2,3-PYRROLIDINEDIONES. II. THERMAL DECOMPOSITION

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In the first paper of this series (1) the preparation of a number of 1,5-diaryl-2,3-pyrrolidinediones (I) was described and the structural character of the hetero-ring was discussed. Mention was made of the observation that compounds with the structure I are thermally decomposed to give carbon dioxide (2, 3) and a cinnamylideneaniline (III) (3). In order to investigate the nature of this unusual reaction we have undertaken a kinetic study of the thermal decomposition process with a view to discovering insofar as such an investigation permits whether the process is materially influenced by strong electrical effects which may be transmitted through the aromatic rings to the reactive pyrrolidine system.[3]

The thermal decomposition represented by Equation 1 is not a general reaction of N-substituted α-ketoamides. A solution of benzylidenepyruvanilide (IV)
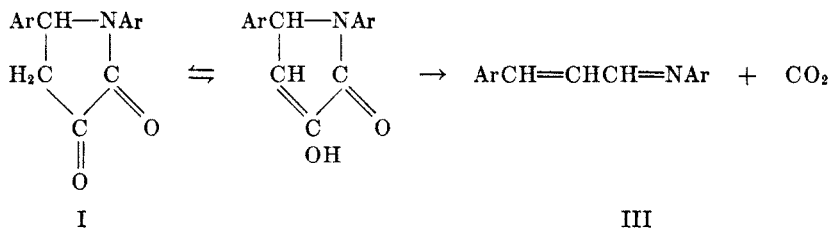
in o-dichlorobenzene was refluxed (179°) for three hours without detectable gas evolution and with subsequent recovery of the anilide unchanged. Therefore structures such as IV cannot be intermediates in the thermal decomposition of compounds with structure I. The addition of pyridine to the refluxing mixture

$$\phi—CH{=}CHCOCONH—\phi$$

IV
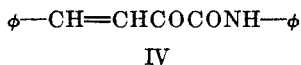
of IV and o-dichlorobenzene had no effect, and pyruvanilide itself (m.p. 104°) appeared stable in a melting point tube even at 200°, at which temperature none of the 1,5-diaryl-2,3-pyrrolidinediones are stable. Pyruvanilide has been reported to decompose with gas evolution at 252°, but neither the gas nor the other decomposition products have been identified (4).
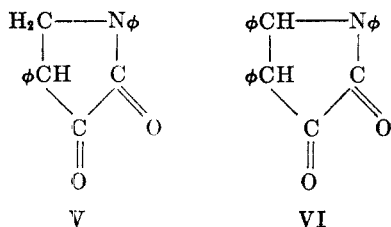
While no extensive investigation of the thermal decomposition of 2,3-pyrrolidinediones other than I was undertaken, a few observations were made on

[3] Cf. Leffler, J. Am. Chem. Soc., 72, 67 (1950), on the effect of such substitution on the mechanism of decomposition of benzoyl peroxides.

the behavior of certain 4-phenyl-2,3-pyrrolidinediones. Thus 1,4-diphenyl-2,3-pyrrolidinedione (V) and 1,4,5-triphenyl-2,3-pyrrolidinedione (VI) are stable

$$
\begin{array}{cc}
\mathrm{H_2C}\text{----}\mathrm{N}\phi & \phi\mathrm{CH}\text{----}\mathrm{N}\phi \\
|\qquad\quad| & |\qquad\quad| \\
\phi\mathrm{CH}\quad\mathrm{C} & \phi\mathrm{CH}\quad\mathrm{C} \\
\diagdown\quad\diagup\ \diagdown & \diagdown\quad\diagup\ \diagdown \\
\mathrm{C}\qquad\mathrm{O} & \mathrm{C}\qquad\mathrm{O} \\
\|\qquad\quad & \|\qquad\quad \\
\mathrm{O}\qquad\quad & \mathrm{O}\qquad\quad \\
\mathrm{V} & \mathrm{VI}
\end{array}
$$

under conditions which decompose 1,5-diaryl-2,3-pyrrolidinediones (I): V melts without decomposition and does not evolve gas even at 250°, and VI may be refluxed for an hour in *o*-dichlorobenzene (179°) with only a slight coloration of the solution. It crystallized out unchanged upon cooling. Borsche (5) carried out a "dry distillation" of VI and obtained stilbene, liquid and gaseous products, and a non-volatile compound $C_{21}H_{17}NO$, whose composition corresponds to a decarbonylation product. Thus it would appear that substitution of the 4-position with an aromatic ring not only stabilizes the 2,3-pyrrolidinedione toward decomposition, but also alters the course of the decomposition.

