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

2,3-PYRROLIDINEDIONES. I. PREPARATION AND STRUCTURE

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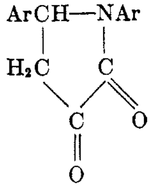
The observation that 1,5-diaryl-2,3-pyrrolidinediones evolve carbon dioxide upon thermal decomposition was first reported by Johnson and Adams (1). Recently investigation of the possibility that such substances might be decarbonylated to β-lactams led to more careful examination of the thermal decomposition reaction and identification of the other decomposition product as a cinnamylideneaniline (2). The obviously unusual character of this "decarboxylation" reaction has led us to examine the nature of the compound which suffers such degradation and to study the reaction mechanism.

Two general methods have been used for the preparation of 1,5-diaryl-2,3-pyrrolidinediones: the first involves the reaction of benzylideneaniline with pyruvic acid in cold glacial acetic acid (3), and the second involves the reaction of benzylidenepyruvic acid with aniline in warm alcohol (3).

1. $ArCH{=}NAr + CH_3COCO_2H \rightarrow$
2. $ArCH{=}CHCOCO_2H + H_2NAr \rightarrow$



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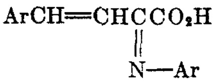
In the present study the second method was found to be more satisfactory because, although benzylidenepyruvic acids are less readily accessible than the corresponding benzylideneanilines, the yields in the critical step were found to be superior and the products more easily purified. Thus only when the benzylidenepyruvic acid failed of ready preparation was the first reaction employed.

It is possible that both methods of preparation may involve a common intermediate by some process of exchange, and it would appear from the present investigation and from earlier work (4, 5) that 2-arylimino-3-benzylidenepropionic acids (II) are indeed formed in both procedures. That rearrangement of



$$ArCH{=}CH\underset{\underset{N-Ar}{\|}}{C}CO_2H$$

II

such acids to compounds of structure I usually occurs upon recrystallization (5), is amply confirmed in the present study.

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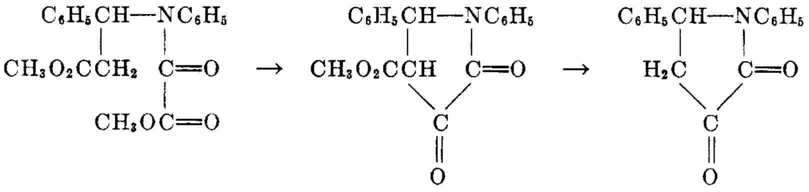
[1] Rackham Predoctoral Fellow 1950–1951.

[2] Abstracted from a portion of the Ph.D. dissertation of Lynn R. Peters, University of Michigan, 1952.

In view of the nature of the reactants it is not surprising that investigations of the well-known Doebner cinchoninic acid synthesis (6) should have had as a by-product considerable information concerning the mode of formation of 2,3-pyrrolidinediones (1, 3, 5, 7–18). Information from these sources, however, is confusing and contradictory, and until the present time no one appears to have offered a satisfactory explanation of the manner in which compounds of structure II are converted into compounds of structure I.

The earliest assignment of the generally accepted structure (I) for the condensation products from reactions such as 1 or 2 was made by Schiff and Bertini (8). Subsequently the 2,3-pyrrolidinedione structure for the neutral condensation products from aldehydes, α-ketoacids, and amines has been accepted almost without exception (see, however, 6 and 7, for other alternatives). The existence of a carbonyl (presumably at position 3) was "established" by the formation of 3(?)-anils (10), which interestingly enough could not be hydrolyzed to the free 2,3-pyrrolidinediones (3). The nature of the reaction with phenylhydrazine remains in doubt as various workers have reported divergent results (3, 5, 19).

It will be seen from the previous paragraph that no one has offered a really convincing proof of structure for these compounds, and indeed, even the existence of the pyrrolidine ring system has not been demonstrated. However, one of the present authors succeeded in preparing I (Ar = C_6H_5) by means of a Dieckmann cyclization of methyl 3-phenyl-3-(N-methoxalyl-N-phenylamino)propionate followed by hydrolysis and decarboxylation (2): Thus the cyclic nature of the system is confirmed.



