IMIDAZOPYRIDINE DERIVATIVES AS POLYMETHINE DYES

III.* 1-METHYL-1H-IMIDAZO[4,5-b]PYRIDINE DERIVATIVES

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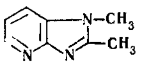
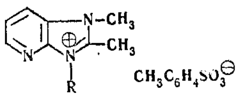
Several new polymethine dyes of the cyanine and merocyanine series with 1-methyl-1H-imidazo[4,5-b]pyridine residues were synthesized, and their colors were studied. Replacement of the benzimidazole residue in the cyanine dyes by a 1-methyl-1H-imidazo[4,5-b]-pyridine residue leads to deepening of the dye color.

We have previously reported the synthesis of some polymethine dyes that contain residues of quaternary salts of 1-methyl(phenyl)-1H-imidazo[4,5-c]pyridines [1, 2]. 1-Methyl-1H-imidazo[4,5-b]pyridine derivatives could be of definite interest as dyes. In this case, because of steric hindrance, it might have been expected that the alkylation of 1,2-dimethyl-1H-imidazo[4,5-b]pyridine (I) would give only the monoquaternary salt and, consequently, dyes that do not contain a pyridine ring nitrogen atom in the onium state. This assumption was confirmed after we had commenced our research by the fact that 3-methyl-3H-imidazo[4,5-b]pyridine reacts with alkylating agents to form the monoquaternary salt at the nitrogen atom of the imidazole ring [3].

Base I was obtained by heating 2-amino-3-methylaminopyridine (II) with acetic anhydride. Compound II was synthesized via the Clark-Lewis and Thompson scheme [4]. The quaternary salts (IIIa, b) were obtained by heating base I with alkyl esters of p-toluenesulfonic acid.



I



III a, b

a) $R = C_2H_5$; b) $R = n\text{-}C_8H_{17}$

The following different types of polymethine dyes were synthesized from quaternary salts III: a symmetrical carbocyanine (IV), unsymmetrical carbocyanine dyes (Va-e, Table 1), dimethylidynemerocyanines (VIa-k, Table 2), a dimerocyanine (VII), and a merocyaninocyanine (VIII).

One should note the lower reactivity of the C-methyl group of III as compared with the methyl group of the diquaternary salt of 1,2-dimethyl-1H-imidazo[4,5-c]pyridine [2], which has a pronounced effect on the yields of the dyes. Thus, for example, symmetrical carbocyanine dye IV could be obtained in a yield of ~5% when IIIa was heated at 190° C with ethyl orthoformate in nitrobenzene in the presence of triethylamine and acetic acid, while a symmetrical carbocyanine dye with a 1-methyl-1H-imidazo[4,5-c]pyridine quaternary salt residue is formed under quite mild conditions (at 130° C in nitrobenzene) [2]. The formation of the dyes is accompanied, in a number of cases, by the appearance of deeply colored products, from which the dyes were freed by chromatography on aluminum oxide.

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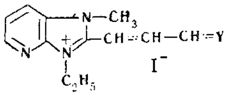
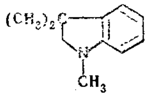
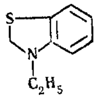
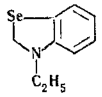
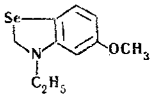
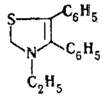
*See [1] for communication II.

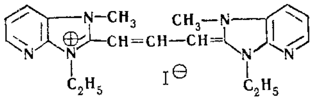
Kazan Scientific-Research Engineering and Design Institute of the Photographic-Chemical Industry. All-Union Scientific-Research and Design Institute of the Photographic-Chemical Industry, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1561-1565, November, 1971. Original article submitted July 14, 1970.

TABLE 1

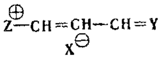


V a-e

Compound	Y	Appearance (from ethanol)	mp, °C	Empirical formula	N, % found	N, % calc.	λ_{max}, nm found (in ethanol)	λ_{max}, nm calc.	λ_{max}, nm symmetrical carbocyanine [8]	Hypsochromic shift, nm	Yield, %
Va		Red needles	150	$C_{23}H_{27}IN_4$	11,6	11,7	520	531	548	11	16,6
Vb		Dark-red needles	237–238	$C_{21}H_{23}IN_4S$	11,2	11,4	520	536	558	16	10,2
Vc		Red needles	248	$C_{21}H_{23}IN_4Se$	10,3	10,4	530	543	572	13	7,4
Vd		Red prisms	262–263	$C_{22}H_{25}IN_4OSe$	9,8	9,9	535	—	—	—	1,8
Ve		Violet prisms	248	$C_{29}H_{29}IN_4S$	9,8	9,5	546	—	—	—	7,7

