POLYMETHINE DYES – 4-METHYLBENZOFURO- AND 4-METHYLBENZOSELENOPHENO[2,3-b]PYRIDINE DERIVATIVES

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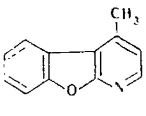
Polymethine dyes of various types were obtained from quaternary salts of 4-methylbenzofuro- and 4-methylbenzoselenopheno[2,3-b]pyridines. It is shown that replacement of the vinylene group in the benzene ring of the benzo[h]-4-quinoline residue by an oxygen or selenium atom gives rise to a larger hypsochromic shift of the absorption maxima of the corresponding cyanine dyes than replacement by a sulfur atom. Dyes with benzofuro[2,3-b]-4-pyridine residues absorb in the shorter-wave region of the spectrum than benzothieno- and benzoselenopheno[2,3-b]pyridine derivatives.

We have previously described [1] polymethine dyes that are 4-methylbenzothieno[2,3-b]pyridine derivatives. It was shown that dyes of this sort absorb in the shorter-wave region of the spectrum than the corresponding 4-methylbenzo[h]quinoline derivatives. It seemed of interest to ascertain the effect on the spectra of the dyes of similar replacement of the vinylene group by an oxygen or selenium atom in the benzo[h]quinoline residues in the cyanines. For this, we synthesized symmetrical and unsymmetrical carbocyanines (III), merocyanines (IV), and p-dimethylaminostyryl dyes (V) that are 4-methylbenzofuro[2,3-b]pyridine (I) and 4-methylbenzoselenopheno[2,3-b]pyridine (II) derivatives:



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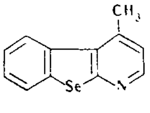

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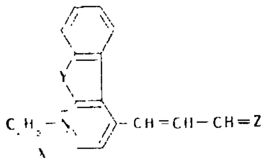

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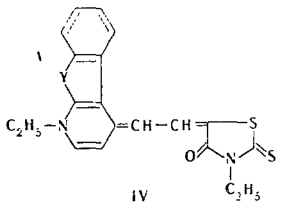

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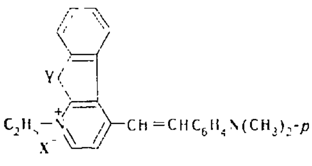

V

Y = O or Se, Z = 1-ethyl-1,4-dihydrobenzofuro- or -benzoselenopheno[2,3-b]-4-pyridylidene, 3-ethylbenzothiazolin-2-ylidene, or 1-ethyldihydro-2(or 4)-quinolylidene, and X^- is an acid residue.

We have previously synthesized the starting 4-methyl-substituted benzofuro- and benzoselenopheno[2,3-b]-pyridines (I and II) and their quaternary salts. The unsymmetrical carbocyanines and dyes IV and V were obtained from the ethiodides of bases I and II by known methods (for example, see [3]). It was found that symmetrical carbocyanines with structure III are practically not formed in the condensation of ethiodides of I and II with ethyl orthoformate, as in the case of salts of furopyridines [4] by heating in acetic anhydride [5], pyridine [6, 7], and nitrobenzene [8]. We were able to synthesize these dyes in 14-16% yields by condensation of the ethiodides of bases I and II with ethoxymethylenemalonic ester in anhydrous ethanol by heating in the presence of triethylamine (see [9]).

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TABLE 1. Absorption Maxima (in Ethanol) of Symmetrical and Unsymmetrical Carbocyanines (III) and Hypsochromic Shifts

Compound	Y	Z	λ_{max}, nm*	Hypsochromic shift [11], nm
III a	CH=CH	1-Ethylbenzo[h]dihydro-4-quinolylidene	736[10]	—
III b	—S—	1-Ethylbenzothieno[2,3-b]dihydro-4-pyridylidene	642[1]	—
III c	—Se—	1-Ethylbenzoselenopheno[2,3-b]dihydro-4-pyridylidene	636	—
III d	—O—	1-Ethylbenzofuro[2,3-b]dihydro-4-pyridylidene	630	—
III e	—O—	3-Ethylbenzothiazolin-2-ylidene	588	6,0
III f	—Se—	3-Ethylbenzothiazolin-2-ylidene	591	6,0
III g	—O—	1-Ethyldihydro-2-quinolylidene	616	2,5
III h	—Se—	1-Ethyldihydro-2-quinolylidene	625	3.5
III i	—S—	1-Ethylbenzo[h]dihydro-4-quinolylidene	689[1, 12]	0
III j	—S—	1-Ethyldihydro-4-quinolylidene	676[1, 12]	0,5
III k	—Se—	1-Ethyldihydro-4-quinolylidene	676	2,5
III *l*	—O—	1-Ethyldihydro-4-quinolylidene	671	0,5

