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SYNTHESIS AND PHYSICAL PROPERTIES OF SOME NEW 4-PYRIDONE EXTRACTANTS

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Abstract—The synthesis and physical properties of N-aryl-3-hydroxy-2-methyl-4-pyridones (aryl = p-NO_2–C_6H_4, p-Cl–C_6H_4, p-CH_3O–C_6H_4 and p-C_2H_5O–C_6H_4) are described and discussed. The acid ionization constants of these compounds were studied by spectrophotometric and potentiometric methods. The pH ranges in which they appear in molecular, cationic or anionic form were determined spectrophotometrically. The distribution of all described compounds between chloroform and aqueous phases of different acidity and ionic strength were determined spectrophotometrically.

INTRODUCTION

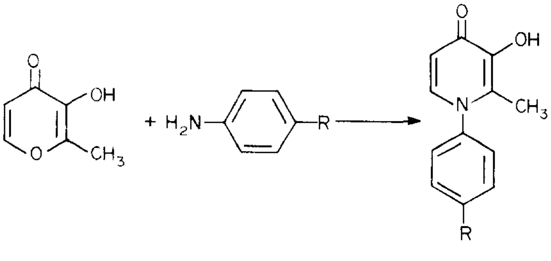
Some very useful characteristics of a few previously studied 3-hydroxy-4-pyridones[1–4] promoted us to continue the investigation of the synthesis and physical properties of new 4-pyridone extractants.

Compounds such as 2-carbethoxy-5-hydroxy-N-(4′-tolyl)-4-pyridone[1–3] and 3-hydroxy-2-methyl-N-phenyl-4-pyridone(I) or 3-hydroxy-2-methyl-N-(4′-tolyl)-4-pyridone(II)[4] appear to be very suitable as selective extractants for gallium(III)[5–6], iron(III)[7–9], vanadium(V)[10–12], uranium(VI)[13], thorium(IV)[14], protactinium(V)[14], zirconium(IV)[15], niobium(V) [2, 15], tantalum(V)[2, 15] and tungsten(VI)[16]. Organic extracts of iron(III), vanadium(V) and uranium(VI)[7–13] are convenient for direct spectrophotometric determination of these metals. In these papers, the selectivity and facile separation of some metals has been stressed as the valuable advantages of such new extractants in comparison with others described in the literature.

Recently we reported fairly simple and efficient synthesis of I and II and some physical characteristics requisite for the explanation of their extraction mechanism[4]. We now report even more simple synthesis of such compounds and also describe some new N-substituted 3-hydroxy-4-pyridones along with their physical characteristics relevant to their extraction abilities.

EXPERIMENTAL

Synthesis of N-aryl-3-hydroxy-2-methyl-4-pyridones. By heating a mixture of 2-methyl-4-pyrone with a 10% excess of an aromatic amine in water at 150°C, N-aryl-3-hydroxy-2-methyl-4-pyridones were obtained in good yield:



R = H(I), CH_3(II), NO_2(III), Cl(IV), OCH_3(V) and OC_2H_5(VI).

The reaction, which probably follows the usual mechanism of transformation of 4-pyrones to 4-pyridones[17], proceeded in some examples with somewhat lower yield than in the reported preparation *via* the corresponding methoxy derivative. Even in such cases, the direct route, described here, saved both material and time.

General procedure. A mixture of 0.05 mole of 3-hydroxy-2-methyl-4-pyrone and 0.055 mole of an aromatic amine in 60 ml of water was sealed in a thick-walled glass tube and heated for 40 hr at 150°C. The crude product obtained on cooling the reaction mixture or by evaporation, was recrystallized from hot water or methanol. Pure compounds I–VI (Table 1) were separated using non-metalic accessories and characterized by elemental analyses, UV, IR and NMR spectra.

IR spectra. All prepared compounds (I–VI) and their methoxy derivatives exhibit the IR band at 1630 cm^{-1} diagnostic for N-aryl-4-pyridone. The band at about 3200 cm^{-1} corresponds to the hydrogen-bonded OH group.

NMR spectra. Due to insufficient solubility in common solvents, NMR spectra were recorded only for compounds I, II, V and VI. However, there were no problems with the methoxy derivatives Ia–VIa (Table 2).

Apparatus. A Perkin–Elmer Coleman 124 spectrophotometer with 1 cm quartz cells was used for recording spectra and all spectrophotometric measurements. A pH-meter, Radiometer model TTT 1, was used for pH-measurements. The IR spectra were recorded on a Perkin–Elmer spectrophotometer, Model 257 in KBr discs. The NMR spectra were recorded with a Varian A-60 spectrometer in $CDCl_3$ at room temperature with TMS as internal standard.