Eight 1,5-diaryl-2,3-pyrrolidinediones (Ia through Ih) were prepared for the present study (1). All eight melt with gas evolution, and *o*-dichlorobenzene solutions of each evolve carbon dioxide upon being heated. The choice of this particular solvent was dictated by previous investigation (3) wherein a solvent was desired with a boiling point somewhat above the decomposition temperature of 1,5-diphenyl-2,3-pyrrolidinedione (161°) (6). The carbon dioxide was identified qualitatively by the precipitation of calcium carbonate from lime water. The corresponding cinnamylideneanilines (IIIa through IIIh) were isolated from the solutions after gas evolution ceased.

Although *o*-dichlorobenzene was used exclusively as solvent in the comparative rate studies because of its low volatility, other solvents (cumene, quinoline, ψ-cumene, *m*- and *p*-dichlorobenzene, oleic acid, phenol, and chlorobenzene) gave solutions from which carbon dioxide was evolved smoothly.

Where the concentration of I in *o*-dichlorobenzene was 2%, considerable darkening occurred upon heating to effect carbon dioxide evolution, and evaporation of the solvent left the cinnamylideneaniline contaminated with tarry residue; indeed, the residues from the decomposition of Ig and Ih appeared to be mostly tar. However, refluxing more dilute (0.2% to 0.4%) chlorobenzene solutions of Ig and Ih under carbon dioxide, followed by reduced pressure distillation of the solvent, afforded easily purified IIIg and IIIh. The reflux time for such operations should be that calculated from rate data for 99% reaction (*cf.* Figure 1).

The first-order rate constants for the thermal decompositions of the eight 1,5-diaryl-2,3-pyrrolidinediones in *o*-dichlorobenzene (0.00159 mole of I in 20 ml. of solvent) are recorded in Table I. These constants are plotted logarithmically against reciprocal absolute temperature in Figure 1. The eight compounds

fall in order of decreasing rates of decomposition as follows (Table II) (temperature 120–140°).

It is apparent that the substituent on the ring nitrogen plays a large part in determining the rate. Thus, the compounds arranged in order of decomposition rates fall into three groups, the members of each group having the same R^2. Here the electron-withdrawing nitro group decreases the decomposition rate. The methoxyl has the opposite effect, suggesting that the methoxyl here acts as an electron source, its electromeric effect outweighing its electron-withdrawing inductive effect. (Observe the series Id, Ib, If; Ic, Ia, Ie; and Ih, Ig.)
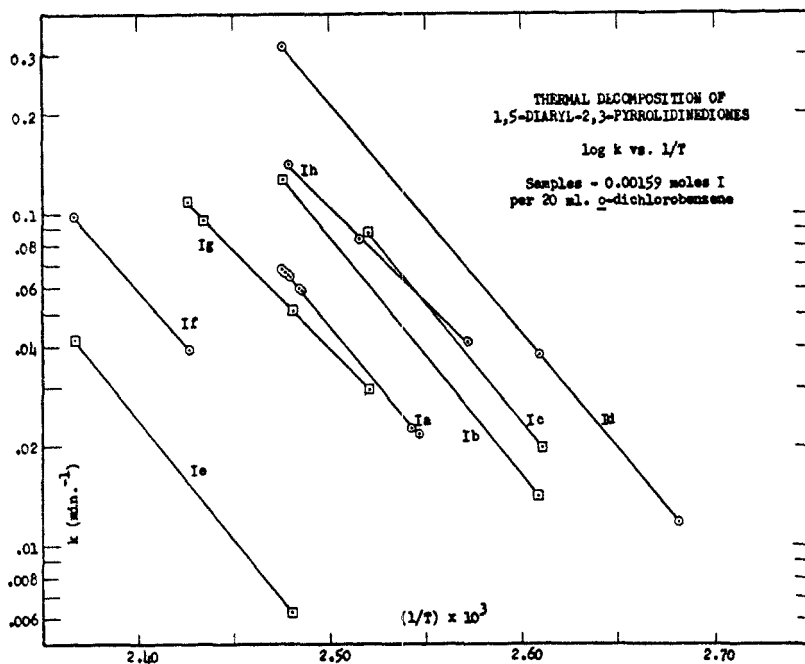

