IMIDAZOPYRIDINE DERIVATIVES AS POLYMETHINE DYES II.* SOME 1-PHENYL-1H-IMIDAZO[4,5-c]PYRIDINE DERIVATIVES AS DYES

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Several new carbo- and dicarbocyanine, merocyanine, and merocyaninocyanine dyes with residues of the quaternary salt of 1-phenyl-1H-imidazo[4,5-c]pyridine were synthesized. The colors of the dyes were studied.

In our previous paper we reported the synthesis of some polymethine dyes which are 1-methyl-1Himidazo[4,5-c]pyridine derivatives [1].

In continuing our study of the synthesis of dyes of this type we obtained the previously undescribed 1-phenyl-2-methyl-1H-imidazo[4,5-c]pyridine (I) by heating 3-amino-4-phenylaminopyridine (II) with acetic anhydride [2]. Dye II was synthesized by the reduction of 3-nitro-4-phenylamino-pyridine (III) with sodium sulfide; III was readily obtained by heating 3-nitro-4-methoxypyridine (IV) [3] with aniline in a sealed tube.

A diquaternary salt (V) was obtained by heating base I with ethyl p-toluenesulfonate.



Various forms of cyanine dyes were synthesized from quaternary salt V: a symmetrical carbocyanine (VI), unsymmetrical carbocyanine dyes (VIIa-f, Table 1), symmetrical and unsymmetrical dicarbocyanines (VIIIa-e, Table 2), a merocyanine (IX), merocyaninocyanines (Xa-c, Table 3), and a dimerocyanine (XI).



One should note the certain increase in the reactivity of the methyl group in V as compared with the diquaternary salt of 1,2-dimethyl-1H-imidazo[4,5-c]pyridine (XII) [1], which is caused by the introduction of an electronegative phenyl group into the 1-position of the imidazopyridine residue. Thus, for example, we were able to obtain mesoalkyl-substituted dicarbocyanine dyes by the condensation of V with 1,1,3,3-tetraalkoxy-2-alkylpropanes [4], but we could not synthesize such dyes from XII.

The absorption spectra of alcohol solutions of the dyes were investigated. Replacement of the methyl group by a phenyl group in the 1-position of the imidazo[4,5-c]pyridine residue of the symmetrical and unsymmetrical carbocyanine dyes causes a slight bathochromic shift of the absorption maximum (3-5 nm); in merocyanines and dicarbocyanines this sort of replacement does not affect the absorption maxima, while a

*See [1] for communication I.

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 $[\]dagger$ The symbols Z⁺ and Z⁺⁺ designate, respectively, a singly and doubly charged 1-phenyl-1H-3,5-diethylimidazo[4,5-c]pyridinium residue.

TABLE 1.



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Comp.	Z'	Appear- ance (from ethanol)	mp	λ_{max} (nm) in eth-	Empirical formula	N, found	% calc.	Yield,	
VIIa	CH ₃ CH ₃ CH ₃ CH ₃	Red prisms	242—243	539	C ₃₀ H ₃₄ I ₂ N ₄	7,7	7,9	21,1	
VIID	S L C,Hs	Red needles	251—252	543	C ₂₈ H _{3C} I ₂ N ₄ S	7,6	7,9	42,3	
VIIc	Se L C ₂ H ₅	Green needles	240—241	552	C ₂₈ H ₃₀ I ₂ N ₄ Se	6,9	7,4	32,4	
VIMI	S N C ₂ H ₅	Violet needles	265—266	550	C32H36I 2N4S	7,1	7,3	47,3	
VIIe		R ed prisms	266—267	561	C ₃₀ H ₃₂ I ₂ N4	8,1	8,0	54,1	
VIIf	$\overbrace{\mathbf{C}_{2}\mathbf{H}_{5}}^{S} \overbrace{\mathbf{C}_{6}\mathbf{H}_{5}}^{C_{6}\mathbf{H}_{5}}$	Red prisms	265—266	555	C ₃₆ H _{3f} I ₂ N ₄ S	7,2	6,9	60,0	

TABLE 2.

$$\begin{array}{c|c} & & & & \\ \hline H & & & \\ N & & & \\ N & & & \\ C_2H_5 & & \\ C_2H_5 & & \\ \end{array} \begin{array}{c} & & & \\ N & & \\ - & & \\ C_2H_5 & \\ - & \\ C_2H_5 & \\ - & & \\ C_2H$$

