STUDIES IN PYRAZOLIDINE CHEMISTRY

XV*. ELECTRONIC SPECTRA OF 4-BENZYLIDENE DERIVATIVES OF 1,2-DIPHENYLPYRAZOLIDINE-3,5-DIONE AND THEIR STABILITY TO CATALYTIC HYDROGENATION IN THE PRESENCE OF RANEY NICKEL

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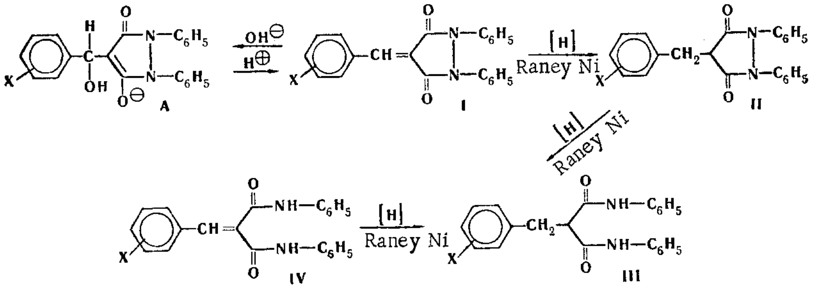
A study of their electronic spectra has led to the hypothesis that 4-benzylidene-1,2-diphenylpyrazolidine-3,5-diones exist in the diketo form in acidic and neutral media and form enolate carbinols (A) in alkaline media. The latter fact explains the stability of the N–N bond of these compounds on catalytic hydrogenation in the presence of a Raney nickel catalyst in alkaline ethanol.

On studying the properties of 4-benzylidene derivatives of 1,2-diphenylpyrazolidine-3,5-dione (DPD), we found that colored solutions of these compounds (Ia-h) in neutral ethanol become decolorized when the solutions are made alkaline. The coloration is regenerated after acidification. This behavior of Ia-h can be explained by the formation of the enolate carbinol (A) through the addition of a hydroxyl ion:



a X=H; b X=NO_2-*p*; c X=Cl-*p*; d X=COOH-*p*; e X=OCH_3-*p*; f X=NH_2-*p*; g X=$N(CH_3)_2$-*p*; h X=$(OCH_3)_2$-*p*, *m*

To confirm the hypothesis put forward, we have studied the electronic spectra of compounds Ia-h in neutral, acidic, and alkaline ethanolic solutions. There is isolated information in the literature [1-4] concerning the electronic spectra of 4-benzylidene derivatives of DPD's in neutral alcoholic solutions. The spectra obtained generally relate to the diketo form. Absorption with a maximum at 240 nm is characteristic for DPD derivatives with a fixed diketo form and also for 4-monosubstituted DPD's [5] in acidified ethanol. The absorption maximum of DPD enolate anions is at 260-268 nm and that of fixed enols [6] at 253 nm.

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*For Communication XIV, see [7].

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TABLE 1. UV Spectra of 4-Benzylidene Derivatives of 1,2-Diphenylpyrazolidine-3,5-dione (I), the Products of Their Hydrogenation (II, III), and Dianilides of Benzylidenemalonic Acid (IV)

Compound	In acidified ethanol		In alkaline ethanol		In neutral ethanol	
	λ_{max}, nm	log ε	λ_{max}, nm	log ε	λ_{max}, nm	log ε
Ia	237 336	4,18 4,09	260	4,41	254 336	4,47 4,13
Ib	247 322	4,14 3,51	262	4,48	250 322	4,52 3,60
Ic	241 342	4,35 4,51	259	4,38	259 342	4,43 4,75
Id	238	4,24	261	4,38	261 348	4,36 3,95
Ie	248 390	4,29 4,30	264	4,47	248 390	4,29 4,30
If	245 460	4,26 5,25	256	4,47	245 460	4,31 5,04
Ig	248 482	4,35 3,98	259	4,66	248 482	4,35 3,95
Ih	235 408	4,25 4,27	265	4,41	259 408	4,29 4,20
IIa	240	4,18	267	4,41	267	4,22
IIf	241	4,29	261	4,46	250	4,47
IIIa	248	4,33	248	4,25	248	4,25
IIIe	246	4,37	246	4,46	246	4,50
III g	250	4,32	250	4,61	250	4,63
II h	247	4,43	247	4,47	247	4,49
IVe	237 322	4,32 4,26	237	4,38	237 322	4,46 4,36
IV g	243 320	4,36 3,84	243	4,29	243 320	4,71 3,74

