carbonate solution, and extracted with chloroform. The solvent was removed by distillation, and the residue was recrystallized from ethanol to give 1.01 g (35.5%) of a product with mp 193-196°C.

C) A mixture of 3 g (14 mmole) of 2-benzylidene-3-oxoquinuclidine, 1.52 g (14 mmole) of phenylhydrazine, and 30 ml of toluene was refluxed for 8 h with removal of the water by azeotropic distillation in the presence of a catalytic amount of p-toluenesulfonic acid. It was then cooled, and the precipitate was removed by filtration and washed with toluene to give 1.42 g (33%) of a product with mp 193-196°C (from ethanol). The substances obtained by the three methods were identical with respect to their IR spectra.

2-(4'-Methoxybenzylidene)-3-oxoquinuclidine Phenylhydrazone (Vb). This compound was synthesized in the same way as phenylhydrazone Va by method A; the reaction time was 8 h. Workup gave a product with mp 176-178°C (from isopropyl alcohol) in 36% yield. Found: C 75.8; H 7.3; N 12.5%. $C_{21}H_{23}N_3O$. Calculated: C 75.6; H 7.0; N 12.6%.

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SYNTHESIS AND PROPERTIES OF SUBSTITUTED 10-PHENYL-10-HYDROXY-10H-PYRIDO[2,3-b]CHROMENES

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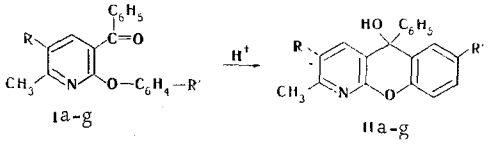
UDC 547.83'814.07:541.124.7

It is shown that 2-aryloxy-3-benzoyl-6-methylpyridines undergo cyclization to the corresponding derivatives of 10-phenyl-10-hydroxy-10H-pyrido[2,3-b]chromenes under the influence of concentrated sulfuric acid in glacial acetic acid. The pK_{R^+} values of the products, which range from −6.28 to −9.27 and correlate with the σ_p^0 and σ_R^0 meta substituent constants, depending on the position of the substituent, were determined by spectrophotometry.

In previous papers [1, 2] we studied the acid–base transformations of 10-aryl-10-hydroxy-pyrido[2,3-b]-chromenes. In order to extend these studies to ascertain the transmission of electronic effects we used a previously described method [1] to synthesize 10-phenyl-10-hydroxy-10H-pyrido[2,3-b]chromenes with substituents in both the benzene and pyridine rings of this heterocyclic system and determined their ionization constants. We used 2-aryloxy-3-benzoyl-6-methylpyridines (Ia-g) as the starting substances [3].



Ia-g IIa-g

Under the influence of concentrated sulfuric acid in glacial acetic acid ketones Ia-g undergo cyclization to give substituted 10-phenyl-10-hydroxy-10H-pyrido[2,3-b]chromenes (IIa-g; Table 1). The rate of cyclization depends on the substituents in both the pyridine ring and in the phenoxy group Ia-g. Compounds IIa-g are colorless crystalline substances. Their structure was confirmed by their IR spectra, in which bands at 3590 cm^{-1} (νOH) are observed, and, in contrast to the spectra of starting ketones Ia-g, a band of a carbonyl group is absent. The UV spectra of alcohol solutions of IIa-g contain maxima at 270 and 292 nm and an absorption band at 220 nm. As in the case of previously described analogous compounds, in sulfuric acid they undergo stepwise conversion with the formation of III ions and IV ions, which is accompanied initially by a bathochromic shift of the spectrum and then by the appearance of maxima at 374-392 and 480 nm.

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 798-800, June, 1982. Original article submitted March 10, 1981.

