Compound	Bp, °C (pressure, mm)	d_4^{20}	n_D^{20}	MR_D found	MR_D calculated	Formula	Cl, % found	Cl, % calculated	Yield, %
I	53—54 (5)	1.170	1.4720	35.83	35.912	$C_6H_{11}ClO_2$	23.23	23.58	60
II	105—106 (3)	1.200	1.4850	33.20	33.121	$C_5H_{11}ClO_2$	24.83	25.63	7
III	58.5—59.5 (3)	1.159	1.4740	35.75	35.912	$C_6H_{11}ClO_2$	23.10	23.58	45
IV	95—97 (2)	1.195	1.4840	33.0	33.143	$C_5H_{11}ClO_2$	24.66	25.63	7

In the present paper, reaction of methylallyl chloride (bp 68°–69°; d_4^{20} 0.918; n_D^{20} 1.4240) and isocrotyl chloride with paraformaldehyde (95%), using the cation exchange resin KU-2 as catalyst, was investigated. The procedure was as follows. A mixture of 15 g paraform, 50 ml elefin, 20 ml dichloroethane, and 20 g KU-2, was refluxed for 8–9 hr. After cooling the catalyst was filtered off, unreacted olefin and dichloroethane distilled off, and finally the reaction product vacuum-distilled over in a current of inert gas. Reaction of methylallyl chloride with paraform gave 4-chloromethyl-4-methyl-1,3-dioxane (I) and 3-chloromethyl-1,3-butanediol (II). Reaction of isocrotyl chloride with paraform gave 4,4-dimethyl-5-chloro-1,3-dioxane (III), and 3-methyl-2-chloro-1,3-butanediol (IV) (table). The physical constants of I–IV cor- those given in the literature [2, 3].

In every case formation of 6–7 g resin was observed.

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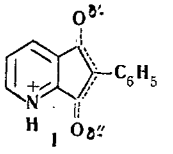
STRUCTURE OF AZAINDAN-1,3-DIONES IN SOLUTION

I. V. Turovskii, Ya. Ya. Linaberg, and O. Ya. Neiland

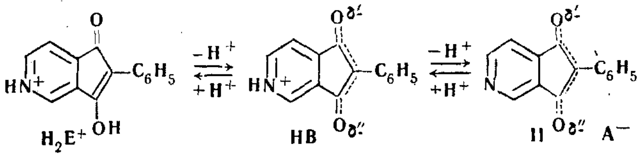
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 3, No. 1, pp. 158–160, 1967

It is shown spectrophotometrically that 2-phenylazaindan-1, 3-diones* can give in solution a cation, a dipolar ion and an anion, and the protolysis constants of the forms of 2-phenyl-4-azaindan-1, 3-dione and 2-phenyl-5-azaindan-1, 3-dione are found.

L. Neiland and G. Vanag presented equilibrium equations for 2-phenyl-4-azaindan-1,3-dione (I), 2-phenyl-5-azaindan-1,3-dione (II), and the corresponding N-methyl derivatives of these azaindan-1,3-diones (III, IV) in solution [1]. For solutions of I and II, in the case of acid solution existence of equilibrium mixtures of N-protonated enol (H_2E^+) and dipolar form (HB) is postulated, and in neutral or alkaline solution, existence of a mixture of dipolar form and anion (A^-).

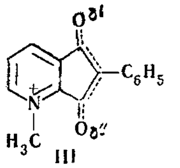


I

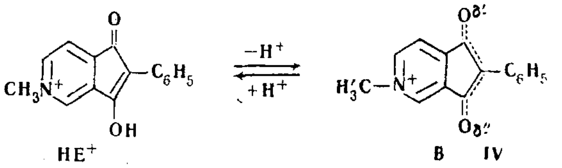


II

Solutions of III and IV consist of an equilibrium mixture of 2 forms, cation with enol structure HE^+, and dipolar ion (B):



III



IV

The Czechoslovakian workers P. Hrnčiar and D. Zacharova [2], having recommended use of II as an acid-base indicator with a color changing range of

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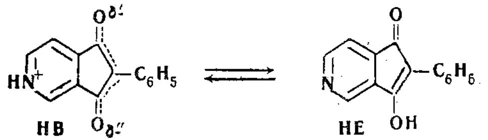
*It is important to note that the name azaindan-1,3-dione is provisional, as all the compounds studied exist in different tautomeric forms.

