SYNTHESIS OF POLYMETHINE DYES FROM δ-ALKOXY-β-PHENYLBUTADIENYL SALTS OF HETEROCYCLIC BASES

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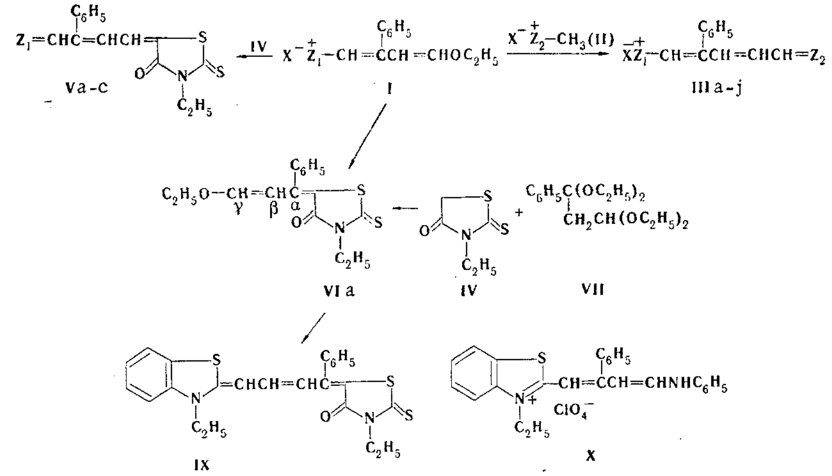
β-Phenyl-substituted dicarbocyanine dyes or β-phenyl-substituted hemicyanine dyes, respectively, are obtained in the condensation of δ-ethoxy-β-phenylbutadienyl salts of heterocyclic bases (I) with quaternary salts of heterocyclic bases or amines. Depending on the reaction conditions, α-phenyl-γ-ethoxyallylidene derivatives of ketomethylene compounds or γ-phenyl-substituted tetramethylidynemerocyanine dyes are obtained in the condensation of I with ketomethylene compounds.

The ethoxy group in δ-alkoxy-β-phenylbutadienyl salts of heterocyclic bases (I) [1] is labile, and I readily react with quaternary salts of heterocyclic bases (II) to give symmetrical or unsymmetrical β-phenyl-substituted dicarbocyanine dyes (III) [2]. The preparation of III has been described [3-5], but the yields of the dyes are low [4-5], and, in addition, relatively hard-to-obtain compounds were used in the synthesis [3].

The reaction of I and II proceeds in the presence of triethylamine in absolute alcohols or in chloroform and gives IIIa-j. If Z_1 and Z_2 have appreciably different basicities (for example if Z_1 is 3-ethylbenzothiazolium and Z_2 is 1-methylpyrrolinylium), it is better to carry out the reaction in chloroform, since a symmetrical β-phenyl-substituted thiadicarbocyanine dye impurity is formed in alcohol. The use of n-butyl alcohol proved to be favorable in the condensation of I and II, which contain 1-ethyl-2-quinolinylium residues (Table 1).



X= I, ClO_4, TsO; Z_1 and Z_2 are nitrogen-containing heterocyclic residues (see Tables 1 and 3).

The formation of γ-phenyl-substituted tetramethylidynemerocyanine dyes (V) might have been expected in the condensation of I with ketomethylene compounds, for example, with 3-ethylrhodanine (IV). However, it was found that the reaction between I and IV proceeds "anomalously."

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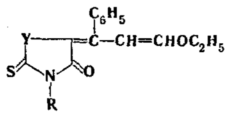
TABLE 1. β-Phenyl-Substituted Dicarbocyanine Dyes (IIIa-j)

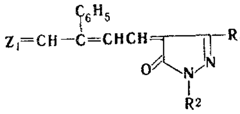
Compound	Z_1	Z_2	X	Condensation solvent	Appearance	mp, °C (from ethanol)	Empirical formula	N, % found	N, % calc.	λ_{max}, nm (log ε)	Yield, %
IIIa	3-Ethyl-2-benzothiazolium	3-Ethyl-2-benzothiazolinyl	I	Ethanol	Green prisms	183	$C_{29}H_{27}IN_2S_2$	4,6	4,7	668 (5,41)	80
IIIb	3-Ethyl-2-benzothiazolium	3-Ethyl-4,5-diphenyl-2-thiazolinyl	ClO_4	Chloroform	Blue needles	175	$C_{37}H_{33}ClN_2O_4S_2$	C 66,5 H 4,9	C 66,4 H 5,0	672 (5,07)	91
IIIc	1-Methyl-2-pyrrolinylium	3-Ethyl-2-benzothiazolinyl	ClO_4	Chloroform	Blue needles	191	$C_{25}H_{27}ClN_2O_4S$	C 61,6 H 5,5	C 61,6 H 5,6	603 (5,24)	42
IIId	3-Ethyl-2-benzothiazolium	3-Ethyl-2-benzothiazolinyl	ClO_4	Ethanol	Green plates	185	$C_{29}H_{27}ClN_2O_4S_2$	4,9	4,9	668 (5,38)	82
IIIe	3-n-Butyl-2-benzothiazolium	3-n-Butyl-2-benzothiazolinyl	ClO_4	Ethanol	Green plates	190	$C_{33}H_{35}ClN_2O_4S_2$	4,5	4,5	672 (5,39)	81
IIIf	3-Ethyl-5,6-dimethyl-2-benzothiazolium	3-Ethyl-5,6-dimethyl-2-benzothiazolinyl	I	Ethanol	Green prisms	197	$C_{33}H_{35}IN_2S_2$	4,4	4,3	682 (5,41)	81
IIIg	3-Ethyl-5-chloro-2-benzothiazolium	3-Ethyl-5-methoxy-2-benzothiazolinyl	ClO_4	Ethanol	Green needles	188	$C_{31}H_{31}ClN_2O_6S_2$	4,2	4,5	688 (5,37)	92
IIIh	3-Ethyl-5-chloro-2-benzothiazolium	3-Ethyl-2-benzothiazolinyl	ClO_4	Ethanol	Green needles	184	$C_{29}H_{26}Cl_2N_2O_4S_2$	4,6	4,9	670 (5,33)	86
IIIi	3-Ethyl-5-methoxy-2-benzoselenazolium	3-Ethyl-5,6-dimethyl-2-benzothiazolinyl	ClO_4	Ethanol	Green prisms	190	$C_{32}H_{33}ClN_2O_5SSe$	4,1	4,2	682 (5,3)	83
IIIj	1-Ethyl-2-quinolinylium	1-Ethyl-2-quinolinyl	ClO_4	n-Butyl alcohol	Green plates	222	$C_{33}H_{31}ClN_2O_4$	5,0	5,0	742 (5,38)	52