0009-3122/82/1806-0605$07.50

TABLE 1. 2-R-3-Methyl-8-R'-10-phenyl-10-hydroxy-10H-pyrido-[2,3-b]chromenes (IIa-g)

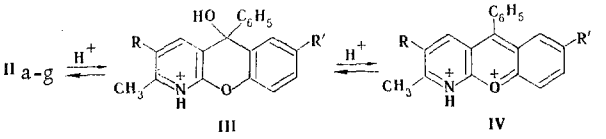
Compound	R	R'	mp, °C	Found, %			Empirical formula	Calculated, %			Yield, %
				Br	Cl	N		Br	Cl	N	
IIa	H	CH_3	229—230			4,8	$C_{20}H_{17}NO_2$[a]			4,6	71
IIb	H	Cl	237—239		10,7	4,4	$C_{19}H_{14}ClNO_2$		10,9	4,3	63
IIc	H	Br	255 (dec.)	21,8		4,0	$C_{19}H_{14}BrNO_2$	21,7		3,8	67
IId	H	F	217—219			4,8	$C_{19}H_{14}FNO_2$			4,5	61
IIe	CH_3	H	219—220			4,8	$C_{20}H_{17}NO_2$[b]			4,6	50
IIf	Br	H	216—217	21,7		3,9	$C_{19}H_{14}BrNO_2$	21,7		3,8	40
IIg	Cl	H	224—225		10,8	4,4	$C_{19}H_{14}ClNO_2$		10,9	4,3	78

[a]Found: C 79.0; H 5.4%. Calculated: C 79.2; H 5.6%. [b]Found: C 79.3; H 5.5%. Calculated: C 79.2; H 5.6%.

TABLE 2. Parameters of the Correlation of the Logarithms of the Indicator Ratios with H_R and pK_{R^+} of 2-R-3-Methyl-8-R'-10-phenyl-10-hydroxy-10H-pyrido[2,3-b]chromenes

Reaction series	Compound	R	R'	λ_{max}[a], nm	lg ε	H_R range	$-pK_{R^+}$[b]	r	s
1	IIa	H	CH_3	384	4,54	5,56—6,90	6,28±0,10	0,999	0,009
1	IIb	H	Cl	387	4,59	8,14—10,53	9,27±0,19	0,997	0,043
1	IIc	H	Br	392	4,56	8,14—10,53	9,24±0,18	0,997	0,043
1	IId	H	F	377	4,53	7,72—10,02	8,91±0,20	0,998	0,032
2	IIe	CH_3	H	382	4,51	6,40—7,28	6,81±0,09	0,996	0,013
2	IIf	Br	H	391	4,41	5,56—7,06	6,31±0,11	0,995	0,027
2	IIg	Cl	H	387	4,43	5,56—6,90	6,34±0,12	0,997	0,017

[a]Data for solutions of pyridinium-benzopyrylium salts of the IV type in 96% sulfuric acid are presented. [b]The pK_{R^+} value of 3-methyl-10-phenyl-10-hydroxy-10H-pyrido[2,3-b]chromene, which is −7.13 [1], was taken into account in the correlation with the substituent constants in both reaction series.



A study of the III ⇄ IV equilibrium in the sulfuric acid—water system by means of the UV spectra showed that a linear relationship between the logarithms of the indicator ratios [log(IV/III)] and the acidity of the medium, which was estimated with respect to the H_R scale [5], is observed. The slopes of this dependence, just as in the case of other similar reaction series [1, 2], differ from unity and range from 0.57 to 0.67. This is probably associated with the fact that the IV ions are doubly charged species that contain both pyridinium and chromenylium rings and the solvation effects for them differ from those for triarylcarbinols, with respect to which the H_R scale was calibrated. The pK_{R^+} values that characterize the III ⇄ IV equilibrium (Table 2) for the compounds of the first reaction series correlate with the σ_p^0 substituent constants [6] ($\rho = -7.5$, $r = 0.990$, $pK^0_{R\,calc} = -7.33$, and $s = 0.172$). The correlation parameters constitute evidence that the electronic effects of the substituents in the 8 position of the heterocyclic system are readily transmitted to the reaction center primarily via an inductive mechanism.

