SYNTHESIS OF BENZIMIDAZOLE DERIVATIVES

III.* NEW IMIDACYANINS

V. M. Zubarovskii and G. P. Khodot

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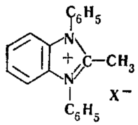
Phenylhalides of 1-phenyl-2-methylbenzimidazole were synthesized and converted to a new type of imidacyanin dye with phenyl groups on both nitrogen atoms of the benzimidazole residue. The heretofore unknown imidadicarbocyanins were obtained from quaternary salts of 1-phenyl-2-methylbenzimidazole (or its derivatives) which contain electronegative substituents in the 5 position.

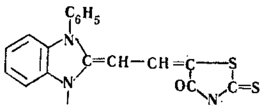
The methyl group of quaternary salts of 2-methylbenzimidazole is of low activity in reactions to prepare cyanin dyes, so that only a few types of imidacyanins are known. A certain increase in the activity of the methyl group in the indicated salts is achieved by the introduction of electronegative substituents into the 1 or 5(6) positions of the benzimidazole nucleus. Substituents on the nitrogen atoms of the heterocycle should apparently have the strongest effect. However, strongly electronegative substituents are split off during salt formation; for example, 1,2-dimethylbenzimidazole methiodide is formed when 1-cyano-2-methylbenzimidazole is heated with methyl iodide. A significant increase in the activity of the methyl group could be expected for 1-phenyl-2-methylbenzimidazole phenylhalides. The latter have not been reported.

We synthesized 1-phenyl-2-methylbenzimidazole phenylchloride (I) by heating N,N'-diphenyl-o-phenylenediamine with acetyl chloride in anhydrous toluene. Imidacyanins with phenyl groups on both nitrogen atoms of the benzimidazole rings – imidadimethinemerocyanin II, unsymmetrical imidathiacarbocyanins III and IV, and symmetrical imidacarbo- and imidadicarbocyanins VII and IX – were obtained from I.

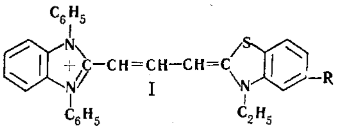


I a, b

I a X=Cl, b X=I



II



III,IV

III R=H; IV R=OCH$_3$

The light-absorption maxima of the symmetrical imidacarbo- and imidadicarbocyanins with electronegative substituents in the 1 or 5 positions are presented in Table 1. Dyes V, VI, XII, and XIII are described in [2, 6]. From a comparison of the absorption maxima of cyanins V, VI, and VII, it can be seen that replacement in V of each ethyl group by a phenyl group leads to a shift of the light-absorption maximum to the long-wave part of the spectrum (5.5 nm, on the average).

Several symmetrical imidadicarbocyanins containing bromo [3], cyano [4], and CF$_3$SO$_2$ [5] groups, and benzoxazole and benzothiazole residues [6] as substituents in the benzene rings of the benzimidazole residues have been described. However, the list of known imidadicarbocyanins is exhausted with the enumerated compounds, and these dyes have received little study. It was of interest to obtain a number of monotypic imidadicarbocyanins to investigate their optical and photographic properties.

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*See [1] for Communication II.

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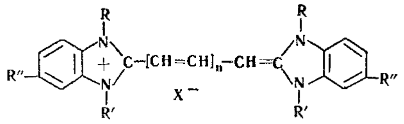
TABLE 1



Dye	R	R′	R″	*n*	X	Mp, °C	Empirical formula	Halogen% found	Halogen% calc	λ_{max},nm	Yield, %
V	C_2H_5	C_2H_5	H	1	I					498[2]	
VI	C_6H_5	C_2H_5	H	1	I					509[2]	
VII	C_6H_5	C_6H_5	H	1	I	309	$C_{41}H_3IN_4$	18,0	18,0	520	45,5
VIII	C_6H_5	C_2H_5	H	2	ClO_4	178	$C_{35}H_{33}ClN_4O_4$	6,1	5,8	605	3
IX	C_6H_5	C_6H_5	H	2	I	215(decom)	$C_{43}H_{35}IN_4$	16,9	17,3	616	13
X	C_6H_5	C_2H_5	CH_3—CO—	2	ClO_4	234(decom)	$C_{39}H_{37}ClN_4O_6$	5,2	5,1	623	25
XI	C_6H_5	C_2H_5	C_2H_5OOC—	2	I	280(decom)	$C_{41}H_{41}IN_4O_4$	16,3	16,3	617	25,5
XII	C_6H_5	C_2H_5	2-Benzoxazolyl	2	I					634[6]	
XIII	C_6H_5	C_2H_5	2-Benzothiazolyl	2	I					637[6]	

Dyes VIII-XIII were synthesized via the method described in [6] by heating the quaternary salts with 1,1,3,3-tetraethoxypropane in nitrobenzene. In some cases, better results were obtained when 1,3,3-triethoxy-1-propene was used. Partial pyrolysis of the starting compounds occurs at high temperatures, and the carbocyanin forms along with the dicarbocyanin; the dicarbocyanin can be freed from traces of the carbocyanin by chromatography (sometimes with difficulty). The method is inapplicable to 1-alkyl-2-methylbenzimidazole alkylhalides since the activity of the methyl group is slight for them.

