PYRAZOLIDINE CHEMISTRY

XVII.* ANOMALOUS BEHAVIOR OF 4-ETHYLIDENE DERIVATIVES OF 1,2-DIPHENYL-3,5-DIOXOPYRAZOLIDINE DERIVATIVES DURING HYDROGENATION OVER RANEY NICKEL

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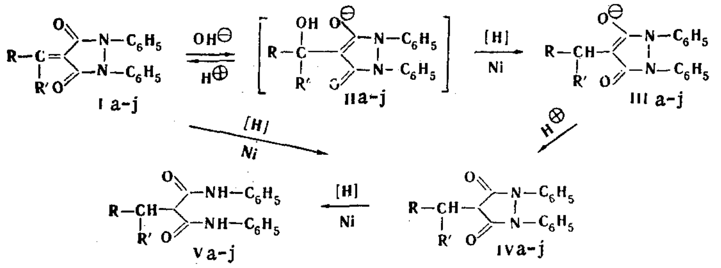
In contrast to 4-benzylidene-1,2-diphenyl-3,5-dioxopyrazolidine and its aromatic and heterocyclic analogs, 4-ethylidene derivatives and their cyclic analogs are hydrogenated at the exocyclic double bond not only in neutral ethanol but also in ethanol in the presence of alkali. The UV spectra of the starting compounds and hydrogenation products in ethanol at various pH values were examined, and the possible reasons for the anomalous hydrogenation of the 4-ethylidene derivatives are discussed.

We previously demonstrated the increase in the resistance of the N−N bond to hydrogenolysis in 4-unsubstituted, 4-monosubstituted [2], and 4-benzylidene derivatives [3] of 1,2-diphenyl-3,5-dioxopyrazolidine (DDP) during hydrogenation over Raney nickel in ethanol in the presence of alkali and expressed an assumption regarding the addition of a hydroxyl ion to 4-benzylidene-DDP to form a carbinol enolate (II).†

In this investigation we have found (Table 1) that the behavior of 4-arylidene-DDP (Ia,c) does not change when the phenyl radical in Ia is replaced by anthryl and furyl residues; in neutral ethanol they are hydrogenated at the C=C and N−N bonds to the corresponding saturated dianilides (Vb, c), while in the presence of alkali they are not hydrogenated and are regenerated on acidification of the solution. 4-Cinnamylidene-DDP (Id), the vinylog of Ia, is hydrogenated only at the noncyclic double bond in ethanol in the presence of alkali to form 4-(γ-phenylpropylidene)-DDP (Ie). The behavior of 4-(α-phenylbenzylidene)-DDP (If) in neutral and alkaline media is similar to the behavior of Ia-c.



I-Va, R = phenyl, R' = H; b, R = 9-anthryl, R' = H; c, R = α-furyl, R' = H; d, R = ω-styryl, R' = H; e, R = phenylethyl, R' = H; f, R = R' = phenyl; g, R = phenyl, R' = methyl; h, R = R' = methyl; i, R,R' = tetramethylene; j, R,R' = pentamethylene.

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*See [1] for communication XVI.

†The work was reported in [4] before the publication of [2, 3].

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TABLE 1. Effect of Conditions on the Hydrogenation of 4-Ylidene-DDP and Characteristics of the Hydrogenation Products

Start. comp.	Hydrogen. temp.^{a}	Hydrogenation products									
		comp.	name	mp	$R_f \times 100^{b}$	empirical formula	found N,%	calc. N,%	IR spectra, cm^{-1} ν_{N-H}	IR spectra, cm^{-1} $\nu_{C=O}$	yield, %
Ib	20, a	Ib	4-(9-Anthrylmethylene)-DDP	223—234^{c}	87, A	$C_{30}H_{20}N_2O_2$	6,4	6,4		1723, 1700	87
Ib	20, n	Vb	9-Anthrylmethylmalonic acid dianilide	249—250^{c}	62, A	$C_{30}H_{24}N_2O_2$	6,0	6,3	3295, 3260, 3200	1670, 1650	67
Ic^{5,6}	20, a	Ic	Furfurylidene-DDP	154—155^{c}	84, A						88
Ic	20, n	Vc	Furfurylmalonic acid dianilide	174—177^{d,e}	16, A	$C_{20}H_{18}N_2O_3$	8,7	8,4	3240	1668	94
Id^{5}	20, a	Ie	4-(γ-Phenylpropylidene)-DDP	90—92^{f}	16. B	$C_{24}H_{20}N_2O_2$	7,6	7,6		1750, 1754	83
Id^{g}	Reflux, n	Ve	γ-Phenylpropylmalonic acid dianilide	249—250^{c}	39, B	$C_{24}H_{24}N_2O_2$	7,5	7,5	3250	1690, 1665	77
If^{5}	20, a	If	4-(α-Phenylbenzylidene)-DDP	262—263^{h}	77, C						96
If	Reflux, n	Vf	α-Phenylbenzylmalonic acid dianilide	292—293^{i,j}	8, C	$C_{28}H_{24}N_2O_2$	6,3	6,7		1676, 1651	60
If	20, n	Vf	α-Phenylbenzylmalonic acid dianilide	220	8, C						
		IVf	4-(α-Phenylbenzyl)-DDP [9]		71, C						
Ig^{5}	20, a	IVg	4-(α-Methylbenzyl)-DDP [9]	143—144^{d,k}	84, C	$C_{23}H_{20}N_2O_2$	7,9	7,9		1744, 1704	75
Ig^{l}	Reflux, n	Vg	α-Methylbenzylmalonic acid dianilide	203—204^{m}	49, C	$C_{23}H_{22}N_2O_2$	7,6	7,8		1680, 1651	79