The pK_{R^+} values of IIe-g (second reaction series) correlate with the σ_R^0 meta substituent constants [6] ($\rho = -4.19$, $r = 0.990$, $pK^0_{R\,calc} = -7.16$, and $s = 0.047$). The correlation with the resonance constants demonstrates the ability of the substituents of the compounds of the second series to enter into conjugation with the pyridinium ring, which bears considerable positive charge. The electronic effects from the latter are transmitted to the reaction center, probably via an inductive mechanism. The reaction constant in this case is lower by a factor of almost two than in the first reaction series. The π electrons of the protonated pyridine ring evidently cannot participate in delocalization of the charge on the chromenylium system, and, in this connection, transmission of the electronic effects by this ring is realized to a lesser extent than transmission by the benzene ring.

EXPERIMENTAL

The IR spectra of solutions of IIa-g in chloroform were recorded with a UR-20 spectrometer. The UV spectra were recorded with a Spectromom-202 spectrophotometer. The ionization constants in the sulfuric acid–water system were determined by spectrophotometry with the same spectrophotometer for $2 \cdot 10^{-5}$ M solutions at 20 ±1°C. The analytical wavelength corresponded to the maximum at 374-392 nm. The equation $pK_R^+ = H_R + \log([IV]/[III])$ was used to find the pK_R^+ values. The pK_R^+ value was found from seven points with a predesignated reliability of 0.98. The results were treated by the method of least squares.

2-R-3-Methyl-8-R'-10-phenyl-10-hydroxy-10H-pyrido[2,3-b]chromenes (IIa-g). A 20-ml sample of concentrated sulfuric acid was added to a solution of 3.5 mmole of Ia-g in 10 ml of acetic acid, and the mixture was heated on a water bath for 1-6 h. It was then poured into water, and the aqueous mixture was neutralized with sodium carbonate. The precipitate was removed by filtration and crystallized from ethanol. This method was used to obtain IIa-g.

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6-AMINO-5-CYANO-1H,4H-PYRAZOLO[3,4-b]PYRANS

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UDC 547.775'779.1'813'461.3'
052.2.07:543.422.51

The reaction of 3-methyl-1-phenyl-5-pyrazolene with arylideneamino nitriles in alcohol leads to the formation of 3-methyl-4(1-aryl-2,2-dicyanoethyl)-5-pyrazolones, which are readily cyclized in the presence of bases to the corresponding 6-amino-5-cyano-3-methyl-4-aryl-1H,4H-pyrazolo[3,4-b]pyrans. The structures of the intermediate and final products were confirmed by the IR, UV, PMR, and mass spectra.

Some derivatives of 2-aminopyrans [1], as well as condensed 2-amino-3-cyanopyrans [2], are pharmacologically active compounds. They have been tested as pesticides [3] and have been proposed as medicinal preparations that have antiallergenic and antiasthmatic activity [2]. 2-Aminopyrans obtained on the basis of 1,3-dicarbonyl compounds and unsaturated nitriles with an active double bond are known [4]. However, very little study has thus far been devoted to 6-aminopyrazolo[3,4-b]pyrans. A single representative of this series, viz., 6-amino-1-phenyl-4,4,5-tricyano-1H,4H-pyrazolo[3,4-b]pyran, which was obtained by the reaction of 3-methyl-1-phenyl-5-pyrazolone with tetracyanoethylene by heating the components in alcohol, has been described in the literature [5]. However, the method does not make it possible to vary the substituents in various positions of the pyran ring. The scope of the method have been extended substantially by a recently published paper [3] in which the addition of malononitrile to 4-arylidene-3-methyl-1-phenyl-5-pyrazolines was studied.

We have developed a simple convenient method for the preparation of 6-amino-5-cyano-3-methyl-1H,4H-pyrazolo[3,4-b]pyrans that consists in the reaction of 3-methyl-1-phenyl-5-pyrazolone with arylidene-malononitriles (method A). It can be recommended for preparative purposes.

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 801-806, June, 1982. Original article submitted May 26, 1980; revision submitted October 28, 1981.

0009-3122/82/1806-0607$07.50