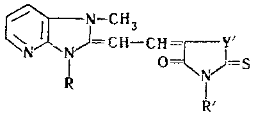


IV

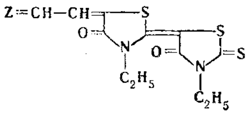


$\overset{\oplus}{Z}-CH=\underset{X^{\ominus}}{CH}-CH=Y$

Va-e*

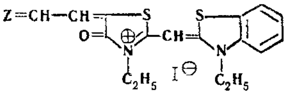


VIa-k



VII

We have investigated the absorption spectra of alcohol solutions of the synthesized dyes. The absorption maximum of the symmetrical carbocyanine dye (IV) at 514 nm is shifted by 24 nm to the long-wave portion of the spectrum as compared with the absorption maximum of 1,1-dimethyl-3,3-diethylimidacarbocyanine iodide [5], while the absorption maximum of dye VIc is shifted to the long-wave portion by 7 nm as compared with the absorption maximum of the corresponding imidadimethinemerocyanine [5].



VIII

Dyes with 1-methyl-1H-imidazo[4,5-b]pyridine residues are more highly colored than the corresponding dyes that contain a 1-methyl-1H-imidazo[4,5-c]pyridine quaternary salt residue ($\Delta\lambda_{max}$ for IV, Vb, and VIc is 11 nm, 20 nm, and 2 nm, respectively) [2]. The hypsochromic shifts of the absorption maxima of a number of unsymmetrical carbocyanines (V) that contain 3,3-dimethylindolenine, benzothiazole, and ben-

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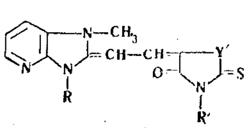
*Here and elsewhere, Z denotes the 1-methyl-1H-imidazo[4,5-b]pyridine residue.

TABLE 2



VI a-k

Compound	R	R′	Y′	mp, °C	λ, nm (in ethanol)	Empirical formula	Found, %			Calc., %			Yield, %
							C	H	N	C	H	N	
VIa	C_2H_5	C_2H_5	O	207	500	$C_{16}H_{18}N_4O_2S$	—	—	17,0	—	—	16,95	6,3
VIb	C_2H_5	CH_3	S	259—260	515	$C_{15}H_{16}N_4OS_2$	—	—	17,1	—	—	16,9	6,0
VIc	C_2H_5	C_2H_5	S	249	518	$C_{16}H_{18}N_4OS_2$	—	—	16,2	—	—	16,17	12,0
VId	C_2H_5	n-C_4H_9	S	188—189	518	$C_{18}H_{22}N_4OS_2$	—	—	14,7	—	—	14,98	8,0
VIe	C_2H_5	CH_2—CH=CH_2	S	236—237	518	$C_{17}H_{18}N_4OS_2$	—	—	15,5	—	—	15,6	3,0
VIf	C_2H_5	C_6H_5	S	258—259	520	$C_{20}H_{18}N_4OS_2$	—	—	14,3	—	—	14,2	5,1
VI g	n-C_8H_{17}	CH_3	S	184—185	522	$C_{21}H_{28}N_4OS_2$	60,3	6,8	—	60,4	6,76	—	12,2
VIh	n-C_8H_{17}	C_2H_5	S	140—141	523	$C_{22}H_{30}N_4OS_2$	61,4	7,1	—	61,25	7,01	—	5,8
VIi	n-C_8H_{17}	n-C_4H_9	S	115—116	523	$C_{24}H_{34}N_4OS_2$	65,9	7,8	—	65,7	7,5	—	14,4
VIj	n-C_8H_{17}	CH_2—CH=CH_2	S	110	523	$C_{23}H_{30}N_4OS_2$	62,4	6,9	—	62,5	6,84	—	13,6
VIk	n-C_8H_{17}	C_6H_5	S	166—167	523	$C_{26}H_{30}N_4OS_2$	65,5	6,4	—	65,3	6,3	—	15,9

zoselenazole residues are quite significant (up to 16 nm, Table 1) as compared with those of the corresponding unsymmetrical carbocyanine dyes with 1-methyl-1H-imidazo[4,5-c]pyridine quaternary salt residues (up to 6.5 nm) [2]. The hypsochromic shift of the absorption maximum for VIc is 9 nm as compared with the corresponding symmetrical dyes. The analogous shift for the dimethylidynemerocyanine with a 1-methyl-1H-imidazo[4,5-c]pyridine quaternary salt residue is 12.5 nm [2], while that for the corresponding imidadimethylidynemerocyanine is 4 nm [5]. From these results, it can be concluded that the 1-methyl-1H-imidazo[4,5-b]pyridine residue in the investigated dyes has lower basicity than the benzimidazole residues in the corresponding dyes, but, as should have been expected, greater basicity than the 1-methyl-1H-imidazo-[4,5-c]pyridine quaternary salt residues.

The synthesized dyes sensitize silver halide emulsions [6].