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A number of authors have suggested that 2,3-pyrrolidinediones are more correctly represented as 3-hydroxy-Δ^3-2-pyrrolinones (19, 20). Although Borsche has reported the preparation of the enol-acetate and benzoate of 1,4,5-triphenyl-2,3-pyrrolidinedione (14) all attempts to obtain enol derivatives of the 1,5-diaryl-2,3-pyrrolidinediones of the present study met with failure. However, the accompanying infrared spectra lend strong support for the enol structure, which is interesting in view of the failure of some of the substances to give characteristic color reactions with alcoholic ferric chloride.

The infrared spectrum of each of the 1,5-diaryl-2,3-pyrrolidinediones prepared in this study shows a band due to the hydroxyl; 2.93 μ in chloroform (Fig. 1) solvent, 3.04 μ in dioxane (Fig. 2); and a band at 6.02 μ attributable to the enolic carbon-to-carbon double bond (21). Likewise there appears but one frequency attributable to the carbonyl group at approximately 5.72 μ. On the other hand, a five-membered cyclic dicarbonyl, exemplified by camphorquinone,

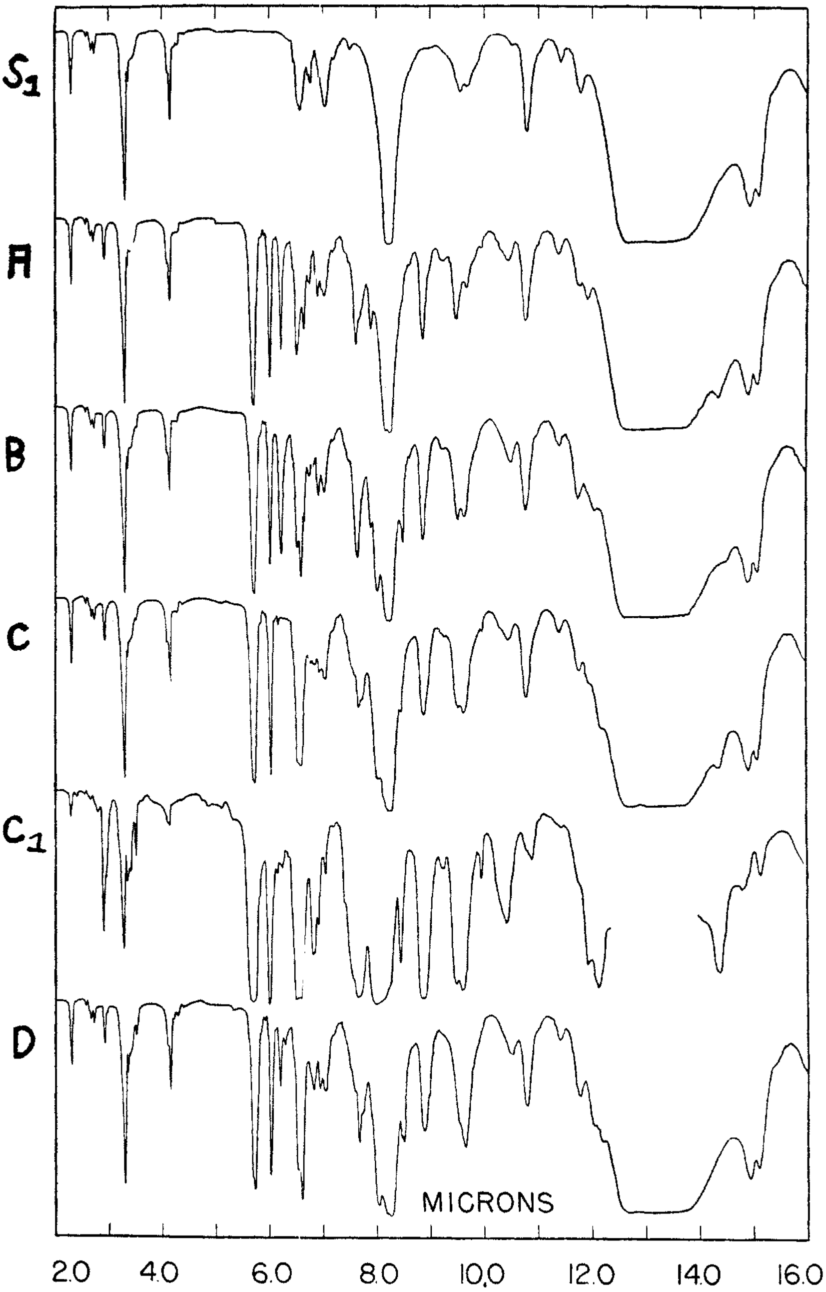

FIG. 1. INFRARED SPECTRA

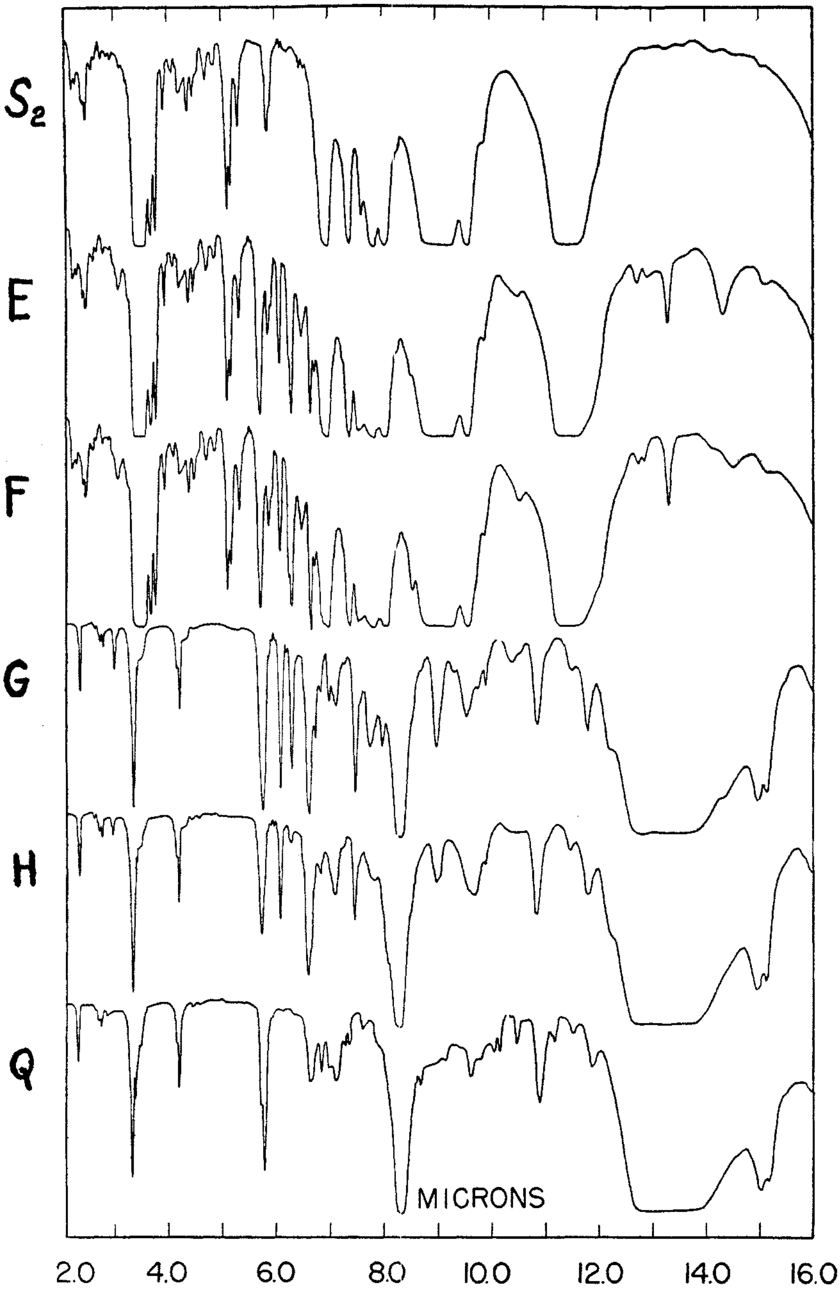

FIG. 2. INFRARED SPECTRA

which cannot enolize, shows two carbonyl frequencies: one at 5.64 μ and one other at 5.71 μ (Fig. 2).[3]

Not all of the pyrrolidinediones were examined in the ultraviolet. However, a careful examination of 1,5-bis(4-methoxyphenyl)-2,3-pyrrolidinedione was made (Fig. 3). The spectrum shows well-defined maxima at two wavelengths: 301 mμ ($\epsilon = 1.34 \times 10^4$) and 225 mμ ($\epsilon = 2.01 \times 10^4$) in ether (Fig. 3). The 225, mμ band may be attributed to ethylenic absorption of the benzene rings (22), and the 301 mμ band, being too intense for unconjugated benzenoid absorption may be attributed to the components of the five-membered ring system. It is to be noted, however, that the wavelength and extinction coefficient of the 301 mμ band are particularly high for two conjugated chromophores. The resolved absorption band in the visible region near 420 mμ exhibited by α-dicarbonyl compounds (22) is not present in the observed spectrum of the ether solution.

