

evaporated to dryness, and the dry residue was treated with absolute alcohol. Removal of the alcohol by distillation gave imidazolidine XII.

2,5,5-Trimethyl-4-phenyl-3-imidazoline 3-Oxide (XV). A) A solution of 0.76 g (0.2 mole) of sodium borohydride in 6 ml of 50% alcohol was added to a cooled (to -20°) solution of 1.28 g (0.05 mole) of 1,5-dihydroxy-2,4,4-trimethyl-5-phenyl-2-imidazolinium chloride (XIV) in 10 ml of alcohol in such a way that the temperature did not rise above -10° . After the entire solution had been added, stirring was continued at -20° for 1 h, after which the temperature was allowed to rise to room temperature, and the mixture was stirred no less than 10 h. It was then diluted with 25 ml of water, and the undissolved precipitate of inorganic salts was removed by filtration. Oxide XV was extracted from the filtrate with ether.

B) The condensation of 0.89 g (0.05 mole) of 2-amino-1-oximino-2-methyl-1-phenylpropane with 0.66 g (0.15 mole) of acetaldehyde was carried out by the method in [12], and the product was obtained in 87% yield. 1-Acetoxy-2,4,4-trimethyl-5-phenyl-2-imidazoline (III) was obtained by the method in [12].

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SYNTHESIS OF BENZIMIDAZOLE DERIVATIVES

IX.* IMIDATRICARBOCYANINES

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A general method for the synthesis of symmetrical imidatricarbocyanines is proposed. A number of dyes of this group were synthesized, and the positions of their light absorption maxima in alcohol solution were determined.

Up until now, only one instance of the formation of an imidatricarbocyanine was known [2]. We have developed a general method for the synthesis of imidatricarbocyanines—condensation of methylphenyl (5-methylphenylamino-2,4-pentadienylidene)ammonium chloride with quaternary salts of substituted 2-methylbenzimidazoles in dimethyl sulfoxide (DMSO) in the presence of sodium alkoxide:

*See [1] for communication VIII.

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TABLE 1. Imidatricarbocyanines

Dye	Starting materials ^a	Variant	R	R'	R''	X	mp, °C ^b	Empirical formula
I	A, H	a	CH ₃	CH ₃	H	Tos	153	C ₅₂ H ₃₄ N ₄ O ₃ S
II	B, H	b	C ₂ H ₅	C ₆ H ₅	H	I	212	C ₃₇ H ₃₅ IN ₄
III	C, H	a	C ₆ H ₅	C ₆ H ₅	H	I	198	C ₄₅ H ₃₅ IN ₄
IV	D, H	b	C ₂ H ₅	C ₆ H ₅	CN	I	215	C ₃₉ H ₃₅ IN ₆
V	E, H	a	C ₂ H ₅	C ₆ H ₅	BO	Tos	219	C ₅₈ H ₄₈ N ₆ O ₃ S
VI	F, H	a	C ₂ H ₅	C ₆ H ₅	BT	Tos	218	C ₅₈ H ₄₅ N ₆ O ₃ S ₃
VII	G, I	b	C ₂ H ₅	C ₆ H ₅	COCH ₃	ClO ₄	164	C ₄₁ H ₃₉ ClN ₄ O ₃

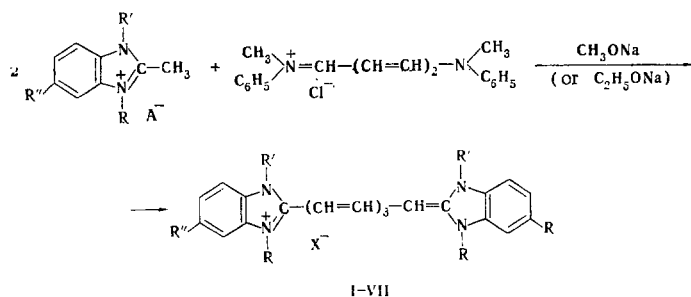
TABLE 1 (cont.)

