 - (*p* - anisyl) - 2(5H)-furanone (IIIi).**—A solution of 7.1 g. (0.05 mole) of *o*-nitroaniline in 50 ml. of absolute ethanol was added with stirring to a solution of 9.5 g. (0.05 mole) of *p*-anisylidenepyruvic acid in 100 ml. of absolute ethanol. The solution was allowed to stand 24 hr. at room temperature, during which time the mass solidified. A small portion was filtered off and found to be insoluble in either dilute sodium bicarbonate or sodium hydroxide solutions, indicating that the α-imino acid had already undergone complete rearrangement to the furanone. The remainder of the reaction mixture was refluxed 45 min. on the steam-bath, cooled, and filtered. There was obtained 7.0 g. of yellow needles melting at 160–161° with gas evolution. Additional product was obtained by concentration of the filtrate bringing the total yield to 9.6 g. (59%). The analytical sample was recrystallized twice from glacial acetic acid and melted at 161–162° with gas evolution.

*Anal.* Calcd. for $C_{17}H_{14}N_2O_5$: C, 62.57; H, 4.32; N, 9.79. Found: C, 52.56; H, 4.11; N, 9.79.

**Reactions Involving Exchange between III and Amines.**—The general procedure for exchange between a sample of II and an amine involved dissolving 1.0 g. of each in 10–20 ml. of ethanol and refluxing the solution for 15–20 min. Upon cooling, the precipitate was filtered off, washed with cold ethanol and dried. Infrared spectra were obtained on the crude products and compared with the spectra of starting material and expected product. This and modified procedures follow. Results are summarized in Table II.

**Reaction of IIIa with *p*-Toluidine. (A).**—The procedure of Bodforss[4] was followed. One gram of 3-phenylamino-5-phenyl-2(5H)-furanone and 2.5 g. of *p*-toluidine were heated together in an oil-bath maintained at 105–115° for 0.5 hr. with continual stirring. During this time some gas evolution was observed. The liquid mass was cooled slightly and glacial acetic acid and absolute ethanol were added. On further cooling of the resulting solution yellow needles melting at 195–203° dec. were obtained. After four recrystallizations from absolute ethanol the product melted at 204–206° dec. and was in the form of white needles.

A mixture of this material and IIf prepared from benzaldehyde, pyruvic acid and *p*-toluidine (below) melted with decomposition at 204–214°. Their infrared spectra are identical. Bodforss[4] recorded a melting point of 187° for his product (presumed by him to be IId).

(B).—To a suspension of 1.0 g. of IIIa in 15 ml. of absolute ethanol was added a solution of 1.0 g. of *p*-toluidine in 5 ml. of ethanol. The mixture was refluxed for 15 min. until a homogeneous solution resulted. On cooling, white plates crystallized out. The crude product was recrystallized from ethanol and melted with gas evolution at 128.5–129.5°. A mixture of this material and IIIa melted at 131–147°. The infrared spectrum, however, corresponded to that of a mixture of IIIa and IIIb. Recrystallization increased the proportion of IIIa in the material (as shown by the spectrum), and no pure IIIb could be isolated from the reaction.

TABLE II

3-ARYLAMINO-5-ARYL-2(5H)-FURANONES (III) + AMINES

| Compound | Amine | Product |
|---|---|---|
| IIIa | *p*-Toluidine | IIIb + IIIa |
| IIIa | β-Naphthylamine | IIIc |
| IIIa | *p*-Anisidine | No exchange obsd. |
| IIIa | *p*-Nitroaniline | No exchange obsd. |
| IIIa | Cyclohexylamine | No exchange obsd.[a] |
| IIIb | Aniline | IIIa |
| IIIb | *p*-Nitroaniline | No exchange obsd. |
| IIId | Aniline | IIIa + IIId |
| IIId | *p*-Nitroaniline | No exchange obsd. |
| IIIe | Aniline | IIIf |
| IIIf | *p*-Anisidine | No exchange obsd. |

[a] A reaction occurred, but the infrared spectrum of the product in no way resembled that of 3-cyclohexylamino-5-phenyl-2(5H)-furanone, whose spectrum was kindly furnished by Dr. Walter L. Meyer.