KEY TO INFRARED ABSORPTION SPECTRA

Figures 1 and 2

SPECTRUM	COMPOUND	SOLVENT*	CONCENTRATION (mmole/ml. of solvent)
S_1	Blank	Chloroform	—
A	Ia	Chloroform	0.108
B	Ib	Chloroform	.107
C	Ic	Chloroform	.107
C_1	Ic	Chloroform	.65
D	Id	Chloroform	.108
S_2	Blank	Dioxane	—
E	Ie	Dioxane	.106
F	If	Dioxane	.109
G	Ig	Chloroform	.106
H	Ih	Chloroform	.0435
Q	Camphorquinone	Chloroform	.106

Instrument. Baird Associates' double beam recording infrared spectrophotometer. Cell length, 0.1 mm.

* No compensation for absorption of solvent except C_1, which is about 50% compensated.

In view of French's generalization (23) that mono-enols or hydroxyl-substituted α,β-unsaturated six-atom cyclic ketones show an intense absorption maximum at 270 ± 5 mμ and Gillam's generalization (24) that the absorption maxima due to conjugated chromophores in a five-atom ring occur at shorter (*ca.* 11–18 mμ) wavelengths than the same system of chromophores in a six-atom ring, one might expect the enol structure to show a band in the region of 265 mμ. Failure to observe such a band, however, cannot be taken as evidence against the enol structure, since the compounds in question are lactams rather than ketones; and no independent evidence concerning differences of this nature is available.

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[3] The authors are indebted to Dr. Nelson J. Leonard for suggestions concerning the use of camphorquinone in this connection.

Thus the spectrographic evidence in both the infrared and ultraviolet regions lends support to the enol structure. While chemical evidence of a conclusive nature is not available, since the usual reagents do not give satisfactory reactions, nevertheless conclusions as to the mode of formation and mechanism of thermal decomposition will be based upon the premise that 1,5-diaryl-2,3-pyrrolidinediones are appreciably enolized.

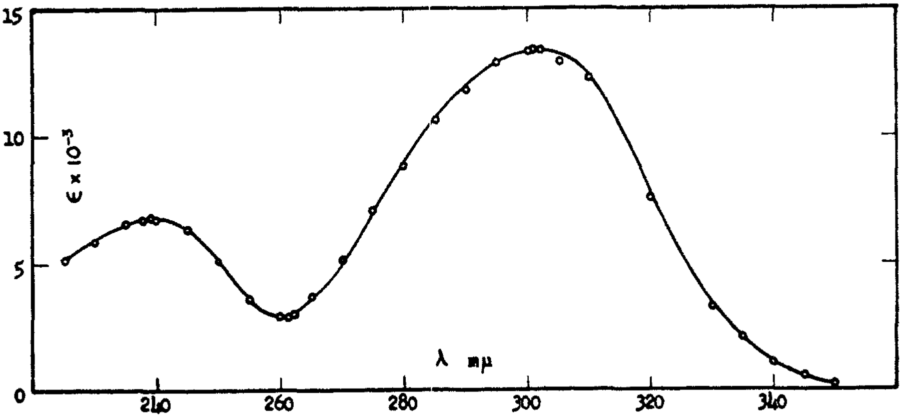

FIG. 3. ULTRAVIOLET SPECTRUM OF Id IN ABSOLUTE ETHER

EXPERIMENTAL[4]

GENERAL METHODS

(*A*). The procedure of Bücherer and Russischwili for preparing Ia from benzylidenepyruvic acid and aniline (3) was adapted to the preparation of compounds Ia through If.

Benzylidine- or anisylidene-pyruvic acid (see below) was dissolved in the minimum volume of absolute ethanol. An absolute ethanolic solution of an equivalent amount of the proper amine was then added dropwise with stirring. Precipitation of a yellow 2-arylimino-3-benzylidenepropionic acid usually began while the amine was being added. The reaction mixture was allowed to stand until no further increase in amount of precipitate was observed (about one-half hour).

If the α-imino acid was to be isolated, the precipitate was filtered off at this point. It usually consisted of a mixture of α-imino acid and a small amount of the corresponding 2,3-pyrrolidinedione. Because of the ease with which the acids rearrange to 2,3-pyrrolidinediones, purification of the acid was in most cases not attempted.