Dye	Found, %			Calculated, %			λ_{max} , nm ^c	Yield, %
	Hal	N	S	Hal	N	S		
I		9.9	5.7		10.1	5.8	685	22
II	19.3	8.6		19.1	8.5		708 (605 ³)	20
III	16.3	7.6		16.7	7.4		719 (616 ³)	40
IV	17.5	12.0		17.8	11.8		725 (618 ⁵)	29
V		8.7	3.2		8.9	3.4	737 (634 ⁴)	25
VI		8.4	9.5		8.7	9.9	742 (637 ⁴)	23
VII	4.8	7.6		4.9	7.8		740 (623 ³)	50

^aAbbreviations: BO is 2-benzoxazolyl, BT is 2-benzothiazolyl, A is 1,2,3-trimethylbenzimidazolium tosylate, B is 1-phenyl-2,3-dimethylbenzimidazolium iodide, C is 1,3-diphenyl-2-methylbenzimidazolium chloride, D is 1-phenyl-2-methyl-3-ethyl-5-cyano-benzimidazolium iodide, E is 1-phenyl-2-methyl-3-ethyl-5-(2-benzoxazolyl)benzimidazolium tosylate, F is 1-phenyl-2-methyl-3-ethyl-5-(2-benzothiazolyl)benzimidazolium tosylate, G is 1-phenyl-2-methyl-3-ethyl-5-acetylbenzimidazolium iodide, H is methylphenyl-(5-methylphenylamino-2,4-pentadienylidene)ammonium chloride, and I is dimethyl(5-dimethylamino-2,4-pentadienylidene)ammonium perchlorate.

^bAll of the compounds melt with decomposition. Dyes V and VI were recrystallized from pyridine-alcohol-water, dye III was precipitated in the form of the iodide from a solution in pyridine, and the remaining compounds were crystallized from acetonitrile.

^cThe absorption maxima of the corresponding symmetrical imidatricarbocyanine are given in parentheses along with a citation to the literature source in which this dye was described.



In place of the above-indicated ammonium salt, one can use its analog — dimethyl(5-dimethylamino-2,4-pentadienylidene)ammonium perchlorate. Sodium methoxide is used in the form of a 2 N solution in methanol, and anhydrous powdered sodium ethoxide is also employed. Except for dye I, the imidatricarbocyanines obtained are stable in the pure state and can be stored for a long time without undergoing changes. However, in dilute solutions in alcohol and other organic solvents the imidatricarbocyanines, because of their high basicities, undergo solvolysis so rapidly that their extinction cannot be measured with a sufficient degree of accuracy.

The light-absorption maxima of the synthesized imidatricarbocyanine range from 685 to 740 nm and are shifted by ~100 nm to the longer-wave portion of the spectrum than the absorption maxima of the corresponding

imidadicarbocyanines [3]. Solutions of the imidatricarbocyanines in organic solvents have considerable fluorescence.

EXPERIMENTAL

The absorption spectra of ethanol solutions of the compounds in the visible region were recorded with an SF-10 spectrophotometer.

Symmetrical Imidadicarbocyanines (I-VII). A) A 1-mmole sample of anhydrous sodium ethoxide was added to a heated (to 50°) solution of 3 mmole of the quaternary salt of a substituted 2-methylbenzimidazole and 1 mmole of methylphenyl(5-methylphenylamino-2,4-pentadienylidene)ammonium chloride in 5-12 ml of dimethyl sulfoxide (DMSO), and the mixture was heated at 90-100° (the temperature of the mixture) for 8-15 min. The dye was isolated by dilution of the mixture with an equal amount of alcohol or excess acetone or ether. The products were crystallized from pyridine-water-alcohol (2 : 1 : 1) or from acetonitrile. They were converted to the iodide by the addition of an aqueous solution of sodium iodide to a pyridine solution of the dye.

B) A mixture of 3 mmole of the quaternary salt of the substituted 2-methylbenzimidazole, 1 mmole of methylphenyl(5-methylphenylamino-2,4-pentadienylidene)ammonium chloride, or dimethyl(5-dimethylamino-2,4-pentadienylidene)ammonium perchlorate, and 6 ml of a 2 N solution of sodium methoxide in methanol was refluxed for 3 min, after which it was cooled, and the precipitate was removed by filtration, washed with alcohol, ether, and water, and crystallized.

Data on the synthesis of dyes I-VII and their properties are presented in Table 1.

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QUINAZOLINES

VI.* REACTION OF ANTHRANILIC ACID AND ITS SUBSTITUTED DERIVATIVES WITH LACTAMS

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A method was developed for the preparation of 2,3-polymethylene-3,4-dihydro-4-quinazolones with substituents in the benzene and polymethylene chains by reaction of anthranilic acid and its substituted derivatives with γ -butyro-, 5-phenyl- γ -butyro-, ϵ -capro-, and α -chloro- ϵ -caprolactams in the presence of dehydrating agents. The corresponding quinazolines were obtained by reduction of the synthesized quinazolones.

2,3-Trimethylene-3,4-dihydro-4-quinazolone (deoxyvasicinone) and quinazoline (deoxypeganine) have been isolated from Peganum harmala [2, 3]. The latter has pronounced anticholinesterase activity.

*See [1] for communication V.

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