**Reaction of IIIa with β-Naphthylamine. (A).**—One gram each of IIIa and β-naphthylamine were dissolved by warming in 20 ml. of ethanol. After refluxing 20 min. and cooling, the solution deposited faintly pink crystals (m.p. 130–135° dec., infrared spectrum identical with that of IIIc). Three recrystallizations from ethanol raised the melting point to 146–148° dec., which was undepressed on admixture with authentic IIIc.

(B).—Two grams of β-naphthylamine and 1.0 g. of IIIa were fused together for 10 min. at 110–120°; 25 ml. of glacial acetic acid was added and the mixture heated to its boiling point. Filtration afforded 0.6 g. of yellow powder, m.p. 285° (gas), which was soluble in dilute bicarbonate. A mixture of this product and authentic 2-phenyl-5,6-benzoquinoline-4-carboxylic acid (as prepared below) melted at 286° (gas).

**2-Phenyl-5,6-benzoquinoline-4-carboxylic Acid.**—To 5.6 g. of β-naphthylamine dissolved in 100 ml. of ether was added a solution of 3.5 g. of pyruvic acid and 4.2 g. of benzaldehyde in 10 ml. of ether. After the solution had stood at room temperature for 24 hr., 4.5 g. of yellow powder was filtered off; m.p. 274.5° (gas). Recrystallization from pyridine–petroleum ether raised the melting point to 290° (gas), reported[9] 296°.

**2-Phenyl-2,3-dihydrofuro[2,3-b]quinoxaline (VIa). (A) From Benzylidenepyruvic Acid.**—A solution of 10.0 g. (0.057 mole) of benzylidenepyruvic acid[24] and 5.0 g. (0.046 mole) of *o*-phenylenediamine in 30 ml. of absolute ethanol was heated on the steam-bath for 10 min. When the solution was cooled, 4.0 g. of orange crystals precipitated; m.p. 240–250°. Recrystallization from chloroform afforded 2.0 g. (17.5%) of yellow needles melting at 247.5–249.5°. The analytical sample was recrystallized twice more from chloroform and twice from ethanol; m.p. 249.5–251.0°. This compound absorbs at 1655 and 1625 cm.$^{-1}$ in the infrared. Its ultraviolet spectrum exhibits maxima at 236 mμ ($\epsilon_{\max}$ $2.57 \times 10^4$) and 380 mμ ($\epsilon_{\max}$ $1.64 \times 10^4$).

*Anal.* Calcd. for $C_{16}H_{12}N_2O$: C, 77.40; H, 4.87; N, 11.28. Found: C, 77.23(S); H, 4.93(S); N, 11.31.

**(B) From 3-Phenylamino-5-phenyl-2(5H)-furanone (IIIa).**—A solution of 3.0 g. of IIIa and 2.0 g. of *o*-phenylenediamine in 30 ml. of absolute ethanol was heated 15 min. on the steam-bath. On cooling, there was obtained 1.5 g. of an orange solid, m.p. 160–170°, which from its infrared spectrum appeared to be a mixture of IIIa and VIa. Two recrystallizations from chloroform gave yellow needles, m.p. 249.5–252.0°. A mixture of this material and the VIa ob-

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(23) W. R. Vaughan and L. R. Peters, *J. Org. Chem.*, **18**, 382 (1953).

(24) E. D. Stecher and H. F. Ryder, THIS JOURNAL, **74**, 4392 (1952).

TABLE III

1,5-DIARYL-3-ARYLAMINO-2(5*H*)-PYRROLONES (II)[a]