TABLE 1. Continued.

Ig	20, n	IVg	4-(α-Methylbenzyl)-DDP	138—139	84, C					
		Vg	α-Methylbenzylmalonic acid dianilide		49, C					
Ih[c]	20, a	IVh	Isopropyl-DDP [15]	142—143[m]	66, C					80
Ih[n]	Reflux, n	Vh	Isopropylmalonic acid dianilide	234—235[d]	56, C	$C_{18}H_{20}N_2O_2$	9,4	9,4	3288, 3147	1676	93
Ih	20, n	IVh	Isopropyl-DDP	137—138	66, C					
		Vh	Isopropylmalonic acid dianilide		56, C					
Ii[10]	20, a	IVi	Cyclopentyl-DDP [10]	171—172[i]	80, D					98
Ii[o]	20, n	Vi	Cyclopentylmalonic acid dianilide	251—252[i]	13, D	$C_{20}H_{22}N_2O_2$	8,7	8,7	3300—3200	1672	76
Ij[8, 10]	20, a	Ij	Cyclohexylidene-DDP	172—173[i]	80, D					99
Ij	50—60, n	IVj	Cyclohexyl-DDP [10]	176—177[i]	75, D					72
Ij	20, n	IVj	Cyclohexyl-DDP		75, D					
		Vj	Cyclohexylmalonic acid dianilide		25, D					
IVj	Reflux, n	Vj	Cyclohexylmalonic acid dianilide	275—276[i]	25, D	$C_{21}H_{24}N_2O_2$	8,0	8,4	3270	1680	72

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[a] Medium: a indicates alkaline and n indicates neutral.

[b] On activity II aluminum oxide containing 2% acetic acid. Systems: A is chloroform–benzene (3:1); B is chloroform; C is ether; D is ethyl acetate.

[c] From benzene.

[d] From aqueous ethanol

[e] With decomposition.

[f] From isopropyl alcohol.

[g] R_f 0.85 (in system B).

[h] From benzene–ethanol.

[i] From ethanol.

[j] mp 285° [7].

[k] mp 152° [9].

[l] R_f 0.89 (in system C).

[m] From ethyl acetate.

[n] R_f 0.76 (in system C).

[o] R_f 0.80 (in system D).

TABLE 2. UV Spectra of DDP (I) and Their Hydrogenation Products

Comp.	In neutral ethanol		In ethanol in presence of alkali		In acidified ethanol	
	λ_{max}, nm	lg ε	λ_{max}, nm	lg ε	λ_{max}, nm	lg ε
Ia	254; 336	4,47; 4,13	260	4,41	237; 336	4,18; 4,09
IVa	267	4,22	267	4,27	245	4,07
Va	248	4,25	248	4,25	248	4,33
Ib	252; 488	5,41; 3,98	260	5,27	252; 488	5,46; 3,98
Vb	233	5,20	233	4,77	233	5,12
Ic	242; 373	4,20; 4,54	260	4,44	242; 373	4,24; 4,67
Vc	249	4,28	249	4,37	249	4,35
Id	245; 386	4,35; 4,35	261	4,43	242; 386	4,21; 4,33
Ie	241; 399	4,23; 3,11	261	4,43	242; 399	4,22; 3,10
Ve	246	4,43	246	4,42	246	4,44
If	248; 337	4,50; 4,53	261	4,48	248; 337	4,42; 4,56
Vf	248	4,40	248	4,43	248	4,34
Ig	248; 356—366	4,37; 2,25	256	4,46	247	4,37
IVg	267	4,43	270	4,41	241	4,22
Vg	248	4,44	248	4,43	248	4,37
Ih	251; 340—370	4,45; 2,85	261	4,50	251; 340—370	4,18; 2,83
IVh	239	4,19	267	4,37	239	4,28
Vh	247	4,44	247	4,37	247	4,41
Ii	259; 344—363	4,52; 2,81	259	4,64	235; 344—363	4,38; 2,80
IVi	269	4,47	269	4,56	239	4,36
Vi	246	4,54	246	4,53	246	4,54
Ij	257; 346—363	4,38; 2,82	260	4,38	249; 346—363	4,18; 2,80
IVj	269	4,20	269	4,20	239	4,20
Vj	247	4,47	247	4,45	247	4,39