To obtain the 2,3-pyrrolidinedione, the reaction mixture frequently was not filtered but was refluxed for the stated time (Table I), allowed to cool, and the 2,3-pyrrolidinedione was collected by filtration. In some cases there was insufficient alcohol to effect complete solution during the refluxing, but this did not prevent the rearrangement. A change from α-imino acid to 2,3-pyrrolidinedione during the refluxing was frequently observable as a change in color of the suspension.

(*B*). The procedure of Bücherer and Russischwili (3) for preparing Ia from benzylideneaniline and pyruvic acid was adapted to the synthesis of Ic, Ie, Ig and Ih.

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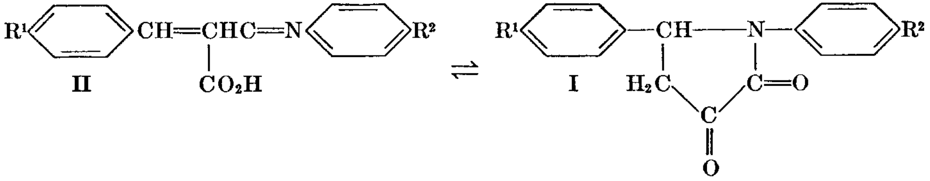
[4] Unless otherwise specified, melting points are uncorrected.

TABLE I

PREPARATION of 1,5-DIARYL-2,3-PYRROLIDINEDIONES AND 2-ARYLIMINO-3-BENZYLIDENEPROPIONIC ACIDS



R¹—	R²—	I	II	GENERAL METHOD	YIELD OF CRUDE II, %	M.P. OF CRUDE II, °C.	TIME OF REFLUX IN PREPARATION OF I	YIELD OF I BASED ON (SUBSTITUTED) PYRUVIC ACID, %	M.P. OF I, °C.	RECRYST. SOLVENT
H	H	Ia	IIa	A	—	141–145°[v]	0.5 hour[u]	79	160–160.5°	Chloroform
CH_3O—	H	Ib*	IIb[x]	A	—	150–151°[v]	0.75 hour[u]	97	153–154°	Toluene
H	CH_3O—	Ic	IIc	A	79	106–116°[v]	Recryst. from EtOH—AcOH (10:1)	61	118–119°	Absolute ethanol
				B	13	100–101°		9		
CH_3O—	CH_3O—	Id*	IId*[y]	A	87[w]	153–154°	Soln. in boiling EtOH—AcOH (8:1)	55	124–125°	Washed with 5% bicarb. sol. and water
H	—NO_2	Ie*[z]	IIe[x]	A	66	—	1 hour[u]	59	d. 181°	CH_3CO_2H or $CHCl_3$
				B	—		2.5 hours[u]	29	m. 187°	
CH_3O—	—NO_2	If*	IIf[x]	A	—	—	4 hours[u]	90 (m.p. 180–181°)	d. 177° m. 188°	CH_3CO_2H or $CHCl_3$
—NO_2	H	Ig*	IIg[x]	B	57	123–125°	Recryst. from 95% ethanol	28	140.5–141.0°	Benzene
—NO_2	CH_3O—	Ih*	IIh[x]	B	—	123–124°	Recryst. from 95% ethanol	27 (m.p. 146–7.5°)	148–149°	Ethanol

* New compound. [u] Color change from bright to pale yellow during refluxing. [v] Color change from yellow to white below the m.p. in the melting point tube. [w] Yield (based on Id) for conversion of Id to IId in methanol. [x] Not previously reported. [y] IId is the only acid which was obtained in a condition known to be suitable for analysis since it is the only member of this series which can be recrystallized without extensive rearrangement. The melting point is given for the pure acid. [z] Procedure A is a new method of preparing Ie.

SPECIFIC COMPOUNDS

1,5-Diphenyl-2,3-pyrrolidinedione (Ia). To the paste resulting from general method *A* (above) using 1.3 g. (0.0074 mole) of benzylidenepyruvic acid and 0.69 g. (0.0074 mole) of aniline, there was added 15 ml. of additional absolute ethanol, and the resulting suspension was refluxed for one-half hour. After cooling, the precipitated 2,3-pyrrolidinedione was filtered from the orange mother liquor and recrystallized from absolute ethanol. It was necessary to wash the solid with cold ethanol to remove all color, leaving 1.47 g. (79%) of white needles; m.p. 158–160° d. (gas). Recrystallization from chloroform gave a product melting at 160–160.5° d. (gas). The reported melting point is 161° d. (3) The scale of this preparation can be increased without affecting the yield.

