sulfonic acid for 4 hr., the solution was dried with sodium carbonate, and chromatographed on alumina. The second 25-ml. fraction to come through the column on elution with benzene was evaporated and the solid was fractionally crystallized from ethanol. After one further recrystallization from ethanol, the solid melted at 143-146°, and on admixture with an authentic sample of the ketal (vide infra) this was undepressed. The infrared spectrum of this sample and that of the authentic ketal were identical.

(b) From 1,5-diphenyl-4-carbethoxy-2,3-pyrrolidinedione (XII). This procedure is due to the research of Covey.¹⁸ A solution of 1.0 g. (0.0031 mole) of 1,5-diphenyl-4-carbethoxy-2,3-pyrrolidinedione (XII)^{6b} in 80 ml. of nitrobenzene was heated until gas evolution commenced and for 12 min. thereafter. The nitrobenzene was then concentrated at the water pump, the resulting solution was evaporated nearly dry in an air stream, and ether was added. The solid was collected and washed with ether, 0.5 g. (65%), m.p. 163-168°. The analytical sample was recrystallized several times from toluene, m.p. 162-163° with softening at 158° (reported⁸ 158–159°). Anal. Caled. for C₁₆H₁₅NO₂: C, 76.47; H, 5.21; N, 5.57.

Mol. Wt., 251. Found: C, 76.54; H, 5.35; N, 5.45. Mol. Wt., 268, 271 (f.p. in camphor).

This compound had an infrared spectrum with absorption bands at 1700 and 1760 cm.⁻¹ which were identical with the strong bands of the product obtained by procedure (a). It was further characterized by means of its derivatives: the anil (V), m.p. 223-225° dec. (heated at 5°/min.) (reported13 227-228° dec.), mixture m.p. undepressed by authentic V, and infrared spectrum identical with that of V; the oxime (IVa), m.p. 238-239° dec. (heated at 16°/min.), no depression of m.p. by authentic IVa, which had an identical infrared spectrum; and the ethylene ketal, m.p. 145-147° from ethanol (see next experiment).

1,5-Diphenyl-3-ethylenedioxy-2-pyrrolidinone (XIII). A suspension of 1.0 g. (0.0030 mole of 1,5-diphenyl-3-anilino-2(5H)-pyrrolone (V) in 10 ml. of ethylene glycol containing 0.3 ml. of methanesulfonic acid was heated on the steam bath for 4 hr., at which time all solid had dissolved. The solution was poured into three times its volume of water and extracted with benzene. After drying with magnesium sulfate, the solvent was evaporated, leaving 0.8 g. (90%) of the ethylene ketal, m.p. 144-146°. After three recrystallizations from ethanol the material was analytically pure. white needles, m.p. 145-146°

Anal. Calcd. for C18H17NO3: C, 73.21; H, 5.80; N, 4.74. Found: C, 73.36; H, 5.85; N, 4.75.

The melting point of this sample was undepressed on admixture with the ketal prepared from either sample of XI, and the infrared spectra of the samples were identical.

ANN ARBOR, MICH.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

1,5-Diaryl-2,3-pyrrolidinediones. IX. Reassignment of Structure¹

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The compound previously described as 1,5-di(*p*-anisyl)-2,3-pyrrolidinedione has been shown to be 5-(*p*-anisyl)-3-(*p*-anisyl)-2,3-pyrrolidinedione has been shown to be 5-(*p*-anisyl)-3-(*p*-anisyl amino)-2(5H) furanone through synthesis of its dihydro reduction product, α -(p-anisylamino)- γ -(p-anisyl)- γ -butyrolactone. This enamino lactone structure applies to all previously reported 1,5-diaryl-2,3-pyrrolidinediones having no other substitution in the heterocyclic ring.

The tautomerism between the enamino lactones (formerly the pyrrolidinediones) and α -arylimino- β -benzylidenepropionic acids is pointed out to be an example of lacto-enoic tautomerism, facilitated by the participation of the free electron pair on the amino nitrogen atom.