EXPERIMENTAL

1,2-Dimethyl-1H-imidazo[4,5-b]pyridine (I). A mixture of 1 g (8 mmole) of 2-amino-3-methylaminopyridine [4, 7] and 8 ml of acetic anhydride was heated at 140°C for 4 h. The excess acetic anhydride was removed by vacuum distillation, and the residue was dissolved in water and neutralized with potassium carbonate. The base was extracted with chloroform to give 1.04 g (84.6%) of colorless plates with mp 166-167°C (from benzene). Found: N 28.3%. $C_8H_9N_3$. Calculated: N 28.6%.

1,2-Dimethyl-1H-imidazo[4,5-b]pyridine Ethyl-p-toluenesulfonate (IIIa). A mixture of 0.73 g (5 mmole) of I and 2.5 g (12.5 mmole) of ethyl p-toluenesulfonate was heated at 130°C for 10 h. The reaction mixture was stirred with acetone, and the precipitate was removed by filtration to give 1.21 g (70.3%) of colorless prisms with mp 164°C [from acetone–alcohol (3 : 1)]. Found: 11.9%. $C_{17}H_{21}N_3O_3S$. Calculated: N 12.1%.

Compound IIIb was obtained under similar conditions and was used without additional purification in the following experiments.

Bis(1-methyl-3-ethylimidazo[4,5-b]pyridine-2,2′)trimethylidynecyanine Iodide (IV). A mixture of 0.34 g (1 mmole) of IIIa, 0.28 g (2 mmole) of ethyl orthoformate, 2.5 ml of nitrobenzene, 0.04 g (0.5 mmole) of acetic acid, and 0.05 g (0.5 mmole) of triethylamine was heated at 190°C for 7 min. The dye was precipitated with ether, chromatographed on aluminum oxide (as a solution in chloroform), and converted to 0.01 g (47%) of red needles of the iodide with mp 269-270°C (from ethanol) and λ_{max} 514 nm (in ethanol). Found: C 51.8; H 5.5%. $C_{21}H_{25}IN_6$. Calculated: C 51.64; H 5.15%.

1-Methyl-3,3′-diethyl(imidazo[4,5-b]pyridine-2-)thiacarbocyanine Iodide (Vb, Table 1). A mixture of 0.34 g (1 mmole) of IIIa, 0.3 g (1 mmole) of 3-ethyl-2-(β-methylthiovinyl)benzothiazolium methylsulfate, 6 ml of dry pyridine, and 0.4 ml of triethylamine was heated at 120°C for 4 h. The dye was precipitated with ether, chromatographed on aluminum oxide (as a solution in chloroform), and converted to the iodide.

Compounds Va, c-e (Table 1) were similarly obtained by the condensation of IIIa, respectively, with 2-(β-acetanilidovinyl)-3,3-dimethylindolenine methiodide, 3-ethyl-2-(β-methoxyvinyl)benzoeselenazolium methylsulfate, 3-ethyl-2-(β-methylthiovinyl)-5-methoxybenzoselenazolium methylsulfate, and 3-ethyl-2-(β-methoxyvinyl)-4,5-diphenylthiazolium methylsulfate.

Dimethylidynemerocyanines (VIb-k, Table 2). A mixture of 1 mmole of the appropriate III, 1 mmole of 3-alkyl(aryl)-5-acetanilidomethylenerhodanine, 5 ml of pyridine, and 0.1 ml of triethylamine was heated at 125°C for 4 h. The dye was purified by chromatography on aluminm oxide (as a benzene solution) and was crystallized as red needles from alcohol.

Compound VIa was similarly obtained by the condensation of IIIa with 3-ethyl-5-acetanilidomethyleneoxazolidinethione.

Dimerocyanine (VII). A mixture of 0.06 g (0.2 mmole) of dimethylidynemerocyanine VIc and 0.05 g of dimethyl sulfate was heated at 120°C for 30 min, the dark-red mass was washed with benzene, and 0.03 g (0.2 mmole) of 3-ethylrhodanine, 2 ml of pyridine, and 0.1 ml of triethylamine were added. The mixture was heated at 120°C for 3 h, and the precipitate was removed by filtration and washed with 5 ml of alcohol to give 0.03 g (34.5%) of violet needles with mp 281-282°C (washed with hot alcohol) and λ_{max} 574 nm (in chloroform). Found: N 15.1%. $C_{21}H_{23}N_5O_2S_3$. Calculated: N 14.8%.

Dimethylidynemerocyaninocyanine (VIII). A mixture of 0.06 g (0.2 mmole) of VIc and 0.05 g of dimethyl sulfate was heated at 120°C for 30 min, 0.06 g (0.2 mmole) of 2-methyl-3-ethylbenzothiazolium tosylate, 3 ml of pyridine, and 0.1 ml of triethylamine were added, and the mixture was heated at 130°C for 2 h. The dye was precipitated with ether and converted to 0.04 g (33.3%) of violet prisms of the iodide with mp 243-244°C (from ethanol) and λ_{max} 600 nm (in ethanol). Found: N 11.25%. $C_{26}H_{28}IN_5OS_2$. Calculated: N 11.2%.

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