| Cpd. | Method (yield, %) | M.p., °C., and solvent | Reported m.p., °C. | Analysis Calcd. for | C | H | N | I.r., cm.⁻¹ |
|---|---|---|---|---|---|---|---|---|
| IIa | A | 224.0–225.5[b]<br>HOAc–EtOH abs. | 227–228[25] | | | | | NH 3280[25]<br>CO 1670[25]<br>CC 1642[25] |
| IId | B(95)[c] | 196–197[b]<br>EtOH abs. | | $C_{23}H_{20}N_2O$ | 81.15 | 5.92 | 8.27 | NH 3310<br>CO 1673<br>CC 1648 |
| | | | | Found | 80.98 | 5.81 | 8.27 | |
| IIe | B(81)[c] | 254–256 d.<br>HOAc | 258[4,d] | $C_{26}H_{20}N_2O$ | 82.95 | 5.36 | 7.44 | NH 3295<br>CO 1670<br>CC 1647 |
| | | | | Found | 82.55 | 5.32 | 7.45 | |
| IIf | A(35) | 214.5–215.0 d.<br>HOAc | 216–217 d.[25] | | | | | NH 3280[25]<br>CO 1670[25]<br>CC 1642[25] |
| IIj | B(97)[c] | 257–258[e]<br>HOAc | 258 d.[4] | $C_{22}H_{17}N_3O_3$ | 71.15 | 4.16 | | NH 3250<br>CO 1692<br>CC 1647 |
| | | | | Found | 70.76 | 4.54 | | |
| IIk | A(38) | 234–235 d.[e]<br>HOAc | 220–221[f] | $C_{22}H_{16}N_4O_5$ | 63.46 | 3.87 | 13.46 | NH 3340<br>CO 1700<br>CC 1640 |
| | | | | Found | (S)63.62 | 3.73 | 13.55 | |
| IIl | A(68) | 196.5–197.0[e]<br>EtOAc | | $C_{22}H_{22}N_2O_3$ | 74.59 | 5.74 | 7.25 | NH 3280<br>CO 1668<br>CC 1640 |
| | | | | Found | 74.53 | 5.54 | 7.21 | |
| IIm | B(91)[c] | 197–198<br>EtOH | | $C_{22}H_{20}N_2O_2$ | 77.50 | 5.66 | 7.86 | NH 3290<br>CO 1670<br>CC 1645 |
| | | | | Found | 77.79 | 5.52 | 8.11 | |
| IIn | B(94.5)[g] | 211–212<br>EtOH | | $C_{23}H_{20}N_2O$ | 81.15 | 5.92 | 8.23 | NH 3280<br>CO 1678<br>CC 1644 |
| | | | | Found | 81.03 | 5.84 | 8.12 | |
| IIo | B(90)[h] | 203–204[e]<br>HOAc | | $C_{22}H_{17}N_3O_3$ | 71.15 | 4.61 | 11.32 | NH 3315<br>CO 1675<br>CC 1643 |
| | | | | Found | 71.19 | 4.56 | 11.37 | |
| IIp | B(87)[i] | 208.5–210.5<br>EtOH | | $C_{23}H_{20}N_2O_2$ | 77.50 | 5.66 | 7.86 | NH 3295<br>CO 1670<br>CC 1648 |
| | | | | Found | 77.47 | 5.57 | 7.88 | |

[a] Compounds IIh and IIi prepared by different method; see text. [b] Also prepared by another method; see text. [c] From IIa by amine exchange. [d] Strictly fortuitous, for the reaction used does *not* afford IIe; see text. [e] Yellow compound. [f] W. Borsche, *Ber.*, **41**, 3884 (1908); no analysis reported. [g] From IIf by amine exchange. [h] From IIk by amine exchange. [i] From IIl by amine exchange.

tained from A melted at 249–251°. Their infrared spectra are identical.

**(II(C) From 3-(*p*-Tolylamino)-5-phenyl-2(5H)-furanone Ib).**—Compound IIIb was treated similarly with *o*-phenylenediamine giving VIa which melted at 247–249° and has an infrared spectrum identical with that of VIa prepared according to procedures A and B.

**2-(*p*-Anisyl)-2,3-dihydrofuro[2.3-b]quinoxaline (VIb).**—*p*-Anisylidenepyruvic acid[23] (5.0 g., 0.024 mole) and *o*-phenylenediamine (2.5 g., 0.023 mole) were dissolved in 25 ml. of absolute ethanol and heated on the steam-bath for 15 min. A copious orange precipitate formed almost immediately and was filtered off after the solution had been cooled; 3.0 g., m.p. 238–245°. Recrystallization from absolute ethanol gave 1.5 g. (23%) of long, silken, orange needles, m.p. 249–250°. The analytical sample was recrystallized again from ethanol and melted at 249.5–250.5°. The infrared spectrum has strong bands at 1600 and 1625 cm.⁻¹. Absorption maxima in the ultraviolet are at 240 mμ ($\epsilon_{max}$ 0.78 × 10⁴) and 400 mμ ($\epsilon_{max}$ 1.9 × 10⁴).

*Anal.* Calcd. for $C_{17}H_{14}N_2O_2$: C, 73.36; H, 5.07; N, 10.07. Found: C, 73.30; H, 5.11; N, 10.06.