RESULTS AND DISCUSSION

The UV absorption spectra

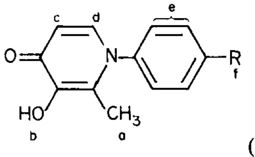
The UV absorption spectrum of III in chloroform has three absorption maxima at 253 nm, 284 nm and 335 nm, the absorption maximum of IV is at 294 nm, and those of V and VI at 292 nm. In ethanol–water mixture the position of maximum absorption depends on the ratio ethanol:water. In these solutions, as well as in chloroform, 4-pyridones are in a molecular form and the shifts of maxima absorption are affected by different solvents. 4-Pyridones are very weak acids. At pH higher than 9, they begin to dissociate and at pH higher than 12 they exist in solution in anionic forms. Maximum absorptions of the anionic forms of IV, V and VI show a bathochromic shift with a simultaneous hypochromic shift. The anionic form of III has two absorption maxima at 309 nm and 266 nm with a hypochromic shift. The UV absorption spectra of III, IV, V and VI in acid solutions show a hypsochromic shift with a simultaneous hypochromic

Table 1. Analytical data of N-aryl-3-hydroxy-2-methyl-4-pyridones

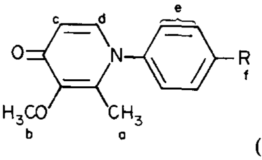
Compound	R	Formula	Anal. calc'd/found (%) C	(%) H	(%) N	(%) Cl	Yield† (%)	M.p. (°C)
I	H	$C_{12}H_{11}NO_2$	71.62 71.38	5.51 5.21	6.96 6.70		35 (69)	222–4
II	CH_3	$C_{13}H_{13}NO_2$	72.54 72.29	6.09 5.85	6.51 6.62		42 (67)	253–5
III	NO_2	$C_{12}H_{10}N_2O_4$	58.53 58.62	4.09 4.11	11.38 11.20		traces (47)‡	294–6
IV	Cl	$C_{12}H_{10}ClNO_2$	61.15 61.21	4.28 4.01	5.94 6.20	15.05 14.95	66 (28)	290–4
V	OCH_3	$C_{13}H_{13}NO_3$	67.52 67.26	5.67 5.45	6.06 5.80		56 (53)	253–5
VI	OC_2H_5	$C_{14}H_{15}NO_3$	68.55 68.45	6.16 5.94	5.71 6.01		74 (56)	218–20

†Figure in parenthesis corresponds to the compound obtained *via* methoxy derivative[4].
‡In the presence of catalytic amount of sulfuric or *p*-toluenesulfonic acid.

Table 2. NMR spectra of 3-hydroxy and 3-methoxy-4-pyridones



(I–VI)



(Ia–VIa)

Compound	*R*	*a*	*b*	*c*	*d* + *e*	*f*
I	H	2.08 (s, 3H)	6.65 (s, 1H)	6.48 (d, 1H; J = 7.8 Hz)	7.2–7.7 (m, 6H)	—
II	CH_3	2.08 (s, 3H)	6.00 (s, 1H)	6.45 (d, 1H; J = 7.8 Hz)	7.0–7.5 (m, 5H)	2.45 (s, 3H)
V	OCH_3	2.10 (s, 3H)	6.58 (s, 1H)	6.40 (d, 1H; J = 7.0 Hz)	6.9–7.5 (m, 5H)	3.95 (s, 3H)
VI	OC_2H_5	2.10 (s, 3H)	6.57 (s, 1H)	6.43 (d, 1H; J = 7.2 Hz)	6.9–7.4 (m, 5H)	1.43 (t, 3H; J = 7.0 Hz) 4.10 (q, 2H; J = 7.0 Hz)
Ia	H	2.08 (s, 3H)	3.91 (s, 3H)	6.45 (d, 1H; J = 7.8 Hz)	7.2–7.7 (m, 6H)	—
IIa	CH_3	2.05 (s, 3H)	3.90 (s, 3H)	6.41 (d, 1H; J = 7.8 Hz)	7.1–7.5 (m, 5H)	2.45 (s, 3H)
IIIa	NO_2	2.21 (s, 3H)	4.00 (s, 3H)	6.52 (d, 1H; J = 7.2 Hz)	7.40 (d, 1H; J = 7.2 Hz) 7.78 (d, 2H; J = 8.8 Hz) 8.53 (d, 2H; J = 8.8 Hz)	—
IVa	Cl	2.04 (s, 3H)	3.92 (s, 3H)	6.47 (d, 1H; J = 7.4 Hz)	7.1–7.7 (m, 5H)	—
Va	OCH_3	2.08 (s, 3H)	3.97 (s, 3H)	6.40 (d, 1H; J = 7.6 Hz)	6.9–7.5 (m, 5H)	3.96 (s, 3H)
VIa	OC_2H_5	2.07 (s, 3H)	3.97 (s, 3H)	6.43 (d, 1H; J = 7.8 Hz)	6.9–7.5 (m, 5H)	1.51 (t, 3H; J = 6.2 Hz) 4.16 (q, 2H; J = 6.2 Hz)

shift for IV, V and VI, as is the consequence of protonation of these reagents.