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*At 558, 607, and 711 nm [10], respectively, for symmetrical carbocyanines and benzothiazole, 2-quinoline and 4-quinoline derivatives (λ_{max}); λ_{max} at 630 and 656 nm [3], respectively, for quino-4-thia- and quino-4,2-carbocyanines (hypsochromic shifts 4.5 and 3.0 nm, respectively).

TABLE 2. Absorption Maxima of Dimethylidynemerocyanines (IV) and p-Dimethylaminostyryl Dyes (V) and Hypsochromic Shifts

Compound	Y	λ_{max} (in ethanol, nm)*	Hypsochromic shift [11], nm
IVa	CH=CH	631[10]	8,0
IVb	—S—	581[1]	11,0
IVc	—O—	576	10,0
IVd	—Se—	580	9,0
Va	CH=CH	557	103,5
Vb	—S—	530[1]	96,0
Vc	—O—	478	142,0
Vd	—Se—	506	117,0

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*λ_{max} 542 nm (in ethanol) [13] for the symmetrical monomethylidyneoxanine, 3-ethylrhodanine derivative.

TABLE 3. Cyanine Dyes

Compound	mp, °C	Empirical formula	Found, %			Calculated, %			Yield, %
			C	H	I	C	H	I	
IIIc	>250	$C_{29}H_{25}IN_2Se_2$	53,4	4,6	24,2	53,5	4,7	24,3	14
IIId	>250	$C_{25}H_{25}IN_2O_2$	62,1	4.4	22.5	62,1	4,5	22,6	16
IIIe	269—271	$C_{25}H_{23}IN_2OS$	56,8	4.4	24.1	57,0	4,4	24,1	47
IIIf	286—287	$C_{25}H_{23}IN_2SSe$	51,1	3.8	21,5	51,0	3,9	21,6	44
IIIg	273—274	$C_{27}H_{25}IN_2O$	62,2	4,7	24,3	62,3	4,8	24,4	39
IIIh	268—269	$C_{27}H_{25}IN_2Se$	55,5	4,1	21,6	55,6	4,2	21,7	41
IIIi	214—216	$C_{31}H_{27}IN_2S$	63,3	4,7	21.5	63,4	4.6	21.6	29
IIIj	215—216	$C_{27}H_{25}IN_2S$	60.3	4,6	23.6	60,4	4,7	23,7	27
IIIk	248—249	$C_{27}H_{25}IN_2Se$	55,6	4,1	21,8	55,6	4,2	21,7	34
III*l*	252—253	$C_{27}H_{25}IN_2O$	62,2	4,6	24,3	62,3	4,8	24,4	31

The data in Table 1 show that replacement of the vinylene group in the carbocyanines by an oxygen atom in one benzene ring of the benzo[h]-4-quinoline residue gives rise to a greater hypsochromic shift of the absorption maxima of the dyes than replacement by a sulfur atom. The 4-methylbenzofuro[2,3-b]pyridine derivatives absorb in a shorter-wave region of the spectrum than the corresponding benzothieno- and benzoselenopheno-[2,3-b]pyridine derivatives.

Merocyanines and p-dimethylaminostyryl dyes with benzofuro- and benzoselenopheno[2,3-b]pyridine residues also absorb in a shorter-wave region of the spectrum than the corresponding benzothieno[2,3-b]pyridine derivatives (Table 2).

A comparison of the hypsochromic shifts of the unsymmetrical carbocyanines (III) and dimethylidynemerocyanines (IV) presented in Tables 1 and 2 shows that the basicities of the benzoselenopheno- and benzofuro[2,3-b]-4-pyridine residues are approximately of the same order as the basicity of the benzo[h]-4-quinoline residue. It follows from the hypsochromic shifts of the p-dimethylaminostyryl dyes that the basicity of the benzoselenopheno[2,3-b]-4-pyridine residue and, to a greater degree, of the benzofuro[2,3-b]-4-pyridine residue is higher than the basicity of both the benzothieno[2,3-b]-4-pyridine and benzo[h]-4-quinoline residues.