Acidities of Azaindandiones

Name	$pK_{H_2E^+}$	pK_{HE^+}	pK_{HB}
2-Phenyl-4-azaindan-1, 3-dione	-0.51 ± 0.07		3.94 ± 0.05
2-Phenyl-5-azaindan-1, 3-dione	-0.16 ± 0.03		5.24 ± 0.03
N-methyl-2-phenyl-4-azaindan-1, 3-dione		-0.86 ± 0.04	
N-methyl-2-phenyl-5-azaindan-1, 3-dione		0.07 ± 0.03	

pH 4.8–5.7, regard the transition as a consequence of a tautomeric change of acid dipolar form (HB) to alkaline enol (HE):



We carried out qualitative and quantitative studies of solutions I–IV, with a view to confirming one or the other equation.

Hydrochloric acid solutions of III and IV show an absorption belonging to the enol forms of indan-1,3-diones; the absorption of neutral or alkaline solutions characterises the dipolar forms. The values of the acidity constants of III and IV, characterizing the transitions $HE^+ \rightleftarrows B + H^+$, are given in the table. The spectra of solutions of I and II at pH 1.8–2.0, and pH 2.8–3.0, respectively, practically coincide with the spectra of alkaline solutions of III and IV, which also shows the presence of dipolar forms of I and II. The similarity between the spectra of hydrochloric acid (9 M HCl) solutions of I and III, and respectively those of II and IV, confirms the N protonation of the enol forms of I and II in such solutions.

If the pH of solutions of I and II is 5 or over, a hypsochromic shift of absorption is observed, due to change of the violet betaine into orange anionic form. Spectrophotometric investigations of solutions of I and II in the pH 3.98–5.28 range show, that the concentration of A^- increases in accordance with the equation

$$\lg\frac{[HB]}{[A^-]} = pK_{HB} - pH.$$

Hence the cause of the change of color of I and II at pH 3–5 and 4–6 respectively, is the shift of the protolytic equilibrium $HB \rightleftarrows A^- + H^+$ and not the tautomeric transition $HB \rightleftarrows HE$. The table gives pK_{HB} values as found spectrophotometrically.

The presence of HE was not detected, hence the amount of it does not exceed 1%. A simple calculation shows that in such a case the acidity of HE is greater than that of HB by not less than two orders of magnitude ($pK_{HE} \leq 2$ for I and ≤ 3 for II). The acidity constants of the enol forms of 2-arylindan-1,3-diones are known to occur inside the limits $2 < pK < 5$; the highest acidity is found in the presence of electron accepting substituents (NO_2, $\overset{+}{N}R_3$) [3]. The extremely high acidity of the N-protonated forms of I and II, as well as of III and IV, is evidently due to the strong inductive effect of the positive charge on the nitrogen atom.

Spectroscopic studies were made on $5 \cdot 10^{-5}$ M solutions of I–IV in water, containing HCl, acetate buffer, or KOH. The concentrations of the hydrochloric acid solutions were checked by titration; their acidity functions (H_0) were determined from the data of [4]. The pH values of the buffer solutions were determined with an Orion pH meter, calibrated with a diphthalate standard solution (pH 4.00).

The pK_{HB} values were corrected for salt effect in accordance with the Debye-Hückel theory.

UV spectra were determined with an SF-4 instrument (length of quartz cell 1 cm), and the other investigations were carried out at 20° ± 0.5°.

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