**Attempted Reduction of 3-(*o*-Nitrophenylamino)-5-(*p*-anisyl)-2-(5H)-furanone (IIIi).**—A solution of 0.326 g. (0.00100 mole) of IIIi in 75 ml. of acetic acid was stirred under 740 mm. of hydrogen with 0.033 g. of platinum oxide. After absorption of 151 ml. (0.00600 mole) of hydrogen, the catalyst and solvent were removed, leaving an intractable solid. Its infrared spectrum is nearly identical with that of VIb.

**Preparation of 1,5-Diaryl-3-arylamino-2(5H)-pyrrolones (II).**—Two general methods were used for the preparation of these compounds. The applicability of a particular procedure depends primarily on the nature of the amines from which the product is derived.

(A) This method is applicable only to compounds in which both N-aryl substituents are the same, and it differs in no way from the previously reported procedure.[25] The starting materials are the amine, benzaldehyde and pyruvic acid.

(B) The amine and IIa (or other II) were refluxed together in acetic acid solution for about 15 min. without prior fusion of the reactants.[26] The product usually crystallized out as soon as the solution was cooled and was filtered off and washed with cold acetic acid and ethanol.

The results of a number of such preparations are summarized in Table III.

**Preparation of 1,5-Diaryl-3-arylamino-2(5H)-pyrrolones (II) from 1,5-Diphenyl-2,3-pyrrolidinedione (I).**—The reaction of I with aniline to give IIa, and of I with *p*-toluidine to give IId was straightforward and yielded products whose infrared spectra, melting points and mixed melting points were identical with those of samples of IIa and IId prepared by method A and B, respectively. An equal weight of the amine was added at once to I suspended in a few ml. of ethanol, and the solution was then warmed on the steam-bath for a few minutes. On cooling, the products crystallized out in excellent yields.

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(25) W. R. Vaughan, *J. Org. Chem.*, **20**, 1613 (1955).

(26) The original procedure used by Bodforss[4] for the reported preparation of IIe and IIj, wherein IIa was fused with a large excess of amine, was first employed. The melt was crystallized from acetic acid (IIe) or from a mixture of acetic and hydrochloric acid (IIj). Purer products in higher yield were obtained by the reported procedure.

**Preparation of 1,5-Diphenyl-3-phenylamino-2(5H)-pyrrolone (IIa) from IVa.**—This procedure obviates the necessity of preparing pure I from IVa. A sample of IIa prepared in this manner was identical in all respects with samples obtained from other procedures. For details *cf.* the similar preparation of IIi, below. A 70% yield of IIa was obtained.

**1-(*p*-Tolyl)-3-oximino-5-phenyl-2-pyrrolidinone** was prepared by the method described by Bodforss[4] for the preparation of I oxime as modified by Meyer.[15] To a solution of 4.0 g. (0.174 g. atom) of sodium in 175 ml. of absolute ethanol was added 10.5 g. (0.151 mole) of hydroxylamine hydrochloride, and the solution was refluxed for 20 min. Then 10.75 g. (0.0304 mole) of IIf was added, and the mixture was refluxed 18 hr., and diluted with 175 ml. of water. After cooling for several hr., a small amount of insoluble material was filtered off, and the filtrate was acidified with glacial acetic acid. After cooling several hr., 4.2 g. of the oxime, m.p. 221.5–222.0°, was filtered off, and the filtrate afforded an additional 1.1 g., m.p. 220–221°. The total yield was 5.1 g. (60%). Five recrystallizations from absolute ethanol raised the melting point to 223–225°. This compound exhibits absorptions in the infrared at 3400, 3060, 1706, 1676 and 1636 cm.$^{-1}$.

*Anal.* Calcd. for $C_{17}H_{16}N_2O_2$: C, 72.84; H, 5.75; N, 9.99. Found: C, 72.40(S); H, 5.55(S); N, 9.79.