The observations that supposed 1,5-diaryl-2,3pyrrolidinediones (I) underwent thermal decarboxylation to cinnamylideneanilines and were tautomeric with α -arylimino- β -benzylidenepropionic acids (II)³ were unprecedented and thus may give rise to doubts concerning the validity of the struc-

$$\begin{array}{ccc} N-Ar' & C_6H_5 & NC_6H_5 \\ \parallel \\ ArCH=CH-C-CO_2H & 0 \\ IIa: & Ar=Ar'=C_6H_5 & III \\ IIb: & Ar=Ar'=p-CH_3OC_6H_4 & III \end{array}$$

(1) Preliminary communication, W. L. Meyer and W. R. Vaughan, J. Org. Chem., 22, 98 (1957).

ture assignment of I. When 1,5-diphenyl-2,3-pyrrolidinedione (III) was synthesized and found to be different from the substance (Ia) previously assigned this structure,⁴ it was of interest to determine the correct structure of I unequivocally.

Examination of the literature indicates that little concrete structural information is available for I. The diphenyl compound (Ia) was originally formulated as the 2,3-pyrrolidinedione by Schiff and Gigli⁵ on the basis of an assumed analogy between the reactions of pyruvic acid and ethyl oxaloacetate with benzylideneaniline, ethyl oxaloacetate affording 1,5-diphenyl-4-carbethoxy-2,3-pyrrolidinedione (IV) under these conditions,⁶ while pyruvic acid led to Ia. The compound IV behaved as was expected for its structure, and although at

(4) W. L. Meyer and W. R. Vaughan, J. Org. Chem., 22, 1554 (1957)

(5) R. Schiff and L. Gigli, Ber., 31, 1306 (1898).
(6) (a) R. Schiff and C. Bertini, Ber., 30, 601 (1897); (b) L. J. Simon and A. Conduché, Ann. chim. et phys., [8] 12,5(1907).

⁽²⁾ National Science Foundation Predoctoral Fellow, 1954-57. Abstracted from a portion of the Ph.D. dissertation of W. L. Meyer, University of Michigan, 1957.

^{(3) (}a) W. R. Vaughan and L. R. Peters, J. Org. Chem., 18, 382 (1953); (b) W. R. Vaughan and L. R. Peters, J. Org. Chem., 18, 393 (1953); (c) W. R. Vaughan and L. R. Peters, J. Org. Chem., 18, 405 (1953); (d) W. R. Vaughan and D. I. McCane, J. Org. Chem., 20, 143 (1955).



that time no unequivocal proof of its structure existed, recent alternate syntheses have confirmed the original formulation of IV.^{3d,7}

In spite of unusual behavior which is not analogous to that of IV, the structure of Ia has been accepted in the literature with but one exception. Garzarolli-Thurnlackh⁸ suggested that it was the isomeric imino lactone (V) (with no experimental evidence), but even he abandoned his formulation in a later publication.^{9,10,10a}: Other early information which would support this structure, or any other, is indeed sparse. Attempted hydrolytic degradation of Ia afforded no well characterized materials.¹¹ Although Bücherer and Russischwili¹¹ isolated a substance which they believed was α -keto- γ -phenyl- γ -anilinobutyric acid from acid hydrolysis, this material was poorly characterized, and the acid was not reconvertible to Ia.

Attempts to prepare ketone derivatives from Ia have failed repeatedly. The anil (VI) is readily prepared,¹² and indeed is found to result even from



heating the substance in ethanol or acetic acid,^{12,18} which treatment presumably causes partial decomposition with liberation of aniline. However, no oxime can be obtained on reaction with hydroxyla-

(10a) Subsequent to our preliminary communication of this work,¹ Wasserman and Koch presented a reformulation of Ia in concurrence with ours. See H. H. Wasserman and R. C. Koch, Chemistry & Industry, 428 (1957).

(11) H. Bücherer and R. Russischwili, J. prakt. Chem., 128, 89 (1930).

(13) R. Ciusa and L. Musajo, Gazz. chim. ital., 59, 796 (1929).

mine,^{8d,11,12,14,15} and with phenylhydrazine, although a multiplicity of products is obtained, none of these appears to be a simple phenylhydrazone.^{3d,11,12,14} Thus the only evidence for a ketonic carbonyl in Ia is the formation of an anil, which cannot be hydrolyzed to the parent "ketone".^{11,16} A reported^{3a} alternate synthesis by hydrolysis and decarboxylation of 1,5-diphenyl-4-carbomethoxy-2,3-pyrrolidinedione might appear to give good foundation to the pyrrolidinedione formulation of Ia. However, this reaction has been found incapable of repetition, by the original investigator and others in this laboratory, and thus doubts may be raised as to the value of conclusions based on this work.