VIII a-e											
Comp.	Z'	R	x	Appearance (from ethanol)	dui	λ _{max} , nm (in ethanol)	Empirical formula	found z	calc. 🐇	Yield, %	
VIIIa	Z+X	H	I	Bronze needles	260— 261	635	C ₃₇ H ₄₁ I ₃ N ₆	8,8	8,8	75	
VIIIP	Z+X-	CH₃	I	Bronze prisms	243— 244	635	C ₃₈ H ₄₃ I ₃ N ₆	8,9	8,8	2,1	
VIIIc	Z+X-	C₂H₅	I	Green prisms	255— 256	635	C ₃₉ H ₄₅ I ₃ N ₆	7,9	8,7	10,2	
VIII d		C ₂ H ₅	ClO4	G reen plates	214— 215	642	C ₃₂ H ₃₆ Cl₂N₄O ₈ S	7,4	7,9	34,1	
VIIJe	Se OCH ₃	C₂H₅	ClO₄	G ree n plat es	240— 242	656	C ₃₃ H ₃₈ Cl₂N₄O₃Se	7,3	7,1	19,4	





Compound	Ζ'	Appearance (from ethanol)	mp	p unit p unit unit unit formula unit o unit		found alc. %		Yield, %
Xa	C ₂ H ₅	Dark-red crystals	283—284	580	$C_{33}H_{35}I_2N_5OS_2$	8,6	8,4	25
Xb	S I C ₂ H ₅	Gray needles	264—265	583	C37H41I2N5OS2	7,5	7,8	25
Xc	C ₂ H ₅	Green crystals	253—254	598	C35H37I2N5OS	8,5	8,43	25

small hypsochromic shift of the absorption maxima of the dyes (5 nm) is observed in the merocyaninocyanine series. The dyes are sensitizers of silver halide emulsions [5].

EXPERIMENTAL

<u>3-Nitro-4-phenylaminopyridine (III)</u>. A mixture of 0.96 g (6.2 mmole) of IV [3], 1.8 ml of aniline, and 5 ml of water was heated in a sealed tube at 160° for 4 h. The oil that separated crystallized on trituration with water. The precipitate was filtered and washed with water to give 1.02 g (76.6%) of yellow needles with mp 116-117° [from water-alcohol (2:3)]. Found %: N 19.6. $C_{11}H_{9}N_{3}O_{2}$. Calculated %: N 19.5.

<u>3-Amino-4-phenylaminopyridine (II)</u>. A solution of 4.8 g (0.02 mole) of sodium sulfide in 20 ml of water was added to a hot solution of 2.15 g (0.01 mole) of III in 10 ml of alcohol. The mixture was heated at 110° for 30 min, and the precipitate was filtered and washed with water to give 1.58 g (85.4%) of colorless needles with mp 170-171° [from alcohol-water (1:1)]. Found %: N 22.2. $C_{11}H_{11}N_3$. Calculated %: N 22.7.

<u>1-Phenyl-2-methyl-1H-imidazo[4,5-c]pyridine (I)</u>. A mixture of 3.7 g (0.02 mole) of II and 10 ml of acetic anhydride was heated at 140° for 5 h. The excess acetic anhydride was removed by vacuum distillation, and the residue was dissolved in water. The solution was made alkaline with potassium carbonate, and the base was extracted with chloroform to give 3.42 g (81.8%) of colorless needles with mp 168-169° (from benzene). Found %: N 20.3. $C_{13}H_{11}N_{3}$. Calculated %: N 20.1.

 $\frac{1-\text{Phenyl-2-methyl-1H-imidazo[4,5-c]pyridinium Ditosylate (V).}{2 \text{ mixture of } 0.42 \text{ g (2 mmole) of I}}$ and 1.2 g (6 mmole) of ethyl p-toluenesulfonate was heated at 125° for 18 h. The resinous mass was washed with dry benzene and triturated with acetone to give 1.12 g (91.8%) of colorless prisms with mp 171-172° [from ethanol-benzene (1:5)]. Found %: N 6.7. C₃₁H₃₅N₃O₆S₂. Calculated %: N 6.9.

Bis (1-phenyl-3,5-diethylimidazo[4,5-c]2,2'-pyridinium)trimethinylcyanine Triperchlorate (VI). A mixture of 0.3 g (0.5 mmole) of V, 0.4 ml of ethyl orthoformate, and 4 ml of pyridine was heated at 130° for 4 h. The dye was precipitated with ether and isolated as the perchlorate. The yield of red needles with mp 254° (from ethanol) was 0.12 g (57.2%); λ_{max} 530 nm (in ethanol). Found %: N 9.8. $C_{35}H_{39}Cl_{3}N_{6}O_{12}$. Calculated %: N 10.0.