**1-(*p*-Anisyl)-3-oximino-5-phenyl-2-pyrrolidinone.**—To 1.6 g. (0.070 g. atom) of sodium, dissolved in 70 ml. of absolute ethanol, 4.2 g. (0.060 mole) of hydroxylamine hydrochloride was added, and the solution was refluxed 20 min. Then 4.7 g. (0.012 mole) of IIl was added and the solution was refluxed 18 hr. Dilution of the solution with 70 ml. of water caused the precipitation of 1.5 g. of unreacted IIl which was filtered off after the solution had been cooled for several hours. The filtrate was acidified with glacial acetic acid, and after cooling for several more hours, 1.5 g. of tan crystals were collected. Treatment with Norit and recrystallization from ethanol gave 1.3 g. (53%, based on 3.2 g. of IIl consumed) of white needles, m.p. 200–203°. Two recrystallizations from ethanol raised the melting point to 206.0–208.5°. One broad absorption at 3400 cm.$^{-1}$ and sharp bands at 1702 and 1661 cm.$^{-1}$ characterize the infrared spectrum of this compound.

*Anal.* Calcd. for $C_{17}H_{16}N_2O_3$: C, 68.90; H, 5.44, N, 9.45. Found: C, 68.90(S); H, 5.39(S); N, 9.39.

**1,5-Diphenyl-3-hydroxy-4-carbethoxy-2(5H)-pyrrolone (VIa).**—The procedure of Southwick and Seivard[27] was followed. From 168 g. (0.80 mole) of the sodium enolate of diethyl oxalacetate and 117 g. (0.65 mole) of benzylideneaniline there was obtained, after recrystallization from ethanol, 83.5 g. (40%) of IVa melting at 173–174° (reported[27] 173–175°).

**1,5-Diphenyl-2,3-pyrrolidinedione (I).**—Five grams (0.0155 mole) of IVa was refluxed 45 min. with 50 ml. of methyl benzoate to which had been added just enough water to permit a pot temperature of 180–185°. Upon cooling, 150 ml. of petroleum ether was added and the mixture was chilled. There was obtained by filtration 3.0 g. of faintly yellow crystals melting at 160–169°. Recrystallization from chloroform–petroleum ether afforded 2.0 g. of white powder melting at 159.0–160.5°. The mother liquors from filtration of the crude product, after being chilled in the refrigerator for 24 hr., afforded 0.9 g. of additional product (m.p. 160.5–162.0°), total yield 2.9 g. (74%). The infrared spectra of the second crop and recrystallized first crop indicated that the compound was relatively pure, since the bands characteristic of the condensation products (principally at 3260 and 1660 cm.$^{-1}$) were practically absent. Melting points of 158–159°,[16] 162–163°,[15] 159–162°[15] and 164–165°[1] have been recorded previously for this compound.

**1,5-Diphenyl-3-(N-pyrrolidyl)-2-(5H)-pyrrolone (IIh).**—To a suspension of 3.7 g. (0.014 mole) of I in 25 ml. of ethanol was added 2.0 g. (0.028 mole) of pyrrolidine. The solution was warmed on the steam-bath for 5 min. As soon as heating was begun the pyrrolidinedione dissolved. Precipitation of IIh commenced about one minute later. The reaction mixture was chilled for a few hours and filtered, whereupon there was obtained 3.5 g. (82%) of light tan powder melting at 159–160°. Four recrystallizations from ethanol afforded white needles melting at 159.5–161.5°. The infrared spectrum shows strong absorptions at 1670 and 1625 cm.$^{-1}$.

*Anal.* Calcd. for $C_{20}H_{20}N_2O$: C, 78.92; H, 6.62; N, 9.20. Found: C, 78.83; H, 6.34; N, 9.15.

**1,5-Diphenyl-3-(N-methyl-N-phenylamino)-2(5H)-pyrrolone (IIi).**—Five grams (0.0155 mole) of IVa was dissolved in 6 ml. of N-methylaniline, and the solution was boiled for 10 min., cooled somewhat, and 20 ml. of ethanol was added. Upon cooling, 4.1 g. of yellow needles melting over a very wide range was obtained. A second crop afforded 0.5 g. of additional product. The combined crude products were dissolved in hot ethanol, except for a small residue which did not dissolve and which was filtered off before the product was permitted to crystallize. Five additional recrystallizations from absolute ethanol were required before a constant melting point of 128.5–131.0° was attained. The infrared spectrum of this compound has bands at 1678 and 1630 cm.$^{-1}$.

*Anal.* Calcd. for $C_{23}H_{20}N_2O$: C, 81.15; H, 5.92; N, 8.23. Found: C, 81.25; H, 5.82; N, 8.26.