The only remaining item of structural information which has been offered is the reduction of α -(*p*-anisylimino)- β -(*p*-anisylidene) propionic acid (IIb) to two products.³⁰ the expected saturated amino acid VIIb and a dihydro saturated (and therefore cyclic) compound. The latter product (VIIIb) arose from reduction of the rearranged form of IIb, the supposed pyrrolidinedione Ib, and was assigned the structure 1,5-di(p-anisyl)-3-hydroxy-2-pyrrolidinone (IX). Aside from the preparation of a benzoyl derivative and microanalyses of the product and its derivative, no evidence was offered for this structure. This rather tenuous data constituted the only "real" evidence for the pyrrolidinedione structure.



When the pyrrolidinedione structure was definitely disproved for Ia,4 reevaluation of several points of the above behavior suggested a possible isomeric formulation for I. The infrared spectra of Ia and the anil VI bear striking similarities to one another. Thus in the spectrum of Ia (Nujol) are found bands at 3310, 1736, and 1656 cm.⁻¹, whereas VI absorbs at 3300, 1674, and 1648 cm. -1 The structure of VI being known,^{4,17} these spectral data would suggest that Ia and VI have an NH function $(3300 \text{ cm}.^{-1})$ and a C==C $(1650 \text{ cm}.^{-1})$ in common; the difference in the third absorption (approximately 62 cm.⁻¹) suggested a lactam-lactone isosterism. The expected difference in the frequency of carbonyl absorptions of lactones and lactams is reported to be 60-80 cm.⁻¹ ¹⁸ with which the

^{(7) (}a) P. L. Southwick and L. I. Seivard, J. Am. Chem. Soc., 71, 2532 (1949); (b) P. L. Southwick and R. T. Crouch, J. Am. Chem. Soc., 75, 3413 (1953).

⁽⁸⁾ K. Garzarolli-Thurnlackh, Monatsh., 20, 480 (1899).

⁽⁹⁾ K. Garzarolli-Thurnlackh, Ber., 32, 2274 (1899).

⁽¹⁰⁾ An enamino lactone structure similar to that of Garzarolli-Thurnlackh⁸ and subsequently found to be correct¹ was suggested to one of us (W.R.V.) by Dr. J. A. King in a private communication subsequent to the publication of the papers of Vaughan and Peters.^{3a,b,c} The suggestion was accompanied by appropriate reassignment of infrared bands with which we now concur (vide infra).

⁽¹²⁾ S. Bodforss, Ann., 455, 290 (1927).

⁽¹⁴⁾ W. R. Vaughan, J. Org. Chem., 20, 1619 (1955).

⁽¹⁵⁾ J. L. Spencer in this laboratory has found that Ia yields the oxime of benzylidenepyruvic acid when treated with hydroxylamine hydrochloride.

⁽¹⁶⁾ O. Doebner and M. Gieseke, Ann., 242, 290 (1887).

⁽¹⁷⁾ W. R. Vaughan, J. Org. Chem., 20, 1613 (1955).
(18) L. J. Bellamy, The Infrared Spectra of Complex Molecules, John Wiley and Sons, Inc., New York, 1954, pp. 153, 176.

difference between the saturated lactones and lactams X and XI⁴ agrees. Thus it appeared that Ia might be 5-phenyl-3-anilino-2(5H)-furanone, and this structure was taken as a working hypothesis for the remainder of the work.¹⁰

$$\begin{array}{c} R \longrightarrow O \\ R \longrightarrow O \\ \\ \hline \\ O \\ X: R = H \text{ or } C_6 H_5 \\ \hline \\ XI: R = H \text{ or } C_6 H_5 \\ \hline \\ XI: R = H \text{ or } C_6 H_5 \\ \hline \\ \end{array}$$

This proposed structure for Ia demands an NH group in the compound of similar character to that in the anil VI. Since the anil affords an N-nitroso derivative from this function,⁴ Ia was subjected to the nitrosation conditions which produced such a change in VI, and a mononitroso derivative which was transparent in the NH region of the infrared was indeed obtained. In all other respects this derivative was analogous to the N-nitroso derivative of VI,⁴ and hence is formulated as 5-phenyl-3-(phenylnitrosamino)-2(5H)-furanone (XII). This supports the proposed structure of Ia by confirm-



ing that the high frequency absorption of the spectrum is due to NH and not OH, and increases the analogy with VI.