Fig. 1. Thermal Decomposition of 1,5-Diaryl-2,3-pyrrolidinediones. log k vs 1/T

The effect of a substituent at R^2 on the rate is less than the effect of the same substituent at R^1. In the 120–140° region, the effect of R^1 is in the same direction as the effect of R^2, although it is smaller. Within a wide range of temperature the introduction of methoxyl at R^1 increases the rate of decomposition. (Observe: Ic, Id; Ia, Ib; Ie, If.) However, since the rates of decomposition of the compounds in which R^1 is a nitro group (If, Ie) are appreciably less temperature dependent than the rates of the other six compounds, introduction of a nitro group at R^1 may either increase or decrease the decomposition rate, depending on the temperature.

The rate constants as determined in this study are sensitive to the medium in which the decomposition occurs. Thus rates of decomposition of Ia in solutions of equal concentration (0.00159 mole Ia to 20 ml. solvent) in quinoline,

oleic acid, cumene, and the dichlorobenzenes (Table III) vary considerably. The three dichlorobenzenes rank *p*-, *m*-, *o*- in order of increasing facilitation of decomposition (Table III).

The observed rate constant is slightly affected by changing the initial concentration, although this does not cause significant deviation from a first order

TABLE I

DECOMPOSITION OF 1,5-DIARYL-2,3-PYRROLIDINEDIONES. RATE CONSTANTS AND ACTIVATION ENERGIES

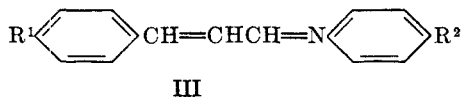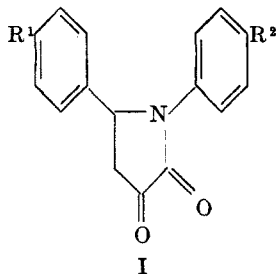Initial Concentration: 0.00159 mole per 20 ml. of *o*-dichlorobenzene

COMPOUND	TEMPERATURE (°C.)	k (±1%) (min.⁻¹ × 10²)	ACTIVATION ENERGY (kcal./mole, ±2%)
Ia	130.8	6.79	31.9
	130.6	6.61	
	130.5	6.57	
	130.4	6.45	
	129.5	5.93	
	129.4	5.83	
	120.2	2.25	
	119.4	2.17	
Ib	130.8	12.7	33.0
	110.2	1.40	
Ic	123.6	8.78	33.0
	109.9	1.97	
Id	130.9	31.5	31.7
	110.1	3.74	
	99.8	1.18	
Ie	149.3	4.13	33.3
	130.0	.620	
If	149.2	9.79	32.4
	138.9	3.82	
Ig	139.0	10.7	27.1
	137.6	9.47	
	130.1	5.13	
	123.6	2.94	
Ih	130.2	14.0	26.4
	124.4	8.37	
	115.7	4.11	

reaction course. Thus Table IV indicates that the constant is greater with the higher concentration.

Quinoline has an appreciable accelerating effect on the rate of decomposition of Ia (Tables III and V). The first order rate constant is approximately linearly proportional to the amount of quinoline added to *o*-dichlorobenzene solutions of identical concentration (Figure 2).

In view of this finding and the strong dependence of the rate on the medium, it is not surprising that the initial concentration should influence the observed rate constant (Table V) inasmuch as the solute and the decomposition product

TABLE II

ORDER OF DECREASING RATES OF DECOMPOSITION OF
1,5-DIARYL-2,3-PYRROLIDINEDIONES (I)

I, III	R¹	R²
Id	CH_3O	CH_3O
Ic	H	CH_3O
Ih	NO_2	CH_3O
Ib	CH_3O	H
Ia	H	H
Ig	NO_2	H
If	CH_3O	NO_2
Ie	H	NO_2

TABLE III

EFFECT OF SOLVENT ON RATE OF DECOMPOSITION OF Ia

Concentration = 0.400 g. (0.00159 mole) per 20 ml.