The alcohol-insoluble residue from the first recrystallization melted at 222–226°. Its infrared spectrum is identical with that of authentic IIa.[28]

**Reaction of I with Piperidine.**—A few drops of piperidine was added to a suspension of 2.0 g. of I in 20 ml. of ethanol. The mixture was warmed for a few min. on the steam-bath, during which time all of the I dissolved, followed almost immediately by the precipitation of some yellow crystals which were filtered off after the mixture was cooled; m.p. 139.0–139.5° dec. This material was soluble in ethanol, methanol, ethyl acetate and nitromethane but almost insoluble in petroleum ether, benzene and acetone. When warmed with any of these solvents in attempted recrystallizations, the compound imparted a purple color to the solution, and no pure product could be isolated. An infrared spectrum of the crude material showed absorptions at 3330, 1670 (with a shoulder at 1685), 1610 and 1595 cm.$^{-1}$.

**1,5,1′,2′-Tetraphenyl-2,4′,5′-trioxo-3,3′-bipyrrolidylidene.**—One gram of IVa was refluxed for 1 hr. in 20 ml. of wet decalin (sufficient water present to maintain a pot temperature of about 185°). During this time crystals began to separate from the hot solution. After the mixture had been cooled, 0.9 g. of light tan crystals was filtered off. Recrystallization from chloroform afforded 0.6 g. of snow-white needles. This product has no well-defined melting point, but decomposes at about 240°. The decomposition point is very sensitive to the rate of heating. Further recrystallizations from chloroform did not alter the infrared spectrum or the decomposition temperature. No satisfactory analysis could be obtained for this material, even though products from several different runs were analyzed after four or five recrystallizations.

*Anal.* Calcd. for $C_{32}H_{24}N_2O_3$: C, 79.32; H, 4.99; N, 5.78. Found: C, 78.32, 78.28(S): H, 5.38, 5.31(S); N, 5.21, 5.19. C, 76.21, 76.31(S); 74.23, 74.14(S); 77.35, 77.41(S); H, 5.01, 4.90(S); 4.68, 4.71(S); 4.82, 4.77(S); N, 5.22, 5.20; 5.33, 5.37; 5.59, 5.64.

**1,5-Diphenyl-3-hydroxy-4-carboxanilido-2(5H)-pyrrolone (IVc).**—1,5-Diphenyl-3-hydroxy-4-carbethoxy-2(5H)-pyrrolone (IVa) (5.0 g., 0.0155 mole) was dissolved by heating in a solution of 5.0 g. (0.054 mole) of aniline in 100 ml. of *cis*-decalin. When the temperature reached about 125° most of the starting material had dissolved and the flocculent white anilide began to separate. Heating was continued for 5 more min. until the temperature reached about 145°. The solution was then cooled, and the product was filtered and washed with petroleum ether (b.p. 60–75°). The yield of crude product was 5.0 g. (87%). The analytical sample was recrystallized from chloroform–petroleum ether, then from absolute ethanol and melted with gas evolution at 232–233°. It is not soluble in 10% aqueous sodium hydroxide solution.

*Anal.* Calcd. for $C_{23}H_{18}N_2O_3$: C, 74.55; H, 4.90; N, 7.57. Found: C, 74.58; H, 5.01; N, 7.43.

**1,5-Diphenyl-3-phenylamino-4-carboxanilido-2(5H)-pyrrolone.**—In a solution of 2 ml. of aniline in 15 ml. of glacial

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[27] P. L. Southwick and L. L. Seivard, THIS JOURNAL, **71**, 2532 (1949).

[28] This compound presumably arose from the presence of a small amount of aniline present in the commercial methylaniline used. Its presence undoubtedly accounts for the difficulty experienced in obtaining the IIi in a pure state, and the reaction has recently been repeated with aniline-free N-methylaniline to give a 78% yield of IIi which was indeed readily purified in two ethanol recrystallizations.

acetic acid was suspended 0.5 g. of IVc. The mixture was refluxed 10 min., during which time the solid dissolved. Water was added to the cloud point, and the solution was cooled, whereupon 0.5 g. (87%) of yellow needles melting at 204°–205° crystallized out. Recrystallization from ethanol–water with decolorization by Norit give white needles with the same melting point. The analytical sample was recrystallized twice from ethyl acetate–petroleum ether, but the melting point was not altered.