Consideration of the proposed structure for I requires that the cyclic dihydro reduction product of Ib obtained by Vaughan and Peters,³⁰ rather than having the structure assigned by these investigators, should be α -(*p*-anisylamino)- γ -(*p*-anisyl)- γ -butyrolactone (VIIIb). Hence it was decided to reduce Ia to the analogous α -anilino- γ -phenyl- γ -butyrolactone (VIIIa) and to synthesize this substance in an unequivocal manner for comparison.



All attempts to reduce Ia to a dihydro product failed. The only material isolated from attempted reduction of this substance under any conditions was α -anilino- γ -phenylbutyric acid (VIIa). This amino acid may have arisen from reduction of the tautomeric form of Ia (IIa), due to unfavorable rates of isomerization and reduction of the two tautomeric forms Ia and IIa. However, in view of the proposed structure of Ia, it could as well have arisen from rapid hydrogenolysis of the VIIIa which was the initial reduction product of Ia. Neither occurrence may be argued a priori from our experimental evidence; however, that the latter is a possibility is shown by the reduction of VIIIa (vide infra) to the amino acid under the same experimental conditions used for the reduction of Ia.

The amino lactone VIIIa was synthesized with the intention of applying the synthesis to the di-(p-anisyl) analog (VIIIb) for comparison with the reduction product of Vaughan and Peters.³⁰ The

$$ArC-CH=CH=CO_{2}H \xrightarrow{Ar'NH_{9}}$$

$$ArC-CH=CH=CO_{2}H \xrightarrow{Ar'NH_{9}}$$

$$ArCCH_{9}CH-CO_{2}H$$

$$i$$

$$NHAr'$$

$$XIIIa: Ar = Ar' = C_{6}H_{5}$$

$$XIIIb: Ar = Ar' = p-CH_{3}OC_{6}H_{4}$$

$$XIIIc: Ar = C_{6}H_{5}; Ar' = p-CH_{3}OC_{6}H_{4}$$

$$Ar \xrightarrow{O} \qquad OH$$

$$i$$

$$Ar \xrightarrow{O} \qquad ArCH-CH_{2}CH-CO_{2}H$$

$$i$$

$$NHAr'$$

$$NHAr'$$

$$VIIIa: Ar = Ar' = C_{6}H_{5}$$

$$XIV: Ar = Ar' = p-CH_{3}OC_{6}H_{4}$$

$$VIIIb: Ar = Ar' = p-CH_{3}OC_{6}H_{4}$$

$$VIIIb: Ar = C_{6}H_{5}; Ar' = p-CH_{3}OC_{6}H_{4}$$

$$VIIIb: Ar = C_{6}H_{5}; Ar' = p-CH_{3}OC_{6}H_{4}$$

$$VIIIc: Ar = C_{6}H_{5}; Ar' = p-CH_{3}OC_{6}H_{4}$$

addition of aniline to β -benzoylacrylic acid has been described by Bougault,¹⁹ although it was not shown conclusively whether the α -amino acid or the β amino acid was the product. One would expect the α -amino acid to result from such a reaction, as addition to the ketone-vinyl system should be favored over addition to the acid-vinyl system.^{20,21} On repetition of Bougault's reaction, the product described him as α -anilino- β -benzoylpropionic acid by (XIIIa) was obtained. On treatment with sodium borohydride, the ketone was reduced, and after acidification and warming for a short time, an amino lactone (VIIIa) was obtained. That this lactone had the α -anilino function was shown by its hydrogenolysis to α -anilino- γ -phenylbutyric acid (VIIa) which was compared with a sample prepared from the α -bromo acid. Thus the addition of aniline to benzoylacrylic acid takes place in the presumed manner.

The synthetic VIIIa has an infrared spectrum very similar to that of Vaughan and Peters'³ reduction product, VIIIa absorbing at 3350 (NH) and 1742 cm.⁻¹ (C=O), and the reduction product VIIIb absorbing at 3320 (NH) and 1758 (C=O). For further evidence along these lines, *p*-anisidine

⁽¹⁹⁾ J. Bougault, Ann. chim. et phys., [8] 15, 491 (1908). See also P. Chabrier et al., Compt. rend., 230, 212 (1950); 226, 1378 (1948); 237, 1420 (1953).