SOLVENT	TEMPERATURE °C.	k (min.$^{-1}$) $\times$ 10^2	TEMPERATURE °C.	k (min.$^{-1}$) $\times$ 10^2
Dichlorobenzene				
para-	130.7	5.05	120.2	1.78
meta-	131.0	5.68	—	—
ortho-	130.8	6.79	120.2	2.25
	129.5	5.93	119.4	2.17
Cumene	130.0	4.53	—	—
Quinoline	129.9	14.0	119.4	5.06
	129.8	13.4		
Oleic acid	—	—	119.0	1.92

TABLE IV

DECOMPOSITION OF Ia IN o-DICHLOROBENZENE FIRST ORDER RATE CONSTANTS

SAMPLE: Ia/solvent	TEMPERATURE °C.	k (min.$^{-1}$) $\times$ 10^2	TEMPERATURE °C.	k (min.$^{-1}$) $\times$ 10^2
0.400 g./20 ml.	130.8	6.79	120.2	2.25
.400 g./10 ml.	130.8	7.61	120.2	2.30
.400 g./5 ml.	130.8	7.64	120.2	2.43

are themselves part of the reaction medium and the anils resulting from thermal decomposition are basic, probably no less so than quinoline. Thus a higher initial concentration of I in a weakly basic solvent such as dichlorobenzene should increase the rate constant, which is exactly the effect observed.

In the light of these data alone it is impossible to do more than speculate regarding the mechanism whereby compounds of structure I are "decarboxylated" to give compounds of structure III. The ready conversion of α-arylimino-β-benzylidenepropionic acids (II) into 1,5-diaryl-2,3-pyrrolidinediones (I) (1)

TABLE V

EFFECT OF QUINOLINE ON THE RATE OF DECOMPOSITION OF Ia

Samples: 0.400 g. Ia per 20 ml. of o-dichlorobenzene plus X grams quinoline

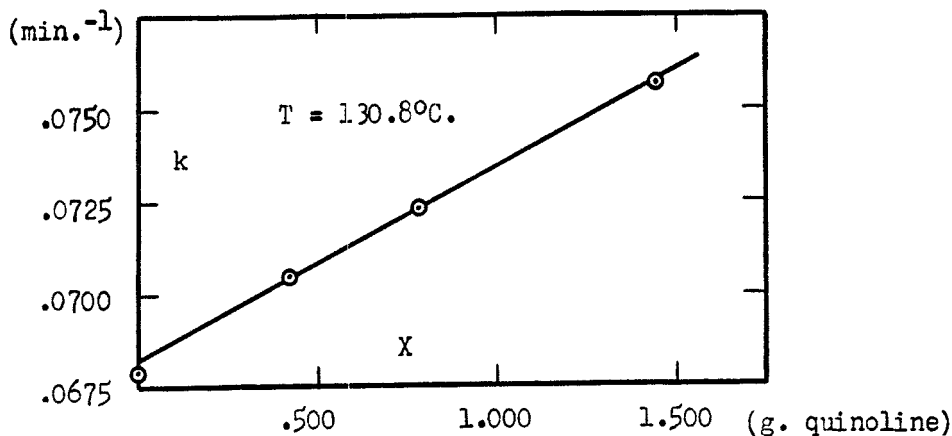| QUINOLINE X, g.	TEMPERATURE °C.	k (min.$^{-1}$) $\times$ 10^2
0.000	130.8	6.79
.422	130.8	7.10
.781	130.8	7.23
1.440	130.8	7.57

FIG. 2. PLOT OF DATA OF TABLE V

suggests strongly that the "decarboxylation" of the latter may result by rapid reconversion of I to II, which then is decarboxylated to III. A consideration of this possibility will be presented in a subsequent communication.

