SYNTHESIS AND SPECTROLUMINESCENT PROPERTIES OF 4-OXO-1,2,3,3a-TETRAHYDROPYRIMIDO[1,2,3-*l*,m]-α-CARBOLINES

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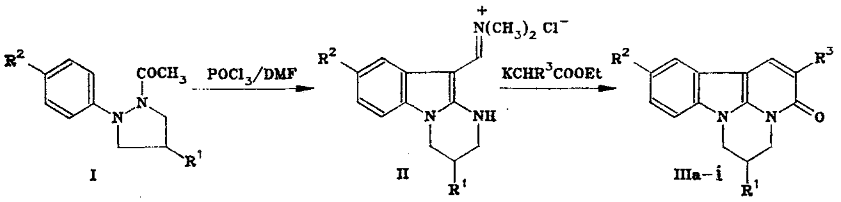
The reaction of 1-acetyl-2-arylpyrazolidines with the DMF—$POCl_3$ complex and subsequent treatment of the iminium salts formed with the potassium enolates of α-substituted acetate esters yielded a series of previously unknown α-carboline derivatives. The spectroluminescent properties of these compounds were studied. Some of the α-carbolines synthesized have a laser effect.

In our previous work [1], we showed that the reaction of 1-acetyl-2-phenylpyrazolidine (I) with the dimethylformamide-$POCl_3$ complex leads to the formation of 1,2,3,4-tetrahydropyrimido[1,2-a]indole-10-methylenedimethyliminium chloride (II). The treatment of salt II with the potassium enolate of ethyl cyanoacetate gave 4-oxo-1,2,3,3a-tetrahydropyrimido[1,2,3-*l*, m]-α-carboline (IIIa) [2].



Tetracyclic α-carboline derivatives IIIa-i had not been described previously in the literature. In this regard, it was of interest to obtain a series of such compounds and study their properties. By using different 1-acetyl-2-arylpyrazolidines and potassium enolates of α-substituted acetate esters, we synthesized a series of α-carbolines IIIa-f. The physical constants and yields of these compounds are given in Table 1. In this case, the intermediates of the reaction of the acetylarylpyrazolidines with the DMF—$POCl_3$ complex were not isolated.

Solutions of III containing cyano, acetyl, and ethoxycarbonyl groups at C-5 fluoresce strongly in chloroform and methanol in the visible and, especially, in the UV region. Measurement of the fluorescence spectra indicated that the emission maxima of these carbolines are in the range from 400 to 430 nm, while the fluorescence quantum yield in some cases is close to unity (see Table 2). The high fluorescence quantum yield is apparently a result of the long conjugation chain in the system of three condensed aromatic rings of the carboline molecule. The introduction of a bromine atom into the benzene ring of the carboline ring (IIIb), as expected, leads to a sharp decrease in the fluorescence quantum yield, which is a manifestation of the "heavy atom effect" [3]. Solutions of 5-nitrocarbolines IIIe-g do not fluoresce at all due to significant intercombinational conversion.

Since some of the α-carbonlines obtained have rather high fluorescence quantum yields, we studied the feasibility of laser generation using three of the compounds synthesized. We found that IIIa, IIIh, and IIIi have a laser effect. Table 2 gives the generation spectrum maxima λ_{gen}^{max}, width of the laser generation spectrum $\Delta\lambda$ (relative to the base), and the laser radiation efficiency η.

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TABLE 1. 4-Oxo-1,2,3,3a-tetrahydropyrimido[1,2,3-*l*,m]-α-carbolines (IIIa-i)

Compound	R^1	R^2	R^3	mp, °C	Found, %		Chemical formula	Calculated, %		Yield, %
					C	H		C	H	
IIIa	CH_3	H	CN	302	72,7	5,1	$C_{16}H_{13}N_3O$	73,0	4,9	82
IIIb	CH_3	Br	CN	324	55,3	3,7	$C_{16}H_{12}BrN_3O$	56,1	3,5	87
IIIc	H	CH_3	CN	328	73,1	5,0	$C_{16}H_{13}N_3O$	73,1	5,0	74
IIId	H	OCH_3	CN	258	69,2	4,6	$C_{16}H_{13}N_3O_2$	69,0	4,7	82
IIIe	CH_3	H	NO_2	295	63,3	4,6	$C_{15}H_{13}N_3O_3$	63,6	4,6	62
IIIf	H	H	NO_2	297	62,3	4,5	$C_{14}H_{11}N_3O_3$	62,4	4,1	68
IIIg	CH_3	Br	NO_2	324	49,4	3,6	$C_{15}H_{12}BrN_3O_3$	49,7	3,3	85
IIIh	CH_3	H	$COOC_2H_5$	212	69,8	6,0	$C_{18}H_{18}N_2O_3$	69,7	5,8	45
IIIi	CH_3	H	$COCH_3$	228	72,6	6,1	$C_{17}H_{16}N_2O_2$	72,8	5,7	51

TABLE 2. Spectroluminescent and Generation Characteristics of α-Carbolines IIIa-i in Ethanol

Compound	λ_{abs}^{max}	λ_f^{max}	φ_f	τ_f	λ_{gen}^{max}	Δλ	η, %
IIIa	372	410	0,72	4,30	446	23	2,1
IIIb	372	402	0,19	1,00	—	—	—
IIIc	372	411	0,51	2,88	—	—	—
IIId	375	415	0,02	3,00	—	—	—
IIIh	372	405	0,91	3,67	423	23	7,1
IIIi	387	431	0,76	4,16	443	29	1,8

EXPERIMENTAL

The absorption spectra were taken on a Pye-Unicam SP-8000 spectrometer. The fluorescence spectra were taken on an Elumin 2M spectrofluorimeter. The fluorescence lifetime was determined from the fluorescence quenching lifetime determined by comparison with a standard compound [4]. The laser generation was studied with transverse pumping of the second harmonic of a ruby laser (λ = 347 nm) and the generation spectra were recorded on an ISP-51 spectrograph.

4-Oxo-1,2,3,3a-tetrahydropyrimido[1,2,3-*l*,m]-α-carbolines IIIa-i (Table 1). A sample of 0.46 ml (5 mmoles) freshly distilled $POCl_3$ was added dropwise to 5 ml dry DMF at 0°C and the solution obtained was maintained at room temperature for 30 min and then a solution of the corresponding 1-acetyl-2-arylpyrazolidine in 3 ml dry DMF was added. The reaction mixture was heated at 70-80°C for 1.5 h and cooled to 0°C. The crystal precipitate was filtered off, washed with dry DMF cooled to 0°C and absolute ether. The indolylmethylenedimethyliminium chloride isolated was dissolved in 5 ml dry DMF and 10 mmoles of the potassium enolate of the corresponding α-substituted acetate ester was added. The mixture was heated at 90-100°C for 1-2 h. After cooling, the reaction mixture was poured into 20 ml water. The precipitate formed was filtered off, washed with water, dried in a vacuum desiccator, and recrystallized from acetonitrile.

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