EXPERIMENTAL

1-Cyano-2-methylbenzimidazole (XIV). Granulated sodium [0.46 g (0.02 g-atom)] was added in two to three doses to a hot solution of 2.65 g (0.02 mole) of 2-methylbenzimidazole in 40 ml of anhydrous xylene, and the mixture was refluxed for 4 h and allowed to stand for 20 h. A warm solution of 7.4 g (0.07 mole) of freshly prepared cyanogen bromide in 20 ml of anhydrous xylene was added, and the mixture was refluxed for 20 min and allowed to stand for a day. Water (40 ml) was added, and the toluene layer was separated and worked up to give 1.65 g (52.5%) of colorless crystals with mp 112° (from alcohol). Found %: N 26.8. $C_9H_7N_3$. Calculated %: N 26.8.

3-Ethyl-5-{β-[1′,3′-dimethyl-2′-benzimidazolinylidene]ethylidene}rhodanine (XV). A salt was formed by heating 0.32 g of XIV with excess methyl iodide (1.5 ml) in a sealed glass tube for 1.5 h at 120 ± 5°. The salt was washed with acetone and was used without further purification to obtain dye XV by the standard method. The latter had mp 297-298° (decomp.) and λ_{max} 511 nm. Found %: N 13.0. $C_{16}H_{17}N_3OS_2$. Calculated %: N 13.1.

The absorption curve and maximum of XV coincide with the absorption curve and maximum of 3-ethyl-5-{β-[1′,3′-dimethyl-2′-benzimidazolynylidene]ethylidene}rhodanine, which we synthesized from 1,2-dimethylbenzimidazole methiodide and 3-ethyl-5-acetanilidomethylenerhodanine to identify XV.

1-Phenyl-2-methylbenzimidazole Phenylchloride (Ia). A solution of 3.0 g (0.04 mole) of acetyl chloride in 7 ml of anhydrous toluene was added in portions with stirring to a solution of 1.0 g (0.004 mole) of N,N′-diphenyl-o-phenylenediamine [7] in 10 ml of anhydrous toluene. The mixture was heated for 2 h on a bath at 120°. After cooling, the precipitate of Ia was filtered and washed with petroleum ether to give 1.0 g of fine, white needles with mp 350-355° (decomp.). The product was used without further purification for the synthesis of dyes.

1-Phenyl-2-methylbenzimidazole Phenyliodide (Ib). Compound Ia (1.0 g) was dissolved in 10 ml of water, the solution was decolorized with a small amount of charcoal, and a hot solution of 3 g of sodium iodide in 5 ml of water was added to the hot filtrate. After 10 min, the precipitate was filtered and washed with water to give 1.2 g of product. The sample for analysis was crystallized twice from alcohol. The product was colorless crystals that decomposed at about 380°. Found %: I 30.2. $C_{20}H_{17}IN_2$. Calculated %: I 30.8.

3-Ethyl-5-{β-[1',3'-diphenyl-2'-benzimidazolinylidene]ethylidene}thiazolidine-2-thion-4-one (II). A mixture of 0.32 g (1.0 mmole) of Ia, 0.28 g (0.9 mmole) of 3-ethyl-5-acetanilidomethylenerhodanine, and 8 ml of triethylamine was refluxed for 1.5 h. The precipitate of dye was filtered from the hot liquid and washed twice on the filter with alcohol and ether to give 0.2-0.25 g (50-61%) of shiny red needles with mp 287.5-288° (from alcohol) and λ_{max} 521 nm. Found %: S 13.9. $C_{26}H_{21}N_3OS_2$. Calculated %: S 14.1.

[1,3-Diphenyl-2-benzimidazole][3'-ethyl-2'-benzothiazole]trimethinecyanin Iodide (III). A mixture of 0.16 g (0.5 mmole) of Ia, 0.23 g (0.5 mmole) of 2-(β-acetanilidovinyl)benzothiazole ethiodide, 7.5 ml of anhydrous pyridine, and 1.5 ml of acetic anhydride was refluxed for 30 min. A solution of 3 g of sodium iodide in 30 ml of water was added to the cold solution. The resulting viscous precipitate of dye was triturated with water until it began to solidify. It was then filtered, dried, chromatographed (Al_2O_3, chloroform), and treated with an aqueous alcoholic solution of sodium iodide to give 0.06 g (20%) of dark-violet, fine crystals with mp 259-260° (decomp.) and λ_{max} 524 nm. Found %: I 21.2. $C_{31}H_{26}IN_3S$. Calculated %: I 21.2.

[1,3-Diphenyl-2-benzimidazole][3'-ethyl-5'-methoxy-2'-benzothiazole]trimethinecyanin Iodide (IV). This was similarly obtained in 21% yield in the form of dark-violet crystals with mp 253° and λ_{max} 534 nm. Found %: I 19.8. $C_{32}H_{28}IN_3OS$. Calculated %: I 20.2.

Imidacarbo- and Imidadicarbocyanins (VII-XI). Compound VII was obtained by heating Ia with orthoformate ester in nitrobenzene and was purified by precipitation from alcohol solution with a sodium iodide solution. The following general method was used for the synthesis of VIII-XI. The starting quaternary salt (0.5 mmole) was dissolved in 10-25 ml of nitrobenzene, 2.5 mmole of 1,1,3,3-tetraethoxypropane or 1.25 mmole of 1,3,3-triethoxy-1-propene was added, and the mixture was heated at moderate reflux for 25 min. It was then cooled and mixed with excess ether. The resulting precipitate of dye was repeatedly washed with ether and two to three times with hot water (by decantation) to remove the starting quaternary salt, dried, and chromatographed (Al_2O_3, chloroform). It was purified by dissolving in pyridine or alcohol, precipitating with an alcoholic or aqueous solution of sodium iodide or chloride, and washing with water and alcohol. The data for VII-XI are presented in Table 1. The UV spectra of ethanol solutions were obtained with an SF-10 spectrophotometer.

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