⁽²⁰⁾ M. M. Fraser and R. A. Raphael, J. Chem. Soc., 2245 (1950).

⁽²¹⁾ N. H. Cromwell, P. L. Creger, and K. E. Cook, J. Am. Chem. Soc., 78, 4412 (1956).

was added to β -benzoylacrylic acid, and the resulting amino keto acid (XIIIc) was reduced and lactonized to α -(*p*-anisylamino)- γ -phenyl- γ -butyrolactone (VIIIc). This amino lactone had an infrared spectrum even more similar to VIIIb, absorbing at 3320 and 1759 cm.⁻¹

With the evidence at hand suggesting that our hypothesis was correct. p-anisidine was added to β -(p-methoxybenzoyl) acrylic acid to yield α -(p-ani $sylamino) - \beta - (p - methoxybenzov) propionic acid$ (XIIIb). This amino keto acid. on treatment with sodium borohydride, was smoothly reduced to an amino hydroxy acid (XIV), but the latter resisted lactonization under conditions which had been successful for the other analogs. Such behavior might suggest that a different type of product was obtained in this case, but the infrared spectrum did not support such a conclusion. The spectrum of the amino keto acid XIIIb was almost indistinguishable from the spectra of the amino keto acids XIIIa and XIIIc, and the spectrum of the amino hydroxy acid XIV was identical with the spectrum of α -(panisylamino)- γ -(p-anisyl)butyric acid (VIIb)³⁰ with the exception of two bands assignable to OH and C=O vibrations. Thus it appears that the non-lactonization of XIV is a property peculiar to this hydroxy acid, possibly due to its insolubility in the reaction medium.

When the amino hydroxy acid XIV was treated with benzoyl chloride in pyridine, lactonization and benzoylation occurred smoothly, and the benzoyl derivative (XV) of the amino lactone VIIIb was isolated. This material was identical in all re-



spects (infrared spectrum and mixture melting point) with the benzoyl derivative of Vaughan and Peters' reduction product,^{3°} and confirms formulation of this reduction product as α -(*p*-anisylamino)- γ -(*p*-anisyl)- γ -butyrolactone (VIIIb).

Thus the structure of Ib must be that of an α amino- γ -lactone containing one double bond. The infrared spectrum and the preparation of an *N*-nitroso derivative from the analogous diphenyl compound Ia require the presence of an NH group in the molecule, and hence the double bond must be endocyclic. The carbonyl groups of the reduced materials VIIIa and VIIIb absorb at higher frequencies in the infrared than do the dehydro compounds Ia and Ib. Thus the double bond must be conjugated with the carbonyl in I, for a β, γ double bond would lead to an enol lactone structure, which would absorb at a higher frequency in the infrared than would the corresponding saturated lactone.²² The foregoing arguments indicate that the only acceptable formulation for Ia and Ib is as 5-aryl-3-arylamino-2(5H)-furanones (I). The similarities in the methods of preparation,^{3a} chemical properties,³ and infrared spectra^{3a} of all known and otherwise unsubsti-



tuted "1,5-diaryl-2,3-pyrrolidinediones"23 requires that all have analogous structures, and hence must be formulated as I. J. 8,10 Thus the 1,5-diphenyl-2,3pyrrolidinedione reported in our previous paper⁴ is the only known compound of this class. This, of course, does not at all apply to 2,3-pyrrolidinediones having other types of substitution.^{3d,7,24} The determination of the enamino lactone structure for I immediately clarifies the tautomeric behavior^{3b,o,d} of I and II.²⁵ This is now seen to be simply an unusually facile case of the reversible lactonization of a β , γ -unsaturated acid, "lacto-enoic tautomerism."26 The extreme ease of interconversion of the "tautomers" in the present system may well be due to the availability of the free electron pair on nitrogen for participation in the electron shift which produces the isomerism:



In this manner, a concerted electron recession from nitrogen to oxygen produces the zwitterionic form of the imino acid II. From consideration of the infrared spectrum of II and its electrical conductivity²⁰ it appears that the imino acid II normally exists as the zwitterion, and hence the system is ideally situ-

⁽²²⁾ Ref. 18, p. 160; F. Ramirez and M. B. Rubin, J. Am. Chem. Soc., 77, 3768 (1955), and references cited therein.

⁽²³⁾ With the exception of the 1,5-diphenyl-2,3-pyrrolidinedione (III) reported in our previous paper,⁴ which was shown to have this structure.