The spectra of the 4-benzylidene DPD's (Ia-h) that we have obtained in acidified ethanol are characterized by two absorption maxima: one in the 237-248 nm range due to the pyrazolidine-3,5-dione ring, and the second in the 315-482 nm range due to an exocyclic double bond. The usual relationship between the donor-acceptor properties of a substituent in the aldehyde residue and the position of the long-wave absorption maximum is observed (Table 1). In alkaline ethanolic solution, in all the 4-benzylidene-DPD's studied (Ia-h), the absorption in the long-wave region disappears and the short-wave band undergoes a bathochromic shift of 10-30 nm, appearing at 256-265 nm, i.e., the region of absorption of DPD enolate anions. Simultaneously there is an increase in the extinction, which is characteristic for the passage from the diketo form to the enolate anion. The spectra in the visible region of compounds Ia-h in neutral ethanol are similar to the absorption spectra in acidified ethanol. In the case of compounds Ia, c, d, and h, the short-wave maximum undergoes a bathochromic shift, falling into the region of the absorption of the enol or the enolate. However, even in these cases the absorption band in the visible region does not change its position. On the basis of the facts given, it may be assumed that the diketo form is characteristic for acid solutions of 4-benzylidene-DPD's and the enolate form (A) for alkaline solutions. In neutral solutions, the diketo form predominates.

Additional evidence for the enolate carbinol structure (A) of compounds Ia-h in alkaline ethanol was obtained in a study of the behavior of these compounds with respect to catalytic hydrogenation in the presence of a nickel catalyst. It has been found previously [7] that the enolate anions of DPD and its 4-monosubstituted derivatives do not undergo hydrogenolysis at the N–N bond on hydrogenation in the presence of Raney nickel; in neutral ethanol, the same compounds form the corresponding dianilides of malonic acid in neutral ethanol. There is much information in the literature [8] on the catalytic hydrogenation in the presence of Raney nickel of 4-ylidene derivatives, including 4-benzylidene derivatives, of DPD with the aim of preparing the corresponding 4-monosubstituted compounds. According to some statements hydrogenation is carried out in neutral solvents at elevated temperature and pressure, and in other cases the hydrogenation conditions are not given. It is stated in individual papers [1, 9, 10] that in the hydrogenation of 4-ylidene derivatives of DPD in the presence of Raney Ni not only the exocyclic double bond but also the N–N bond of the heterocycle is saturated. The behavior of 4-ylidene derivatives on hydrogenation in alkaline solutions has not been described.

We performed the hydrogenation of compounds Ia-h in neutral ethanol at 20°C and 40-50°C and at the boiling point of the solution in the presence of an excess of catalyst without a feed of hydrogen, and in alkaline solution at 20°C. Type W-5 catalyst was used. It was found that in neutral solution at 20°C, compounds Ia, e, g, and h hydrogenate at the C=C and N–N bonds with the formation of the corresponding saturated dianilides (IIIa, e, g, h) (Table 2). Some of the final hydrogenation products (IIIe and g) were obtained by independent synthesis via the hydrogenation of the corresponding unsaturated dianilides (IVe and g). The latter were synthesized by condensing malondianilide with p-methoxy- and p-dimethylaminobenzalde-