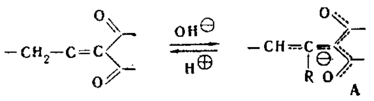
When neutral ethanol solutions of DDP I are refluxed in the presence of Raney nickel, saturated dianilides Va-c and Ve-j are formed. As in the hydrogenation in neutral ethanol, the reaction proceeds through the corresponding saturated, substituted IV, as can be judged from the detection of IVf-h in the catalyzates (Table 1) and their disappearance during additional hydrogenation.

In contrast to the 4-benzylidene-DDP and their analogs, the 4-ethylidene-DDP (Ig,h) are hydrogenated at the exocyclic double bond to form the corresponding 4-monosubstituted DDP (IVg,h), not only in neutral ethanol but also in ethanol in the presence of alkali. The cyclic analog of 4-isopropylidene-DDP, viz., 4-cyclopentylidene-DDP (Ii), behaves similarly. 4-Cyclohexylidene-DDP (Ij) is not hydrogenated in ethanol in the presence of alkali.

The presence of an absorption band with a maximum at 241-251 nm (log ε 4.3-4.6) and a second absorption band at 340-400 nm is characteristic for the spectra of all of the DDP (I) in acidic ethanol (Table 2). One's attention is drawn to the relatively low intensity and elongated character of this band in the case of the 4-ethylidene-DDP and their analogs (Ig-j) as compared with the 4-benzylidene-DDP and their analogs (Ia-d). The spectra in neutral ethanol are similar to the spectra in acidic ethanol; as for the benzylidene derivatives [3], in some cases one notes a bathochromic shift of the short-wave band, which can be explained by the solvatochromic effect of the solvent.

As in the case of 4-benzylidene-DDP [2], the absorption band in the visible region in the spectra of all of the DDP (Ib-j) in ethanol in the presence of alkali vanishes, while the short-wave band is shifted bathochromically by 10-24 nm, entering into the absorption region of an enolate and, as a rule, becomes more intense and broader. This makes it possible to assume that carbinol enolates II are formed in this case. At the same time, the absorption maxima of DDP I in alkali are shifted by 6-12 nm to the short-wave region as compared with the position of the absorption maxima of the 4-monosubstituted saturated DDP IV obtained from them, which indicates the existence of a definite difference in the structures of the enolates of these compounds (II and III).

Considering the high lability of the hydrogen of the methyl groups of 4-ethylidene-DDP, which is observed in sulfonation reactions [11] and in reactions with aldehydes [12] and diazonium salts [13], it can be assumed that the hydrogenation of Ig-i in alkaline media proceeds through mesomeric carbanion A, which is formed on dissolving them in ethanol in the presence of alkali, as has been demonstrated for 4-ethylidene and 4-cycloalkylidene derivatives of Meldrum acid [14].



The formation of this anion is apparently hindered in the case of a cyclohexylidene substituent (Ij) as a consequence of its nonplanar configuration which, in addition, can also hinder the adsorption of Ij on the catalyst.

The explanation of the reason for the anomalous hydrogenation of 4-ethylidene-DDP requires additional investigation.

EXPERIMENTAL

As described in [2,3], I and IV were hydrogenated in the presence of W-5 Raney nickel catalyst. The effect of the conditions on the direction of the hydrogenation and the characteristics of the compounds obtained are presented in Table 1.

4-(9-Anthrylmethylene)-DDP (Ib). A mixture of 5 g (0.001 mole) of 1,2-diphenyl-3,5-dioxopyrazolidine, 5 g (0.025 mole) of 9-anthraldehyde, and 100 ml of ethanol was refluxed on a water bath for 2 h. The precipitate that formed on cooling was recrystallized from benzene to give 8.4 g (87%) of an orange-red compound with mp 233-234° (Table 1).

Substituted Malonic Acid Dianilides (Vb,c,e-j). A total of 0.001-0.002 mole of starting I in 20 ml of ethanol was hydrogenated in the presence of 1-2 g of W-5 Raney nickel until hydrogen absorption ceased. The filtrate after removal of the catalyst was evaporated to dryness, and the residue was recrystallized. The characteristics of the new compounds obtained are presented in Tables 1 and 2.

The IR spectra of mineral oil suspensions were obtained with an IKS-14 spectrometer with NaCl and LiF prisms. The electronic spectra of solutions in 96% ethanol and in ethanol containing 0.35% HCl or 0.1% KOH (1 to $4 \cdot 10^{-5}$ and $5 \cdot 10^{-4}$) were obtained with an SF-4a spectrophotometer.

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