DETERMINATION OF RATES OF CARBON DIOXIDE EVOLUTION

Apparatus. (Figure 3) The reaction vessel and manometer were adapted from the apparatus of Hinshelwood (7). Constant temperature was provided by refluxing a pure liquid[4] contained in a flask attached to the standard taper joint

[4] In some runs, a constant positive air pressure was maintained in the outer jacket to achieve a temperature higher than the atmospheric boiling point. Due to difficulty of pressure regulation and the necessity for sealing all joints, this modification was not commonly employed.

at the base of the outer glass jacket. Solutions within the reaction vessel were vigorously stirred by means of a glass covered piece of nail (2 mm. diam. × 22 mm.) which was turned magnetically by a magnet mounted on an inverted stirring motor beneath the vessel. Pressure within the reaction vessel was determined by the level of mercury in the open manometer, a 4 mm. (i.d.) glass tube rigidly mounted beside a meter stick. Temperature was read from a 90–160° thermometer placed in the well extending into the center of the reaction vessel.

Description of procedure. The tip (A) of the reaction vessel (R.V.) was opened with an oxygen torch by blowing through the male joint C. A weighed amount of pyrrolidinedione (0.00159 mole in all runs plotted in Figure 1) was introduced
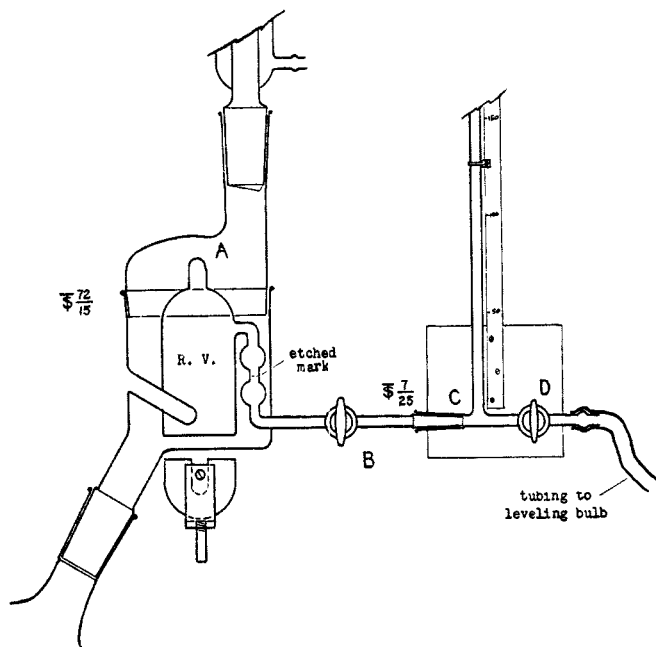

FIG. 3. THERMAL DECOMPOSITION APPARATUS

into the reaction vessel through A with a small funnel. Solvent (20 ml. of *o*-dichlorobenzene in all the runs of Figure 1) was poured in through the same funnel. The glass-encased piece of nail was dropped in and A was resealed. The apparatus was then assembled as shown (Figure 3), with a thermometer in the well, B open, and D closed. With the stirrer running, the liquid in the lower flask was heated rapidly until the condensate rose above point A. Stopcock B was closed, and mercury was allowed to rise in the manometer through D. B was then opened just enough to let mercury fill the upper of the two small bulbs in the arm of the reaction vessel. The mercury was drained from the manometer and B was opened suddenly so that the surge of mercury from the reaction vessel out through the tube would force any large air bubbles from the tube and stopcock B. This process was repeated if necessary to eliminate bubbles from B. By

opening D enough mercury was then let into the manometer so that with B open the mercury level stood at the etched mark between the two bulbs in the arm of the reaction vessel. Time was noted to the nearest second, temperature taken to the nearest 0.1 degree and the manometer was read to the nearest 0.5 mm. Enough mercury was then let into the manometer through D to raise the level about 10 mm. D was then closed and B opened. When the mercury level again was forced down to the etched mark, time, temperature and pressure were noted as before, and this process was repeated until there was no further increase in pressure. (Final pressure.)

The final pressure (P_f) was determined in this manner for compounds Ia–f and Ih. Compound Ig apparently underwent further thermal decomposition, so that pressure did not stop increasing in a reasonable length of time. In this case P_f was taken to be that pressure which made the plot of ln ($P_f - P_t$) linear with time, in the manner of Schenkel and Klein (8).

For each run there thus were obtained a set of 20 to 40 time-pressure data and a P_f, corresponding to complete decomposition.