TABLE 2. Hydrogenation of Compounds I, II, and IV

Starting material		Hydrogenation conditions			Hydrogenation product		Conditions for chromatography*
compound	name	temp., °C	medium	compound	name	$R_f \times 100$	
Ia	4-Benzylidene-DPD [11]	20	Neutral	IIIa	Benzylmalondianilide	90	A
Ia	4-Benzylidene-DPD	40–50	Neutral	IIa	4-Benzyl-DPD [12]	20	A
Ia	4-Benzylidene-DPD	20	Alkaline	Ia	4-Benzylidene-DPD	36	A
IIa	4-Benzyl-DPD	20	Neutral	IIIa	Benzylmalondianilide	90	A
IIa	4-Benzyl-DPD	20	Alkaline	IIa	4-Benzyl-DPD	20	A
Ic	4-p-Chlorobenzylidene-DPD	20	Neutral	IIIa	Benzylmalondianilide	90	A
Ic	4-p-Chlorobenzylidene-DPD	20	Alkaline	Ic	4-p-Chlorobenzylidene-DPD	38	A
Ib	4-p-Nitrobenzylidene-DPD [13]	20	Neutral	IIf	4-p-Aminobenzyl-DPD [14]	18	B
Ib	4-p-Nitrobenzylidene-DPD†	20	Alkaline	If	4-p-Aminobenzylidene-DPD [14]	84	B
If	4-p-Aminobenzylidene-DPD	20	Neutral	IIf	4-p-Aminobenzyl-DPD	18	B
Ie	4-p-Anisylidene-DPD [13]	20	Neutral	IIIe	p-Anisylmalondianilide	18	C
Ie	4-p-Anisylidene-DPD	40–50	Neutral	IIIe	p-Anisylmalondianilide	18	C
Ie	4-p-Anisylidene-DPD	20	Alkaline	Ie	4-p-Anisylidene-DPD	80	C
IVe	p-Anisylidenemalondianilide‡	40–50	Neutral	IIIe	p-Anisylmalondianilide	18	C
IVe	p-Anisylidenemalondianilide	20	Alkaline	IIIe	p-Anisylmalondianilide	18	C
Ig	4-p-Dimethylaminobenzylidene-DPD	20	Neutral	IIIg	p-Dimethylaminobenzylidenemalondianilide	18	C
Ig	4-p-Dimethylaminobenzylidene-DPD	20	Alkaline	Ig	p-Dimethylaminobenzylidene-DPD	75	C
IVg	p-Dimethylaminobenzylidenemalondialdehyde**	50–60	Neutral	IIIg IIIg	p-Dimethylaminobenzylidenemalondianilide p-Dimethylaminobenzylidenemalondianilide	18 18	C C
IVg	p-Dimethylaminobenzylidenemalondialdehyde	20	Alkaline	IIIh	Veratrylmalondianilide	17	C
Ih	Veratrylidene-DPD [13]	20	Neutral	Ih	Veratrylidene-DPD	77	C
Ih	Veratrylidene-DPD	20	Alkaline				

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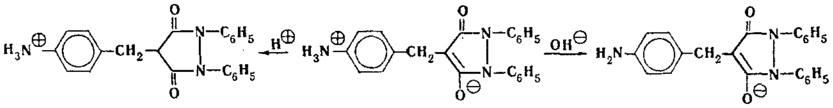
* Conditions for chromatography: A) alumina of activity grade II with the methanol–benzene (1:1) solvent system; B) alumina of activity grade II containing 2% of CH_3COOH with the ethyl acetate–ethanol (1:1) system; C) alumina of activity grade II containing 2% of CH_3COOH with the chloroform–benzene (3:1) system.

† R_f (in system B) 0.30.

‡ R_f (in system C) 0.48.

** R_f (in system C) 0.45.

hydes. In the case of the p-chloro derivative (Ic), moreover, chlorine split off, and the end-product was compound IIIa. The p-aminobenzylidene derivative (If) hydrogenated only at the C=C bond with the formation of the 4-p-aminobenzyl derivative (IIIf). 4-p-Nitrobenzylidene-DPD (Ib) also hydrogenates only to 4-p-aminobenzyl-DPD (IIIf). The resistance of the latter to the cleavage of the N–N bond in neutral ethanol can be explained by the stabilization of the molecule through the formation of an internal salt of the enolate-anionic structure (IIIf) as is also indicated by the UV spectra of this compound taken in neutral, in acidic, and in alkaline ethanol:



4-p-Amino-DPD, the bipolar structure of which is confirmed by its IR spectrum [6], also has an absorption maximum at 252 nm in neutral ethanol. The product of the hydrogenation of the 4-p-carboxy derivative could not be isolated. The hydrogenation of compounds Ia-h in neutral ethanol at 40-50°C and at the boil with a catalyst without the feed of hydrogen led to the same products as hydrogenation at 20°C. Only when Ia was hydrogenated at 40-50°C was compound IIa isolated in quantitative yield. When compounds Ia-h were hydrogenated in alkaline ethanol (1% of KOH) no absorption of hydrogen was observed, and when the solution was acidified the starting material separated out quantitatively; 4-p-Nitrobenzylidene-DPD (Ib), yielded 4-p-aminobenzylidene-DPD (If).