3-Benzylidene-2-phenyliminopropionic acid (IIa). This compound was obtained by general method *A*. After thorough washing with absolute ethanol, the crude product melted at 141–145° d. (gas), the color changing gradually from bright yellow to light tan during the heating to about 100°. The melting point reported by Bodforss, who used the same method of preparation, is 158°, "the same as that of Ia." (5).

5-(4-Methoxyphenyl)-1-phenyl-2,3-pyrrolidinedione (Ib). *p*-Anisylidenepyruvic acid, 11.00 g. (0.0533 mole), and aniline, 4.96 g. (0.0533 mole), were combined according to method *A* and the resulting orange suspension was refluxed for 45 minutes on a steam-bath. The yellow solid became colorless as soon as the solvent reached the boiling point. After cooling, the mixture was filtered, and the solid was washed with cold absolute ethanol. The product was slightly yellow: yield, 14.5 g. (97%). It was recrystallized from toluene by dissolving at steam-bath temperature and cooling to 5°. The precipitate was washed thoroughly with ether and absolute ethanol to remove all color; m.p. 153–154° d. (gas) after darkening at 151°. The melting point was unchanged by subsequent recrystallization from alcohol.

Anal. Calc'd for $C_{17}H_{15}NO_3$: C, 72.58; H, 5.38; N, 4.98.

Found:[5] C, 72.84; H, 5.45; N, 5.04.

3-Anisylidene-2-phenyliminopropionic acid (IIb). A portion (0.079 g.) of the orange solid obtained by general method *A* at ice-bath temperature was extracted with 2.5% sodium bicarbonate solution. The white insoluble residue, 0.017 g. (21%), was Ib. The basic extract, when acidified with 5% hydrochloric acid afforded a yellow precipitate of crude IIb. On heating in a melting point tube, the yellow IIb gradually became lighter colored and was white by 130°. The m.p., 150–151° d. (gas), was undepressed by admixture of IIb with Ib.

1-(4-Methoxyphenyl)-5-phenyl-2,3-pyrrolidinedione (Ic). (*A*). By following general method *A*, there was obtained from 4.2 g. (0.024 mole) of benzylidenepyruvic acid and 2.9 g. (0.024 mole) of *p*-anisidine, 5.3 g. (79%) of crude yellow Ic; m.p. 106–116°. The crude acid (5.23 g.) was dissolved in the minimum amount (*ca*, 140 ml.) of boiling ethanol-acetic acid (10:1 by volume). Cooling the resulting dark brown solution caused precipitation of needles. More product was obtained by concentration of the mother liquors. Recrystallization of the combined precipitates from absolute ethanol afforded 4.14 g. (61%) (two crops) of a slightly colored product. Washing by slurrying with cold alcohol gave a nearly white product melting at 118–119° d. (gas), which yellowed and acquired a cinnamaldehyde-like odor on exposure to light. Bodforss (5) reported m.p. 118° d.

3-Benzylidene-2-(4-methoxyphenylimino)propionic acid (IIc). The crude acid, m.p. 106–116°, obtained by general method *A* at ice-bath temperature could not be purified by recrystallization since it was converted to Ic on solution in any organic solvent. Solution in aqueous sodium bicarbonate followed by fractional precipitation with dilute hydrochloric acid gave products melting between 106° and 119° whose decomposition points were not depressed by admixture with Ic. Bodforss (5) reported the compound melted at 114° without purification.

1,5-Bis(4-methoxyphenyl)-2,3-pyrrolidinedione (Id). A mixture of Id and IId was precipitated according to general method *A* from 4.41 g. (0.0214 mole) of *p*-anisylidenepyruvic acid and 2.64 g. (0.0214 mole) of *p*-anisidine. To the orange reaction mixture there was

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[5] Micro-Tech Laboratories; Skokie, Illinois.

added enough acetic acid-ethanol (1:8 by volume) to dissolve the solids at the boiling point. About 425 ml. of solvent was required. The hot solution was filtered, seeded with Id, and cooled in an ice bath for three hours. The resulting yellow precipitate was filtered and slurried with 5% aqueous sodium bicarbonate solution until the color was removed. The residue, a mat of nearly white hairlike crystals was washed with water (by decantation) until the washings were neutral to litmus. Yield, 3.65 g. (55%); m.p. 124–125° d. (gas).