*Anal.* Calcd. for $C_{29}H_{23}N_3O_2$: C, 78.18; H, 5.20; N, 9.43. Found: C, 78.22; H, 5.29; N, 9.41.

**Hydrolysis of Vc.**—In 10 ml. of glacial acetic acid was dissolved 0.1 g. of Vc, and 5 ml. of 5% hydrochloric acid was added. The solution was heated to 80° at which temperature a white flocculent precipitate began to appear. The mixture was heated 3 min. longer and cooled. The precipitate after filtration and drying melted at 230–232° (undepressed on admixture with IVc). Its infrared spectrum is identical with that of IVc.

**Attempted Decompositions of IVc and Vc.**—In separate experiments 0.1 g. each of IVc and Vc were dissolved in solutions of 2 drops of aniline in 10 ml. of methyl benzoate. The solutions were refluxed for 25 min. and cooled. The starting materials were recovered unaltered. The same result was obtained when these compounds were boiled with aniline in the absence of solvent.

**Hydrolysis of 1,5-Diphenyl-3-phenylamino-4-methyl-2-(5H)-pyrrolone (Vb).**—To 0.5 g. (0.0015 mole) of Vb,[1,29] dissolved by gentle warming in 10 ml. of glacial acetic acid, was added 10 ml. of concentrated hydrochloric acid. The solution was refluxed 10 min., and then water was added to the hot solution to incipient crystallization. Upon cooling, the white crystals were filtered off, washed with water, and then with ethanol. White needles (0.3 g., 73%) were obtained which melted at 214–216°. The product was identified as 1,5-diphenyl-3-hydroxy-4-methyl-2(5*H*)-pyrrolone (IVb) by comparison of melting points (reported[1] 213.0–213.5°) and infrared spectrum with those of an authentic sample of IVb and by a mixture melting point, which was undepressed.

**1,5-Diphenyl-3-(N-piperidyl)-4-carboxpiperidido-2(5H)-pyrrolone (Vd).**—A solution of 1.0 g. of IVa in a mixture of 5 ml. of piperidine and 15 ml. of quinoline was heated to 190°, during which time some piperidine was allowed to distil slowly. The solution was refluxed 20 min. at this temperature and poured into 100 ml. of 10% hydrochloric acid. The gummy material which precipitated was recrystallized from ethanol–water, then from dioxane–water to yield a white powder melting at 175–205° dec., which was taken up in benzene–petroleum ether and filtered from some insoluble material. Evaporation of the solvents followed by two recrystallizations from dioxane–water afforded a small amount of white needles, m.p. 167.0°–168.5°.

*Anal.* Calcd. for $C_{27}H_{31}N_3O_2$: C, 75.49; H, 7.27; N, 9.78. Found: C, 75.53; 75.51(S); 75.34, 75.26; H, 7.48; 7.37(S); 6.96, 7.06; N, 9.48, 9.54.

In a similar experiment the only product isolated was IVd, m.p. 240–243° after recrystallizations from benzene and chloroform. Its identity was confirmed by means of a mixture melting point with IVd prepared by the hydrolysis of Vd and identity of their infrared spectra.

It was subsequently found that Vd was more readily obtainable in pure condition by the following procedure. A solution of 5.0 g. (0.0155 mole) of IVa in 50 ml. of decalin was heated with sufficient piperidine to maintain the boiling point at 170–180°. The solution was allowed to cool somewhat and petroleum ether (b.p. 60–75°) was added until crystallization began. A yellow powder (4.0 g., m.p. 130–150°) was obtained. Recrystallization from alcohol–water gave 1.7 g. of fine white needles melting at 167–169°. A small additional amount was obtained from the filtrate; total yield 2.1 g. (32%). The infrared spectrum is identical with that of Vd as prepared above.

**1,5-Diphenyl-3-hydroxy-4-carboxpiperidido-2(5H)-pyrrolone (IVd).**—In 15 ml. of glacial acetic acid was dissolved 0.50 g. (0.011 mole) of Vd. An equal volume of 10% hydrochloric acid was added and the solution was heated to the boiling point. As it warmed up crystals began to separate. The mixture was refluxed for 10 min., during which time the dark red color of the original solution was dissipated. The white granular crystals (0.35 g., 95%) were filtered off and melted at 242.0–243.5° (gas). After two recrystallizations from chloroform the compound melted at 241–242° (gas).