The gas in the reaction vessel was tested by disassembling the apparatus (while warm) with stopcock B closed. The tip C was placed in a small beaker of lime water while B was opened slowly to release the gas gently into the lime water.

Calculation of rate constants. Temperature and volume being kept constant, the change of pressure is linearly proportional to the amount of carbon dioxide formed (and thus to the pyrrolidinedione decomposed): $\Delta p = \Delta n \left(\dfrac{RT}{V} \right)$, assuming an ideal gas.

Since the initial amount of pyrrolidinedione is proportional to the total change in pressure, $P_f - p_{i(\text{nitial})}$, the amount of pyrrolidinedione undecomposed at any time t is proportional to the difference between the final pressure and the pressure at time t, i.e., $P_f - p_t$. Values of $P_f - p_t$ were calculated for each of the pressures measured during the decomposition and the natural logarithm of each $P_f - p_t$ was determined. This process gave a set of 20 to 40 time-ln p data for each run, which were plotted. In all runs, most of the points, with exception of a few at the initial stage of the reaction before temperature stability had been reached and some at the end of the reaction where pressure change was so slow that time could not be determined accurately, showed no significant deviation from a straight line. This linear plot indicates that the decompositions follow a first order course (9). The slope of the ln p *vs.* time plot was determined by the method of averages (10). It is equal to the first order rate constant (9).

Precision of measurements. Reaction temperature, as read on a 90–160° thermometer stayed within 0.1° of the reported value throughout the run. At 130°, the activation energy being 32 kcal., a rate constant changes 1.1% for each 0.1° change in temperature (Figure 1).

The manometer was read to the nearest millimeter. Errors in pressure due to temperature fluctuations are due largely to change of vapor pressure of solvent

with temperature, an error estimated[5] to be less than 1 mm. per 0.1°. No corrections in manometer readings for changes in barometric pressure were made, since these changes were negligible during any one run.

An important possible source of error is the determination of P_f. Secondary decomposition and barometric changes would combine to introduce uncertainty in this value. In a typical run, a two-mm. error in P_f would cause 1.8% change in the rate constant. The erroneous P_f imparts a perceptible curve to the plot of ln $P_f - p_t$ *vs.* time, however. Two mm. is probably the maximum error in P_f, so that the rate constants determined in the described manner should be reproducible within less than 2%.

The precision of the rate constants is demonstrated by the four runs on Ia around 130°. When these constants are corrected to 130.6° on the basis of 31.9 kcal./mole activation energy (1.1% per 0.1°), the four constants, now for supposedly identical runs, become 6.64, 6.61, 6.64, and 6.59. The maximum deviation is less than 1%.

Because of the high reaction temperature, any solubility of carbon dioxide in the solvent was neglected, as has been commonly done previously (12–14). The linearity of the log $P_f - p_t$ *vs.* time plots indicates that the effect is negligible. Stirring rates, molar concentrations, and volumes of samples were made the same in all runs to minimize indeterminate errors and make the results as comparable as possible.

Activation energies. Activation energies, E_a were determined from the usual

equation relating E_a to the rate constant k (15): $E_a = RT^2 \dfrac{d(\ln k)}{dT}$. Thus the slope

of the plot of log k against $1/T = -0.4343E_a/R$. The slopes of the straight lines best representing this relationship (Figure 1) were determined mathematically [by least squares calculation (16) where three or more points were available]. The activation energies [(slope) (2.303) (1.987) calories/mole] are listed in Table I. Where a temperature interval of ten degrees was used in the calculation of the activation energy, the 0.2° uncertainty due to two temperature readings introduces a 2% uncertainty in the value of the activation energy.

<div align="center">EXPERIMENTAL[6]</div>

Benzylidenepyruvanilide (IV). To 0.95 g. of pyruvanilide (17) was added 0.61 g. (0.00575 mole) of benzaldehyde and a solution of 0.3 g. of sodium hydroxide in 20 ml. of water. After a few minutes' shaking a yellow precipitate of benzylidenepyruvanilide (IV resulted). This was filtered off and recrystallized from 90% ethanol; m.p. 154–156°. The mother liquor from the first filtration of the reaction mixture continued to deposit the compound for several days. The melting point of this product is not depressed by admixture with authentic IV prepared according to the method of Bodforss (18) by condensing pyruvanilide

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[5] Vapor pressure data: (11).