Anal. Calc'd for $C_{18}H_{17}NO_4$: C, 69.46; H, 5.51; N, 4.50.
Found:[6] C, 69.36; H, 5.31; N, 4.83.

Ultraviolet absorption spectra. (*cf.* Fig. 3) 301 mμ $\epsilon = 1.34$ x 10^4, 225 mμ $\epsilon = 2.01$ x 10^4.

3-Anisylidene-2-(4-methoxyphenylimino)propionic acid (IId). (*A*). The mixture of Id and IId obtained by general method *A* from *p*-anisylidenepyruvic acid and *p*-anisidine was filtered and the precipitate was extracted with 5% sodium bicarbonate solution leaving a small residue of white hair-like crystals of Id. The yellow IId was reprecipitated from its sodium salt solution with dilute hydrochloric acid. It was recrystallized from absolute methanol affording clusters of yellow needles, m.p. 153–154° d. (gas).

Anal. Calc'd for $C_{18}H_{17}NO_4$: C, 69.46; H, 5.51; N, 4.50.
Found:[6] C, 69.31; H, 5.56; N, 4.77.

(*B*). The same acid was obtained by boiling 2.10 g. of Id in 100 ml. of absolute methanol for about 10 minutes. The Id turned yellow and began to dissolve as soon as the methanol was added to it. During the heating, the acid precipitated. After the reaction mixture had cooled, the product was filtered and dried. Yield, 1.82 g. (87%); m.p. 152.5–153.5° d. (gas), undepressed by Id from (A).

1-(4-Nitrophenyl)-5-phenyl-2,3-pyrrolidinedione (Ie). From 1.35 g. (0.0077 mole) of benzylidenepyruvic acid and 1.06 g. (0.0077 mole) of *p*-nitroaniline there was obtained 1.50 g. (66%) of crude Ie according to general method *A*, using a reflux time of one hour. After recrystallization from glacial acetic acid and washing with absolute ethanol, the light-yellow product melted at 184–192° d. with darkening from about 180°; yield, 1.35 g. (59%). It was recrystallized from acetonitrile; m.p. 187° d. (gas) with darkening from 181°. The product appeared identical with Ie prepared in 29% yield by refluxing an absolute ethanolic solution of *p*-nitroaniline, benzaldehyde, and pyruvic acid for 2.5 hours according to the procedure of Borsche (10), who reported m.p. 188–189°. The melting point of a mixture of the two products was undepressed.

5-(4-Methoxyphenyl)-1-(4-nitrophenyl)-2,3-pyrrolidinedione (If). General method *A*, applied to 7.59 g. (0.0367 mole) of anisylidenepyruvic acid and 5.06 g. (0.0367 mole) of *p*-nitroaniline gave about 400 ml. of a bright yellow suspension which was refluxed four hours on a steam-bath, cooled and filtered. A single recrystallization from chloroform afforded 10.0 g. of light yellow product darkening at 176° and melting at 181° d. (gas). A second crop of 0.8 g., m.p. 180° d., was obtained by evaporation of mother liquors from the recrystallization. Recrystallized three times from glacial acetic acid and washed with cold absolute ethanol to remove brown color, the light yellow product melted at 188° d. (gas) after darkening at 177°. It then was recrystallized from chloroform to give a microcrystalline powder having the same melting point as before.

Anal. Calc'd for $C_{17}H_{14}N_2O_5$: C, 62.57; H, 4.33; N, 8.59.
Found:[6] C, 62.71; H, 4.23; N, 8.61.

5-(4-Nitrophenyl)-1-phenyl-2,3-pyrrolidinedione (Ig). N-(*p*-Nitrobenzylidene)aniline, 5.3 g. (0.023 mole), prepared according to Fischer (25), was dissolved in 55 ml. of glacial acetic acid. The solution was cooled to partial freezing, and to it was added slowly a solution of 2.1 g. (0.023 mole) of pyruvic acid in 5 ml. of ether. The reaction mixture turned brown immediately, and then a yellow product precipitated. After standing one hour at room temperature, the mixture was filtered and the yellow solid was washed with ether and dried. This substance, m.p. 123–125° d. (gas), was soluble in 5% sodium bicarbonate solu-

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[6] Clark Microanalytical Laboratory; Urbana, Illinois.

tion and was evidently IIg, 3.87 g. (57%). It was dissolved by boiling with 400 ml. of absolute ethanol for about 15 minutes. Three crops of reddish-brown crystals, m.p. 138–140° d. (gas), totalling 2.46 g., were obtained. Recrystallization from benzene,[7] gave orange-yellow prisms; m.p. 140.5–141° d. (gas), with slight darkening from 125°; yield, 1.917 g. (28% from pyruvic acid). The compound is insoluble in 5% sodium bicarbonate solution.