EXPERIMENTAL

The absorption spectra of the dyes in ethanol were recorded with an SF-2 spectrophotometer.

4-Methylbenzofuro- and Benzoselenopheno[2,3-b]pyridines (I and II). These compounds were obtained by our previously described method [2]. Base II was also synthesized by condensation of 14.5 g (0.02 mole) of the double tin salt of 2-aminobenzo[b]selenophene hydrochloride with 3 g of methyl vinyl ketone by the method in [14]. Workup gave 1.45 g (24.5%) of a light-yellow oil with bp 158-162° (4-5 mm), in agreement with the data in [2].

Cyanine Dyes (Table 3). Symmetrical carbocyanines IIIc and IIId were synthesized by heating a mixture of 0.68 g (0.002 mole) of the ethiodide of I or 0.8 g (0.002 mole) of the ethiodide of II, 0.30 g (0.0014 mole) of ethoxymethylenemalonic ester, 5 ml of anhydrous ethanol, and 0.1 g (0.001 mole) of triethylamine on a boiling-water bath for 1 h. Unsymmetrical carbocyanines IIIe-III*l* were obtained by heating 0.34 g (0.001 mole) of the ethiodide of I or 0.4 g (0.001 mole) of the ethiodide of II with an equimolar amount of 2-β-acetanilidovinylbenzothiazole ethiodide or 2-β-acetanilidovinylquinoline ethiodide in 4-6 ml of acetic anhydride at 125-130° (20-30 min) in the presence of 0.1 g (0.001 mole) of triethylamine. The symmetrical and unsymmetrical carbocyanines were purified by chromatography on neutral aluminum oxide and by recrystallization from ethanol.

3-Ethyl-5-(1'-ethylbenzofuro[2,3-b]dihydropyridylidene-4'-ethylidene)rhodanine (IVc). This compound was obtained by condensation of 0.34 g (0.001 mole) of ethiodide I with 0.03 g (0.001 mole) of 3-ethylrhodanine in 5 ml of anhydrous ethanol in the presence of 0.1 g (0.001 mole) of triethylamine by heating on a boiling-water bath for 60 min. The dye was purified by the method used for carbocyanines to give 0.090 g (24%) of violet needles with mp 290-292° (from ethanol). Found: C 62.6; H 4.6; N 16.7%. $C_{20}H_{18}N_2O_2S_2$. Calculated: C 62.8; H 4.7; N 16.8%.

3-Ethyl-5-(1'-ethylbenzoselenopheno[2,3-b]dihydropyridylidene-4'-ethylidene)rhodanine (IVd). This compound was synthesized from 0.4 g (0.001 mole) of the ethiodide of II by the method used to prepare dye IVc. Workup gave 0.10 g (23%) of violet needles with mp 238-239° (from ethanol). Found: C 53.8; H 4.0; N 14.3%. $C_{20}H_{18}N_2OS_2Se$. Calculated: C 53.9; H 4.0; N 14.4%.

4-(p-Dimethylaminostyryl)benzofuro[2,3-b]pyridine Ethiodide (Vc). This compound was obtained by condensation of 0.34 g (0.001 mole) of the ethiodide of I with 0.17 g (0.011 mole) of p-dimethylaminobenzaldehyde in 5 ml of pyridine in the presence of 0.085 g (0.001 mole) of piperidine by heating on a boiling-water bath for 35 min. Workup gave 0.098 g (21%) of dark-violet prisms with mp 148-149° (from ethanol). Found: C 58.7; H 4.9; I 26.9%. $C_{23}H_{23}IN_2O$. Calculated: C 58.7; H 5.1; I 27.1%.

4-(p-Dimethylaminostyryl)benzoselenopheno[2,3-b]pyridine Ethiodide (Vd). This compound was synthesized from 0.4 g (0.001 mole) of the ethiodide of II by the method used to prepare dye Vc. Workup gave 0.1 g (19%) of dark-violet prisms with mp 210-211° (from ethanol). Found: C 51.7; H 4.2; I 23.8%. $C_{23}H_{23}IN_2Se$. Calculated: C 51.8; H 4.3; I 23.8%.