Thus, the 4-benzylidene derivatives of DPD are resistant to the hydrogenolysis of the N–N bond in alkaline ethanol, like the 4-monosubstituted derivatives of DPD [7]. This is in favor of the enolate carbinol structure of Ia-h in alkaline ethanol.

We previously [7] convinced ourselves that the increase in the resistance of the N–N bond to hydrogenolysis in the enolate anions of substituted DPD's is not connected with the action of the alkali on the catalyst, since the fixed enol 4-n-butyl-1,2-diphenyl-3-methoxypyrazolin-5-one is not hydrogenated in neutral ethanol. Additional facts indicating the absence of an influence of the alkali on the catalyst were obtained by studying the hydrogenation of unsaturated dianilides – compounds IVe and g in alkaline ethanol. These compounds, like the saturated dianilides (IIIa, e, g) are incapable of enolization, as is shown by the constancy of the absorption maximum in the UV spectra of these compounds taken in acidic, alkaline, and neutral ethanol (Table 1). It was found that compounds IVe and g undergo hydrogenation at the C=C bond not only in a neutral but also in an alkaline medium, unlike the corresponding cyclic compounds (Ie and g), which undergo no change on hydrogenation in alkaline ethanol.

In the hydrogenation of 4-benzylidene-DPD the exocyclic double bond is apparently saturated first. This follows from the behavior of 4-aminobenzylidene-DPD (If) and 4-nitrobenzylidene-DPD (Ib), and is confirmed by the fact that in the hydrogenation of 4-benzylidene-DPD (Ia) at 40-50°C in neutral ethanol, 4-benzyl-DPD (IIa) is obtained. In the case of compounds Ic-h, it was impossible to isolate the intermediate hydrogenation products (IIc-h, respectively) in the pure state; however, even in these cases the C=C bond is hydrogenated first. This conclusion may be drawn from the appearance in the IR spectra of the products of the incomplete hydrogenation of compounds Ie and g of absorption bands with maxima at about 1750 cm^{-1} which are characteristic for the diketo form of 4-monosubstituted DPD's [5]. In the IR spectra of the initial compounds (Ie and g), and also in those of the corresponding saturated and unsaturated dianilides (IIIe, g and IVe, g), carbonyl absorption is at lower frequencies (Table 3). The results of the chromatography of the products of the incomplete hydrogenation of compounds Ie and g (Table 3) lead to similar conclusions.

EXPERIMENTAL

The starting materials were obtained by methods given in the literature (Table 2). The homogeneity of the substances was established chromatographically.

4-p-Chlorobenzylidene-DPD (Ic). A mixture of 0.76 g (0.003 mole) of 1,2-diphenylpyrazolidine-3,5-dione, 0.85 g (0.006 mole) of p-chlorobenzaldehyde, and 15 ml of ethanol was boiled for 2 h. After cooling, 0.9 g (81%) of a red crystalline substance with mp 145-146°C (from ethanol) was obtained. Found, %: Cl 9.30; N 7.82. $C_{22}H_{15}ClN_2O_2$. Calculated, %: Cl 9.47; N 7.47.

TABLE 3. IR Spectra and R_f Values of the Products of the Incomplete Hydrogenation of the 4-Benzylidene Derivatives of 1,2-Diphenylpyrazolidine-3,5-dione (Ie and g)

Compound	ν_{CO}, cm^{-1}	$\nu_{C=C}$, cm^{-1}	R_f*
Ie	1718 1685	1625 1590	0,8
IIIe	1685 1660	1605	0,18
IVe	1680 1650	1615 1605	0,48
Alcoholic catalyzate Ie	1745 1720 1708 1685 1676	1615 1594	0,18; 0,37; 0,8
Ig	1708 1678	1618 1600	0,75
IIIg	1680	1605	0,18
IVg	1680 1650	1620 1605	0,45
Alcoholic catalyzate Ig	1742 1720 1710 1680	1615 1600	0,18; 0,35; 0,75