*Anal.* Calcd. for $C_{22}H_{23}N_2O_3$: C, 72.91; H, 6.12; N, 7.73. Found: C, 76.69(S); H, 6.30(S); N, 7.55.

**1,5-Diphenyl-3-phenylamino-4-carboxpiperidido-2(5H)-pyrrolone (Ve). (A) From 1,5-Diphenyl-3-(N-piperidyl)-4-carboxpiperidido-2(5H)-pyrrolone (Vd).**—A mixture of 0.50 g. (0.00116 mole) of Vd and 2.0 g. (0.021 mole) of aniline was dissolved in 25 ml. of glacial acetic acid, and the solution was refluxed for 10 min. Water was added to the cloud point, and 0.40 g. (79%) of yellow, granular crystals, m.p. 215–225°, precipitated. The analytical sample, m.p. 233–236°, was recrystallized twice from 95% ethanol.

*Anal.* Calcd. for $C_{28}H_{27}N_3O_2$: C, 76.86; H, 6.22; N, 9.61. Found: C, 76.64; H, 6.24; N, 9.53.

(B) **From 1,5-Diphenyl-3-hydroxy-4-carboxpiperidido-2-(5H)-pyrrolone (IVd).**—A mixture of 0.20 g. of IVd and 10 drops of aniline was refluxed in 10 ml. of glacial acetic acid for 10 min. Addition of water to the cloud point precipitated white crystals, which upon recrystallization from alcohol melted at 233–234°. A mixture of this material and the Ve obtained by procedure A above melted at 233–234°, and their infrared spectra are identical.

**Hydrolysis of Ve.**—Compound Ve (0.2 g.) was dissolved with heating in a mixture of 5 ml. of glacial acetic acid and 5 ml. of 5% hydrochloric acid. The solution was refluxed 15 min. On cooling, a white solid separated; m.p. 240.0–242.5°. It is identical with IVd as shown by identical infrared spectra and undepressed mixture melting point.

**1,5-Diphenyl-3-oximino-4-carboxanilido-2-pyrrolidinone.**—To a mixture of 15 ml. of pyridine and 15 ml. of ethanol was added 2.5 g. (0.0068 mole) of IVc and 2.5 g. (0.036 mole) of hydroxylamine hydrochloride. The resulting solution was refluxed 3 hr. on the steam-bath. The solution was then poured into 100 ml. of ice-cold, dilute hydrochloric acid. The aqueous mixture was chilled for 2 hr., and the pale yellow precipitate was collected. The crude product was triturated with a little hot benzene and cooled. The resulting white powder (1.8 g., 69%) was filtered off and melted at 190–200°. The analytical sample was recrystallized successively from ethanol, chloroform–petroleum ether and ethyl acetate. It melted at 213–215° with gas evolution and was in the form of white prisms. The infrared spectrum has bands at 3280, 3040, 1710, 1687 and 1660 $cm.^{-1}$.

*Anal.* Calcd. for $C_{23}H_{19}N_3O_3$: C, 71.67; H, 4.97; N, 10.90. Found: C, 71.71; H, 5.09; N, 10.89.

**1,2-Diphenyl-2,3-dihydro-3-carbethoxy-1-pyrrolo[2.3-b]-quinoxaline (IX).**—A mixture of 1.0 g. (0.0031 mole) of 1,5-diphenyl-3-hydroxy-4-carbethoxy-2(5*H*)-pyrrolone (IVa) and 1.0 g. (0.0091 mole) of *o*-phenylenediamine was dissolved by heating in 5 ml. of glacial acetic acid. The solution was refluxed 5 min. On cooling there precipitated 1.1 g. of orange crystalline powder, m.p. 205–210°. Recrystallization from a mixture of ethanol and acetic acid afforded 0.4 g. (32%) of yellow needles, m.p. 215.0–217.5°. The analytical sample was recrystallized twice more from an ethanol–acetic acid mixture; m.p. 215–216°.

*Anal.* Calcd. for $C_{25}H_{21}N_3O_2$: C, 75.93; H, 5.35; N, 10.63. Found: C, 75.82; H, 5.42; N, 10.63.

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(29) Kindly furnished by Dr. I. S. Covey.