Acid ionization constants of reagents

Ionization of the 4-pyridones in aqueous solutions is represented by the equilibrium:

$$HX \rightleftharpoons H^+ + X^- \quad (1)$$

and the ionization constant can be defined as:

$$K_a = \frac{[H^+][X^-]}{[HX]} \quad (2)$$

being

$$pK_a = pH + \log[HX] - \log[X^-]. \quad (3)$$

The pK_a values were determined by potentiometric titrations and spectrophotometrically[18]. The compounds (1×10^{-3} M in 35% aqueous ethanol) were titrated with 0.01 M aqueous sodium hydroxide solution. The pK_a values (9.70 ± 0.1 for III, 9.85 ± 0.1 for IV, 10.04 ± 0.1 for V and 10.03 ± 0.1 for VI) were calculated according to the eqn (3).

The UV absorption spectra of III, IV, V and VI show differences between maxima absorption of the molecular and anionic form. The greatest differences between the absorbances of these two forms are at 282 nm and 309 nm for III, at 286 nm and 317 nm for IV and at 284 nm and 315 nm for V and VI. Therefore, these wavelengths were chosen for the measurements. At pH values between 9 and 11 the solutions contained both forms. Series of solutions, having the pH values in this range were prepared and their absorbances were recorded. An ammonia buffer was employed to control the pH. The p*K* values 9.62 for III at 309 nm, 9.74 for IV at 317 nm and

9.86 for V and VI at 315 nm were calculated according to the eqn (4) and 9.70 for III at 282 nm, 9.83 for IV at 286 nm and 9.96 for V and VI at 284 nm were calculated according to the eqn (5).

$$pK = pH + \log\frac{A_A - A}{A - A_M} \qquad (4)$$

$$pK = pH + \log\frac{A - A_A}{A_M - A}. \qquad (5)$$

In these equations, A_A represents the absorbance of the anionic form of the reagent, A_M the absorbance of the molecular form and A the absorbance obtained at a given pH (the mixture of the anion and the undisociated molecule).

Table 3. The distribution of reagents between chloroform and aqueous perchlorate or chloride solution or distilled water

Composition of aqueous phase	Distribution coefficient, D			
	III	IV	V	VI
H_2O	20	120	126	350
0.1 M NaCl (or 0.1 M $NaClO_4$, or 1 M NaCl, or 1M $NaClO_4$)	20	122	128	355
0.09 M NaCl + 0.01 M HCl (or 0.09 M $NaClO_4$ + 0.01 M $HClO_4$)	6.2	26	11.0	37
0.01 M HCl (or 0.01 M $HClO_4$)	6.0	26	11.0	37
0.9 M NaCl + 0.1 M HCl (or 0.9 M $NaClO_4$ + 0.1 M $HClO_4$)	0.4	2.1	1.4	3.7
0.1 M HCl (or 0.1 M $HClO_4$)	0.4	2.0	1.4	3.6

The results were represented as mean values. The relative error was maximum 5%.

Distribution of the reagents between chloroform and aqueous phase. The distribution of III, IV, V and VI between chloroform and aqueous solutions of different acidity and ionic strength was studied. The concentrations of these compounds in the aqueous phase were measured spectrophotometrically using standard concentration–absorbance curves established previously. These measurements were made at 277 nm for III and at 279 nm for IV, V and VI for acidic (0.1 M and 0.01 M) perchlorate or chloride solutions and at 282 nm for III, at 286 nm for IV and at 284 nm for V and VI for distilled water and 0.1 M and 1 M NaCl or $NaClO_4$. The solutions of all the reagents in the concentration range used obey Lambert-Beer's law so that straight lines were obtained. The aqueous media were saturated with chloroform and then equilibrated with an equal volumen of solutions of III, IV, V and VI in chloroform for 1 hr. Three different concentrations of the reagents were used. The same results were obtained if the initial concentration in chloroform were 1×10^{-4} M, 5×10^{-4} M, or 1×10^{-3} M. The results are shown in Table 3. Distribution of all these reagents is independent on the following factors: (1) their initial concentration in chloroform in the range studied, (2) the mineral acid used in the aqueous phase and (3) ionic strength of the aqueous phase. Distribution depends only on the acidity of aqueous phase. An increase in acidity causes higher solubility of all the reagents in the aqueous phase as the result of higher solubility of the cationic form.

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