	120°	130°	140°
Cymene.......... b.p. 175°	169 mm.	229 mm.	305 mm.
Isobutylbenzene.. b.p. 167°	200 mm.	271 mm.	363 mm.

[6] Melting points uncorrected.

with benzaldehyde in the presence of aniline. The reported melting point is 153°. Our procedure is superior to that of Bodforss for preparing pure benzylidenepyruvanilide.

A determination of the molecular weight of this compound by freezing point depression in camphor indicated that benzylidenepyruvanilide prepared by the described methods is not dimeric: Calc'd 251; Found 270.

1,4-Diphenyl-2,3-pyrrolidinedione (V). This was prepared according to Borsche (5). The product, crystallized from benzene, darkens at 202° with m.p. 212-214°. No gas is evolved at or below 250°. The reported m.p. is 208° (5).

1,4,5-Triphenyl-2,3-pyrrolidinedione (VI). This was prepared according to Borsche (5). The crude product (57% yield) was recrystallized from acetic acid: large prisms, m.p. *ca* 253° after darkening and softening from 210°. Further recrystallization failed to improve the melting point which is reported to be 250° (5), needles from acetic acid. The compound is highly fluorescent (blue); the fluorescence is destroyed by melting.

THERMAL DECOMPOSITIONS

Solvents for the decompositions were prepared as follows: *o-Dichlorobenzene.* Eastman practical *o*-dichlorobenzene was distilled through a short column at 746 mm. The fraction boiling at 175.8-177.2° (uncorr.) was used. *Chlorobenzene.* Eastman white label chlorobenzene was distilled through an 8-in. column packed with glass helices. The fraction boiling at 127.4-128.8° (uncorr.) was collected. *p-Dichlorobenzene.* Dow Chemical Co. "Paradow", m.p. 155-156°. *m-Dichlorobenzene.* This was prepared from Eastman white label *m*-chloroaniline by the Sandmeyer reaction according to the procedure of *Organic Synthesis* for preparing *m*-chlorobenzaldehyde, b.p. 170.8-171.8° (short column). *Cumene.* Eastman white label, redistilled, b.p. 148-148.7°. *Quinoline.* Synthetic quinoline was boiled with acetic anhydride and distilled twice. B.p. 228-232°/747 mm. *Oleic acid.* Merck, U. S. P.

Benzylidenepyruvanilide (IV) 170 mg., and 3 ml. of *o*-dichlorobenzene were refluxed two hours. No gas evolution was detected. Evaporation of half the solvent caused precipitation of pure starting material. Two ml. of *o*-dichlorobenzene and two drops of dry pyridine were added to the mixture, and refluxing was continued 45 minutes longer. The solution darkened slightly, but evaporation of the solvent left the starting material as the only identifiable product.

1,4,5-Triphenyl-2,3-pyrrolidinedione (VI) was refluxed one hour in *o*-dichlorobenzene. A very slight pink color developed during the heating. No gas evolution was detected. After two days the compound was recrystallized unchanged in white needles.

N-(p-Methoxycinnamylidene)aniline (IIIb) *from Ib.* A mixture of 0.5 g. of Ib and 25 ml. of *o*-dichlorobenzene was refluxed 15 minutes. Carbon dioxide (lime water test) was evolved and the solution darkened even below the boiling point. The solvent was evaporated under an air jet. The brown residue was recrystallized twice from benzene. The product, light yellow, turning brown on exposure to air, melted at 125-127°. The melting point reported (19) for the expected *p*-methoxycinnamylideneaniline is 125°.

N-Cinnamylidene-p-anisidine (IIIc) *from Ic.* A solution of 0.448 g. of Ic in 20 ml. of *o*-dichlorobenzene was heated at 110° in the described kinetic apparatus (Figure 3) until no more carbon dioxide was given off (five hours). The dark brown solution was then evaporated to dryness under an air stream. The residue was taken up in hot carbon tetrachloride and filtered. Cooling the resulting brown solution in an ice-bath caused precipitation of IIIc. Recrystallized twice from ethanol, this product melted at 121-122°. A mixture melting point with authentic IIIc prepared from cinnamaldehyde and *p*-anisidine according to Senier and Gallagher (20) was 121-122°; reported, 119° (corr.).