⁽²⁴⁾ P. L. Southwick, E. P. Previc, J. Casanova, Jr., and E. H. Carlson, J. Org. Chem., 21, 1087 (1956).

⁽²⁵⁾ There is no doubt concerning the structure of II. Vaughan and Peters³⁰ confirmed the structure of IIb through reduction to VIIb, which was prepared in an alternate fashion. Vaughan¹⁷ has reduced IIa to the saturated amino acid VIIa, and this has been shown identical with the authentic sample prepared from the bromo acid in the usual manner. (26) R. P. Linstead and H. N. Rydon, J. Chem. Soc., 580 (1933).

ated for the reversal (cyclization) of the isomerism through initial attack of the carboxylate anion at the γ -carbon atom:



This example of tautomeric behavior is unique in that no proton shift is needed to complete the isomerization.

It has been suggested^{3b,o} that the decarboxylation of I proceeds through an initial rapid isomerization to II, which is the actual decarboxylating species and loses carbon dioxide in the rate determining step of the reaction. This is certainly a possible, and even probable mechanism for the decarboxylation, but the inverse mechanism cannot be excluded; i.e., the cyclic form may lose carbon dioxide in the slow step, the imino acid cyclizing to this in a preliminary rapid isomerization. Such a possibility is supported by the rapid formation of the ring form (I) from the chain form (II) on warming for recrystallization, suggesting that I is the more stable tautomer at increased temperatures. Also, consideration of the rate and equilibrium data of Vaughan and Peters³⁰ for the lone measurable example of the tautomerism, with exactly the same assumptions as were made by these authors, indicates the cyclization, as well as the ring-opening, reaction to be many times more rapid than the decarboxylation. Thus the same kinetic order for decarboxylation would be anticipated for either mechanism. Both mechanisms fit all the known facts, and with the evidence at hand, it is not possible to determine which is correct.

EXPERIMENTAL

All melting and boiling points are uncorrected. Infrared spectra were obtained from Nujol mulls, unless otherwise noted, by means of a Perkin-Elmer Model 21 infrared spectrophotometer. Microanalyses are by Spang Microanalytical Laboratory, Ann Arbor, Mich.

5-Phenyl-3-anilino-2(5H)-furanone (Ia). (a) Aniline was condensed with benzylidenepyruvic acid⁸⁴ according to the method of Vaughan and Peters.^{3a}

(b) By utilizing acetic acid as a solvent, it was found unnecessary to isolate pure benzylidenepyruvic acid from its salt. Sodium benzylidenepyruvate^{3d} was dissolved in the minimum amount of glacial acetic acid, and with stirring there was added at room temperature one equivalent of aniline in acetic acid. Precipitation was complete in 30 min. The solid was filtered off and washed with ethanol. By addition of an equal volume of ethanol to the filtrate, a second crop was obtained. The yield was 70%, m.p. 160.5-161.0° dec. (reported^{3a} 160.0-160.5° dec.).

Reduction of 5-phenyl-3-anilino-2(5H)-furanone (Ia). To a suspension of 270 mg. (1.07 mmoles) of Ia in 40 ml. of absolute alcohol was added a spatula tipful of 5% palladiumon-carbon catalyst (Baker and Co., Inc.), and the mixture was stirred under one atmosphere of hydrogen at 25°. After 1 hr., absorption of hydrogen had ceased, 64 ml. (114% of 2 equivalents) being taken up. The catalyst was filtered off, washed well with ethanol, and the ethanol evaporated to leave 213 mg. (79%) of white solid which after one recrystallization from ethanol melted at 181–185° dec. (heated at 5°/min.) and showed no depression of m.p. on admixture with the authentic sample (vide infra) of α -anilino- γ -phenylbutyric acid (VIIa). The infrared spectrum of this material was indistinguishable from that of the authentic sample.

A methyl ester hydrochloride was prepared by treatment with methanolic hydrogen chloride; after one recrystallization it melted at 157-159°: mixture m.p. with the authentic sample 157-160°.

 α -Anilino- γ -phenylbutyric acid (VIIa). In 10 ml. of ethanol was dissolved 1.5 g. (0.0061 mole) of α -bromo- γ -phenylbutyric acid²⁷ and approximately 2 g. of aniline. The solution was refluxed for 2 days. On cooling, white crystals of the anilino acid VIIa precipitated and were filtered. After one recrystallization from ethanol there was collected 1.1 g. (71%) of the product, m.p. 184–186° dec. One further recrystallization from ethanol and one from ethanol-acetic acid produced the analytical sample, m.p. 186–188° dec. (reported¹⁷ 192–194° dec.).