* Conditions for chromatography in Table 2.

p-Anisylidenemalondianilide (IVe). A mixture of 2.0 g (0.0079 mole) of malondianilide, 2.38 g (0.0172 mole) of anisaldehyde, and 0.05 g of piperidine was heated at 220-230°C for 30 min. After cooling, 1.85 g (63%) of a yellow crystalline substance with mp 200-201°C (from dichloroethane) was obtained. Found, %: N 7.44. $C_{23}H_{20}N_2O_3$. Calculated, %: N 7.53.

p-Dimethylaminobenzylidenemalondianilide (IVg). A mixture of 0.254 g (0.001 mole) of malondianilide and 0.298 g (0.002 mole) of p-dimethylaminobenzaldehyde was fused at 200-220°C for 30 min. Then the melt was ground with ether, giving 0.82 g (21%) of a yellow substance with mp 229-230°C (from dichloroethane). Found, %: N 10.84. $C_{24}H_{23}N_3O_2$. Calculated, %: N 10.91.

Catalytic hydrogenation was carried out under the conditions described previously [7] on 0.25-0.5 g of the substance, using 1-2 g of type W-5 Raney nickel catalyst and 20 ml of ethanol. The yield of hydrogenation products was 80-95%. The conditions for the hydrogenation and chromatography of compounds I-IV are given in Table 3.

4-p-Aminobenzylidene-DPD (If). A solution of 0.25 g of 4-p-nitrobenzylidene-DPD (Ib) in 20 ml of 1% ethanolic caustic potash solution was hydrogenated in the presence of 1 g of catalyst until the absorption of hydrogen ceased. After the removal of the catalyst, the filtrate was acidified and diluted with water. This gave 0.16 g (64%) of a yellow crystalline substance with mp 239-240°C (from dichloroethane). Found, %: N 12.03. $C_{22}H_{17}N_3O_2$. Calculated, %: N 11.82.

4-p-Aminobenzyl-DPD (IIf). 0.25 g of compound Ib in 20 ml of ethanol was hydrogenated in the presence of 1 g of catalyst until the absorption of hydrogen ceased. The catalyst and the precipitate that had appeared towards the end of hydrogenation were filtered off and treated with 1% alcoholic KOH solution. The filtrate after the elimination of the catalyst was neutralized and evaporated. The residue was treated with water, giving 0.19 g (76%) of a yellow substance, mp 193°C (from ethanol). Found, %: N 11.67. $C_{22}H_{19}N_3O_2$. Calculated, %: N 11.75.

p-Anisylmalondianilide (IIIe). The hydrogenation of compounds Ie and IVe gave a white crystalline substance, mp 218-219°C (from aqueous methanol) with yields of 64 and 91%, respectively. Found, %: N 7.47. $C_{23}H_{22}N_2O_3$. Calculated, %: N 7.48.

p-Dimethylaminobenzylmalondianilide (IIIg). When compounds Ig and IVg were hydrogenated until the absorption of hydrogen ceased, a white crystalline substance, mp 232-233°C (from ethanol) was obtained with a yield of 80-81%. Found, %: N 10.93. $C_{24}H_{25}N_3O_2$. Calculated, %: N 10.84.

Incomplete Hydrogenation of 4-p-Anisylidene-DPD (Ie) and 4-p-Dimethylaminobenzylidene-DPD (Ig). A suspension of 0.005 g of compound Ie (Ig) in 40 ml of ethanol was hydrogenated in the presence of 2 g of catalyst until half the calculated amount of hydrogen had been absorbed. The ethanolic filtrate was evaporated to dryness. The residue was dissolved in chloroform, and its IR spectrum was recorded and it was chromatographed (Table 2). The catalyst was treated with chloroform. The chloroform extract was analyzed similarly, and only the starting material was found in it.

The IR spectra were taken on an IKS-14 double-beam spectrophotometer with an NaCl prism with the substances in the form of suspensions in paraffin oil and in chloroform solution.

The electronic spectra were recorded on an SF-4 spectrophotometer in ethanol, in 80% ethanol containing 0.35% of HCl, and in 0.1% KOH in ethanol at concentrations of $1\text{-}4 \cdot 10^{-5}$ mole/liter.

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