N-(p-Methoxycinnamylidene)-p-anisidine (IIId) *from Id.* A solution of 0.400 g. of Id in 20 ml. of *o*-dichlorobenzene was heated at 131° for 30 minutes. The reaction mixture was blown down to dryness, leaving a brownish-yellow partially crystalline residue, which was recrystallized twice from absolute ethanol. Brownish plates, liquefying at 164-166°, melt clearing at 178°. The reported melting point of IIId is: solid, 167°, liquid crystal, 180° (19).

N-Cinnamylidene-p-nitroaniline (IIIe) *from Ie*. A solution of 0.171 g. of Ie in 50 ml. of cholorobenzene was refluxed 12.5 hours under carbon dioxide. The chlorobenzene was distilled off under carbon dioxide at 20 mm., leaving a yellow solid residue which was dissolved in hot acetonitrile (*ca*. 1.5 ml.). On cooling the solution, 0.088 g. of yellow crystals, m.p. 121–124° was obtained. A second crop, 0.025 g., m.p. 120–123°, was combined with the first crop and recrystallized from acetonitrile and then from absolute ethanol: prisms, m.p. 123–124°.

Anal. Calc'd for $C_{15}H_{12}N_2O_2$: C, 71.40; H, 4.80; N, 11.11.

Found:[7] C, 71.59; H, 4.84; N, 11.18.

N-(p-Methoxycinnamylidene)-p-nitroaniline (IIIf) *from If*. A solution of 0.520 g. of If in 20 ml. of *o*-dichlorobenzene was decomposed at 149° in the described apparatus (Figure 3) until no further change in pressure was observed (50 minutes). Evaporation of the *o*-dichlorobenzene under an air jet left 0.452 g. of brownish-yellow crystalline residue. Two recrystallizations from absolute ethanol afforded 0.267 g. of IIIf, orange-yellow needles liquefying at 146.5–151°, melt clearing at 160–161°.[8] After two further recrystallizations from acetonitrile the transition points were I, 150–151°, II, 162–162.5° and these were unchanged by subsequent recrystallizations from acetonitrile.

Anal. Calc'd for $C_{16}H_{14}N_2O_3$: C, 68.09; H, 5.00; N, 9.93.

Found:[7] C, 67.88; H, 4.91; N, 9.96.

N-(p-Nitrocinnamylidene)aniline (IIIg) *from Ig*. A solution of 0.193 g. of Ig in 50 ml. of chlorobenzene was refluxed under carbon dioxide for 60 minutes. The light yellow solution became golden yellow. The chlorobenzene was distilled off under carbon dioxide at 18 mm., leaving a brownish-yellow crystalline residue which was dissolved in boiling absolute ethanol. The yellow precipitate resulting from cooling the enthanolic solution to 0° was recrystallized from acetonitrile: golden yellow needles, m.p. 122–125°. Recrystallized again from acetonitrile and then from 50% acetonitrile-absolute ethanol, the product, 0.069 g., melted at 125–126°. After solidifying on cooling in the melting point tube, remelting occurred at 129–129.5°. Reported (21): Yellow needles (absolute alcohol), m.p. 132–133°.

Anal. Calc'd for $C_{15}H_{12}N_2O_2$: C, 71.40; H, 4.80; N, 11.11.

Found:[9] C, 71.65; H, 4.65; N, 11.14.

N-(p-Nitrocinnamylidene)-p-anisidine (IIIh) *from Ih*. A solution of 0.500 g. of Ih in 25 ml. of chlorobenzene was refluxed for 45 minutes in an oxygen-free atmosphere. The solution became black. The chlorobenzene was distilled off at 20 mm. leaving a black solid containing traces of orange crystals. An orange solid and a trace of white solid sublimed together from this black residue at 140°/0.05 mm. The whole sublimate was recrystallized from absolute ethanol: m.p. 162–165°, 0.07 g. A constant melting point was achieved by two further recrystallizations from ethanol: liquefy 164–166°, clear melt, 168.5°.

Anal. Calc'd for $C_{16}H_{14}N_2O_3$: C, 68.09; H, 5.00.

Found:[7] C, 68.01; H, 5.05.

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