Anal. Calcd. for C₁₆H₁₇NO₂: C, 75.27; H, 6.71; N, 5.49. Found: C, 75.41; H, 6.52; N, 5.45.

A benzene-soluble methyl ester hydrochloride was prepared by refluxing in methanolic hydrogen chloride. Recrystallization was effected by dissolving in a small amount of benzene, passing in dry hydrogen chloride, adding petroleum ether (b.p. 60–75°) to the warmed solution to saturation, and cooling. After several recrystallizations by this procedure, the analytical sample melted at 157–159°.

Anal. Calcd. for C₁₇H₂₀ClNO₂: C, 66.77; H, 6.59; Cl, 11.60; N, 4.57. Found: C, 66.84; H, 6.69; Cl, 11.71; N, 4.60.

The anilino acid VIIa and its methyl ester hydrochloride were shown to be identical with the anilino acid of Vaughan¹⁷ obtained by reduction of α -phenylimino- β -benzylidenepropionic acid (IIa) and the methyl ester hydrochloride prepared from it. The melting points and infrared spectra of the samples were identical, and mixture melting points were undepressed.

5-Phenyl-3-(phenylnitrosamino)-2(5H)-furanone (XII). To a solution of 300 mg. (1.2 mmoles) of 5-phenyl-3-anilino-2(5H)-furanone (Ia) in 7 ml. of hot glacial acetic acid there was added dropwise a solution of 100 mg. of sodium nitrite in 2 ml. of water. The mixture became bright orange colored. Water was added to the hot solution to incipient precipitation and the solution was cooled. The tan solid which precipitated was filtered off and the mother liquors were allowed to stand for several days to collect a second crop. The total yield was 150 mg. (45%), m.p. 216.0-216.5° dec., after several recrystallizations from acetic acid (fine lemon-yellow needles). The infrared spectrum of the sample was transparent in the high frequency region.

Anal. Calcd. for C10H12N2O3: C, 68.56; H, 4.32; N, 10.00. Found: C, 68.71; H, 4.17; N, 10.14.

 α -Anilino- γ -phenyl- γ -butyrolactone (VIIIa). To a solution of 647 mg. (2.40 mmoles) of α -anilino- β -benzoylpropionic acid (XIIIa)^{19, 28} in 20 ml. of 5% sodium bicarbonate was added a solution of 200 mg. of sodium borohydride in 5 ml. of water. This was allowed to stand at room temperature for 12 hr., and then was acidified with hydrochloric acid. The suspension was warmed on the steam bath for 3 hr. and allowed to stand overnight at room temperature. Excess 5% sodium bicarbonate was added and the solid was filtered off, washed with 5% sodium bicarbonate and water, and dried. This yielded 395 mg. (65%) of the anilino lactone VIIIa, m.p. 118-124°. Several recrystallizations

⁽²⁷⁾ E. Fischer and W. Schmitz, Ber., 39, 2208 (1906).

⁽²⁸⁾ The authors are indebted to Prof. P. A. S. Smith for a sample of β -benzoylacrylic acid used in this work.

from ethanol produced small white platelets of analytical purity, m.p. 128-129°.

Anal. Caled. for C₁₆H₁₅NO₂: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.84; H, 6.02: N, 5.59.

Reduction of α -anilino- γ -phenyl- γ -butyrolactone (VIIIa). α -Anilino- γ -phenyl- γ -butyrolactone (VIIIa) (258 mg., 1.02 mmoles) was reduced exactly as was 5-phenyl-3-anilino-2(5*H*)-furanone (Ia) above. There was absorbed 112% of one equivalent of hydrogen in 1 hr., and 200 mg. (77%) of α -anilino- γ -phenylbutyric acid (VIIa) was obtained, m.p. 183-186° dec. (heated at 5°/min.) after one recrystallization from ethanol. On comparison with authentic material, in-frared spectra were superimposable and the mixture m.p. was 184-188° dec.