 $\frac{1-\text{Phenyl}-3,5,3'-\text{triethyl}(\text{imidazo}[4,5-c]-2-\text{pyridinium})\text{thiacarbocyanine Diiodide (VIIb, Table 1).}}{\text{mixture of } 0.3 \text{ g} \text{ (0.5 mmole) of V, } 0.17 \text{ g} \text{ (0.5 mmole) of } 3-\text{ethyl}-2-(\beta-\text{methylthiovinyl})\text{benzothiazonium}}$

methyl sulfate, 4 ml of pyridine, and 0.2 ml of triethylamine was heated at 130° for 4 h. The dye was precipitated with ether, chromatographed on aluminum oxide (chloroform solution), and converted to the iodide.

Unsymmetrical carbocyanines VIIa and VIIa,c-f (Table 1) were similarly obtained by condensation of V, with, respectively, 1,3,3-trimethyl-2-(β -methylthiovinyl)indolenine methyl sulfate, 3-ethyl-2-(β -methylthiovinyl)benzoselenazolium methylsulfate, 3-ethyl-2-(β -methylthiovinyl)-6,7-tetramethylenebenzothiazolium methylsulfate, 1-ethyl-2-(β -anilinovinyl)quinolinium tosylate, and 3-ethyl-2-(β -anilinovinyl)-4,5-di-phenylthiazolium iodide. Acetic anhydride (about 0.2 ml per 0.50 mmole of V) was also added to obtain VIIe and VIIf.

<u>Dimethinylmerocyanine (IX)</u>. A mixture of 0.45 g (0.75 mmole) of V, 0.23 g (0.75 mmole) of 3-ethyl-5-acetanilidomethylenerhodanine, 6 ml of pyridine, and 0.15 ml of triethylamine was heated at 130° for 5 h. The dye was precipitated with ether to give 0.43 g (94.4%) of red needles with mp 200-201° (from ethanol) and λ_{\max} 520 nm (in ethanol). Found %: N 9.0. $C_{30}H_{32}N_4O_4S_3$. Calculated %: N 9.2.

Dimethinylmerocyaninocyanines (Xa-c, Table 3). A mixture of 0.25 mmole of IX and 0.2 ml of dimethyl sulfate was heated at 130° for 40 min. The quaternary salt of the appropriate heterocyclic base (0.25 mmole), 4 ml of pyridine, and 0.1 ml of triethylamine were added, and the mixture was heated at 130° for 3-4 h. The dye was precipitated with ether and converted to the iodide. The iodide was crystallized from alcohol.

<u>Dimerocyanine (XI)</u>. A mixture of 0.15 g (0.25 mmole) of IX and 0.2 ml of dimethyl sulfate was heated at 130° for 45 min, 0.05 g (0.25 mmole) of 3-ethylrhodanine, 4 ml of pyridine, and 0.1 ml of triethylamine were added, and the mixture was heated at 130° for 4 h. The dye was precipitated with ether to give 0.12 g (66.6%) of red-brown crystals with mp 270-271° (from ethanol) and λ_{max} 560 nm (in ethanol). Found %: N 9.8. C₂₉H₃₃N₅O₆S₄. Calculated %: N 10.3.

Bis (1-phenyl-3, 5-diethylimidazo[4,5-c]-2, 2'-pyridinium) pentamethinylcyanine Triiodide (VIIIa, Table 2). A mixture of 0.3 g (0.5 mmole) of V, 0.12 ml of 1,1,3,3-tetraethoxypropane, and 4 ml of pyridine was heated at 120° for 2 h. The dye was precipitated with ether and converted to the iodide. The iodide was crystallized from ethanol. Compounds VIIIb, c were similarly obtained (Table 2).

<u>1-Phenyl-3,5,3',10-tetraethyl (imidazo[4,5-c]-2-pyridinium)thiadicarbocyanine Diperchlorate (VIIId, Table 2)</u>. A mixture of 0.53 g (0.85 mmole) of V, 0.22 g (0.85 mmole) of 3-ethyl-2-(γ -ethyl- γ -formylallylidene)benzothiazoline [6,7], 4 ml of pyridine, and 1 ml of acetic anhydride was heated at 110° for 35 min. The dye was precipitated with ether and converted to the perchlorate. The perchlorate was crystallized from alcohol. Compound VIIIe was similarly obtained (Table 2).

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