Anal. Calc'd for $C_{16}H_{12}N_2O_4$: C, 64.86; H, 4.08; N, 9.45.

Found:[6] C, 65.18; H, 4.12; N, 9.45.

1-(4-Methoxyphenyl)-5-(4-nitrophenyl)2,3-pyrrolidinedione (Ih). N-(*p*-Nitrobenzylidene)-*p*-anisidine, 12.0 g. (0.047 mole), m.p. 132–134°, prepared according to Pope and Fleming (26), was dissolved in enough warm acetic acid to make 550 ml. of solution. The solution was cooled to 24°, at which temperature it was just saturated. A solution of 4.5 g. (0.051 mole) of pyruvic acid in 10 ml. of absolute ether was then added with stirring. After about two hours precipitation seemed to be complete and the product (bright orange, soluble in 5% sodium bicarbonate solution) was filtered off. After being washed with absolute ethanol and ether it melted at 123–124° d. (gas). This appears to be IIh. Recrystallization from 95% ethanol gave 4.2 g. (27%) of yellow-orange Ih, m.p. 146–147.5° d. (gas). A second recrystallization from alcohol raised the m.p. to 148–149° d. (gas).

Anal. Calc'd for $C_{17}H_{14}N_2O_5$: C, 62.63; H, 4.33; N, 8.59.

Found:[6] C, 62.80; H, 4.18; N, 8.59.

The acetic acid filtrate from the original reaction mixture was diluted with three times its volume of water and the precipitate was recrystallized from alcohol, affording an additional 2.65 g. of Ih.

Benzylidenepyruvic acid. This substance was prepared according to Reimer (27) by condensing benzaldehyde with pyruvic acid in the presence of sodium hydroxide. The wet sodium salt was washed with methanol to facilitate drying. The acid was dried *in vacuo* over potassium hydroxide and calcium chloride.

p-Anisylidenepyruvic acid. To a cooled solution of 74 g. (0.54 mole) of *p*-anisaldehyde and 48 g. (0.54 mole) of pyruvic acid in 270 ml. of ethanol was added slowly with stirring 32.8 g. of sodium hydroxide in 328 ml. of water. The temperature of the reaction mixture was kept below 10° until the addition of the sodium hydroxide was complete. Stirring was maintained while the mixture was allowed to come to room temperature. After 30 minutes there was obtained a thick yellow paste which, after standing two hours with occasional stirring, was filtered with the help of a rubber dam. A solution prepared by dissolving this moist yellow sodium salt in six liters of water at room temperature was filtered and treated dropwise with vigorous stirring with concentrated hydrochloric acid until precipitation of yellow product was complete. The product was filtered and dried *in vacuo* over calcium chloride: yield, 74 g. (66%); m.p. 128–131°. The reported m.p. is 131° (28). This procedure is faster than that of Reimer (29), who did not specify the yield. The present procedure on a 0.05-mole scale gave a yield of 73.6%.

p-Nitrobenzylidenepyruvic acid. *p*-Nitrobenzaldehyde (1.04 g., 0.0069 mole), was dissolved by warming in 4.1 g. (0.046 mole) of pyruvic acid. The solution was cooled slightly and 3 drops of methanesulfonic acid was added. After standing six days at room temperature the partially crystallized reaction mixture[8] was filtered. The crystalline product was recrystallized four times from benzene: m.p. 136–139° d. (gas), with darkening below the melting point. This m.p. was unchanged by recrystallization from chlorobenzene. Ciusa (30) whose procedures could not be repeated, reported m.p. 117°. The compound dissolved in 5% aqueous sodium bicarbonate giving a yellow solution.

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[7] Three days' standing at 5° was required for crystallization to be substantially complete.

[8] The *p*-nitrobenzaldehyde tended to crystallize from the reaction mixture during the early stages of the reaction. It was redissolved by warming gently. The condensation product began to precipitate after several days.

Anal. Calc'd for $C_{10}H_7NO_5$: C, 54.30; H, 3.19; N, 6.33.
Found:[6] C, 54.73; H, 3.27; N, 6.48.

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