 α -(*p*-Anisylamino)- β -benzoylpropionic acid (XIIIc). In a solution of 1.0 g. of sodium carbonate in 10 ml. of water was dissolved 1.0 g. (5.7 mmoles) of β -benzoylacrylic acid and 1.0 g. (8.1 mmoles) of *p*-anisidine. After standing for 16 hr. at room temperature, the solution was acidified with acetic acid, precipitating an oil which soon solidified. This was filtered and washed well with ether, yielding 1.3 g. (77%) of XIIc. Several recrystallizations from benzene produced the analytical sample, m.p. 134–135° dec.

Anal. Caled. for C₁₇H₁₇NO₄: C, 68.19; H, 5.72; N, 4.68. Found: C, 67.79; H, 5.66; N, 4.53.

 α -(p-Anisylamino)- γ -phenyl- γ -butyrolactone (VIIIc). The sodium borohydride reduction of XIIIc was carried out by a procedure identical with that used for the preparation of VIIIa above. The product was recrystallized from ethanol, m.p. 147-148° (21% yield).

Anal. Caled. for $C_{17}H_{17}NO_4$: C, 72.07; H, 6.05; N, 4.94. Found: C, 72.01; H, 6.02; N, 4.93.

 α -(p-Anisylamino)- β -(p-methoxybenzoyl)propionic acid (XIIIb). The addition of p-anisidine to β -(p-methoxy-

benzoyl)acrylic acid¹⁹ [prepared from β -(*p*-methoxybenzoyl)propionic acid²⁹] was carried out as was the preparation of XIIIc above. The product was obtained in quantitative yield; m.p. 144.5-145.0° dec. after several recrystallizations from benzene.

Anal. Caled. for $C_{18}H_{19}NO_5$: C, 65.64; H, 5.82; N, 4.25. Found: C, 65.69; H, 5.79; N, 4.25.

 α -(*N*-Benzoyl-p-anisylamino)- γ -(p-anisyl)- γ -butyrolactone (XV). To a solution of 1.0 g. (0.0030 mole) of XIIIb and 0.5 g. of sodium carbonate in 20 ml. of water was added 0.5 g. (0.013 mole) of sodium borohydride. After standing at room temperature for 12 hr. acidification with acetic acid precipitated the amino hydroxy acid XIV, which could not be induced to lactonize. This hydroxy acid was dissolved in warm pyridine and treated with benzoyl chloride. After warming for a few minutes, the solution was poured into excess 3% sodium carbonate solution. The XV came down as an oil which soon crystallized and was recrystallized from ethanol, m.p. 157-161°. Several further recrystallizations produced small white needles of analytical purity, m.p. 164.5-165.5° (reported³⁰ 169.5-170.0°).

164.5-165.5° (reported³⁰ 169.5-170.0°). Anal. Calcd. for C₂₅H₂₃NO₅: C, 71.95; H, 5.55; N, 3.36. Found: C, 71.82; H, 5.53; N, 3.37.

When compared with the material erroneously described by Vaughan and Peters³⁰ as the benzoate of 1,5-di-(p-anisyl)-3-hydroxy-2-pyrrolidinone, this compound was found identical in all respects, and the mixture melting point was undepressed.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

1,5-Diaryl-2,3-pyrrolidinediones. X. Phenylhydrazine Derivatives

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Structures of two of the three products of the reaction of 5-phenyl-3-anilino-2(5H)-furanone (I) with phenylhydrazine have been reassigned. One of these, 1,5-diphenyl-2,3-pyrrolidinedione-3-phenylhydrazone (XI) was found to be tautomeric with benzylidenepyruvanilide phenylhydrazone (IX), a new type of tautomerism for which the term "lactam-enamide" is proposed.

5-Phenyl-3-anilino-2(5*H*)-furanone (I), the compound formerly described as 1,5-diphenyl-2,3-pyrrolidinedione (II), affords three distinct products on treatment with phenylhydrazine.²⁻⁵ These compounds, A, B, and C, have been variously formulated in the literature, but inasmuch as they have been considered derived from and analogous to II (which was an incorrect structure), the reformula-

tion of II as I,⁶ which may isomerize reversibly to III, has made a re-evaluation of these derivatives desirable.



The simplest of the reaction products of I with phenylhydrazine is A, first obtained by Bücherer and Russischwili³ and later examined by Vaughan and McCane.⁴ This substance, A, has the molecular formula $C_{16}H_{14}N_2O_2$, and arises by substitution of aniline by phenylhydrazine.⁴ By analogy with the

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