LITERATURE CITED

1. P. I. Abramenko and V. G. Zhiryakov, Zh. Org. Khim., 1, 1132 (1965).
2. P. I. Abramenko, V. G. Zhiryakov, L. A. Balykova, and T. K. Ponomareva, Khim. Geterotsikl. Soedin., 6, 796 (1974).
3. F. M. Hamer, The Cyanine Dyes and Related Compounds, New York—London (1964).
4. P. I. Abramenko and V. G. Zhiryakov, Khim. Geterotsikl. Soedin., No. 4, 475 (1975).
5. W. König and W. Meyer, J. Prakt. Chem., 109, 324 (1925).
6. F. M. Hamer, J. Chem. Soc., 3160 (1928); 2606 (1929).
7. F. M. Hamer, J. Chem. Soc., 2796 (1927).
8. A. van Dormael, J. Liebeer. Sci. Ind. Phot., 20, 451 (1949).
9. N. N. Sveshnikov and N. S. Stokovskaya, Zh. Vses. Khim. O-va, No. 7, 111 (1962).
10. N. I. Fisher and F. M. Hamer, Proc. Roy. Soc. (London), 154A, 703 (1936).

11. P. I. Abramenko and V. G. Zhiryakov, Khim. Geterotsikl. Soedin., No. 12, 1611 (1972).
12. V. G. Zhiryakov and P. I. Abramenko, Trudy Gosniikhimfotoproekt, 1, 18 (1968).
13. M. V. Deichmeister, I. I. Levkoev, and E. B. Lifshits, Zh. Obshch. Khim., 23, 1529 (1953).
14. P. I. Abramenko and V. G. Zhiryakov, Khim. Geterotsikl. Soedin., No. 2, 227 (1965).

SYNTHESIS AND SOME PROPERTIES OF BENZO-1,2,3-THIASELENAZOLIUM SALTS

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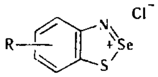
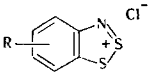
The reaction of selenious acid on benzo-1,2,3-dithiazolium salts (Herz salts) gives benzo-1,2,3-thiaselenazolium salts, which were previously obtained from o-aminothiophenols. This reaction, which involves exchange of sulfur by selenium in the heteroring, occurs only under conditions in which the products of hydrolysis of the Herz salts — benzo-3H-1,2,3-dithiazole 2-oxides — are in equilibrium with them.

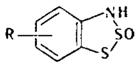
Benzo-1,2,3-thiaselenazolium salts (I) were previously obtained by reaction of selenious acid with o-aminothiophenol hydrochlorides [1]. We have found that the same heterocycles (Ia-c) are formed by the action of selenious acid on benzo-1,2,3-dithiazolium salts (IIa-c) in alcohol, acetic acid, and formic acid.



I a-e



II a-e



III a-e

I-III a R=H; b R=5-Cl; c R=6-Cl; d R=6-CH_3O; e R=6-C_2H_5O

Herz salts with donor substituents (IId,e) react in acetic and formic acids only to give admixtures of salts Id,e, which are distinctly recordable in the PMR spectra. When the acidity of the medium is reduced by the addition of sodium acetate, the reaction of IId with selenious acid in acetic acid gives Id as the final product. The 6-dimethylamino and 6-phenylamino derivatives of the Herz salt do not undergo reaction under these conditions.

Replacement of sulfur by selenium was not observed in concentrated hydrochloric and sulfuric acids or when selenium tetrabromide was used in place of selenious acid.

Thus the ability of Herz salts IIa-e to undergo reaction with selenious acetate decreases as the electron-donor properties of the substituents increase and the acidity of the medium increases. The same relationship is also observed for the ability of Herz salts to undergo hydrolysis to give benzo-3H-1,2,3-dithiazole 2-oxides (IIIa-e).

This made it possible to assume that the reaction with selenious acid does not proceed directly with the cations of II but rather through a step involving sulfoxides III. In fact, sulfoxides II react vigorously with selenious acid in acetic and formic acids to give salts I, which were isolated in the form of the chlorides. The mechanism of this transformation of sulfoxides III to cations of I remains unclear, since the assumption that the reaction proceeds through a step involving prior nucleophilic opening of the heterorings of III under the influence of a protic solvent or selenious acid is not in agreement with the fact that this transformation can also be carried out in aprotic media (by the action of selenium dioxide on IIIc,d in anhydrous dimethylacetamide, acetonitrile, nitrobenzene, and xylene). Nevertheless, the possibility of the preparation of salts I directly from

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