TABLE 2. α-Phenyl-γ-ethoxyallylidene Derivatives of Ketomethylene Compounds (VIa-g)



Compound	Y	R	Appearance	mp, °C (from ethanol)	Empirical formula	Found, % C	Found, % H	Found, % N	Found, % S	Calc., % C	Calc., % H	Calc., % N	Calc., % S	λ_{max}, nm (log ε)	Yield, %
VIa	S	C_2H_5	Yellow prisms	108	$C_{16}H_{17}NO_2S_2$	60,2	5,3	4,2	20,1	60,2	5,4	4,4	20,1	410 (4,6)	81
VIb	S	CH_3	Yellow prisms	157	$C_{15}H_{15}NO_2S_2$				21,1				21,1	408 (4,5)	83
VIc	S	$CH_2—CH=CH_2$	Yellow prisms	108	$C_{17}H_{17}NO_2S_2$				19,5				19,3	410 (4,58)	82
VId	S	n-C_4H_9	Yellow prisms	81	$C_{18}H_{21}NO_2S_2$	62,4	6,0			62,2	6,1			410 (4,53)	82
VIe	S	C_6H_5	Yellow needles	181—182	$C_{20}H_{17}NO_2S_2$	65,2	4,6	3,6	17,4	65,4	4,7	3,8	17,5	410 (4,57)	84
VIf	O	C_2H_5	Resinous mass	—	$C_{16}H_{17}NO_3S$	63,1	5,3	4,4		63,3	5,6	4,6		378 (4,47)	70
VIg	C_6H_5N	CH_3	Resinous mass	—	$C_{21}H_{20}N_2O_2S$	69,6	5,3	7,5		69,2	5,5	7,7		412 (4,5)	72

TABLE 3. γ-Phenyl-Substituted Tetramethylidynemerocyanine Dyes (VIIa-g)



Compound	Z_1	R_1	R_2	Appearance	Mp, °C (from ethanol)	Empirical formula	Found, %		Calc., %		λ_{max}, nm (log ε)	Yield, %
							C	H	C	H		
VIIIa	3-Ethyl-2-benzothiazolinyl	CH_3	C_6H_5	Blue prisms	100	$C_{29}H_{25}N_3OS$*	—	—	—	—	608 (5,07)	39
VIIIb	1,3,3-Trimethyl-4,5-benzo-2-indoleninyl	CH_3	C_6H_5	Blue needles	272	$C_{35}H_{31}N_3O$	82,3	6,0	82,5	6,1	614 (4,97)	40
VIIIc	3-Ethyl-2-benzothiazolinyl	CH_3	o-ClC_6H_4	Blue needles	140	$C_{29}H_{24}ClN_3O$	70,0	4,5	69,9	4,8	610 (5,01)	38
VIIId	3-Ethyl-2-benzothiazolinyl	C_6H_5	C_6H_5	Blue prisms	226	$C_{34}H_{27}N_3OS$	77,8	5,1	77,7	5,2	612 (4,98)	48
VIIIe	3-Ethyl-5-methoxy-2-benzothiazolinyl	CH_3	C_6H_5	Blue prisms	195	$C_{30}H_{27}N_3O_2S$	N 8,3		N 8,5		623 (5,03)	43
VIIIf	3-Ethyl-5-methoxy-2-benzothiazolinyl	C_6H_5	n-C_6H_{13}	Blue needles	205	$C_{35}H_{37}N_3O_2S$	74,4	6,3	74,6	6,6	616 (5,1)	41
VIIIg	3-Ethyl-5,6-dimethyl-2-benzothiazolinyl	CH_3	C_6H_5	Blue prisms	252	$C_{31}H_{29}N_3OS$	75,3	6,0	75,7	6,0	620 (5,1)	52

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*Found: N 9.0%. Calculated: N 9.1%.

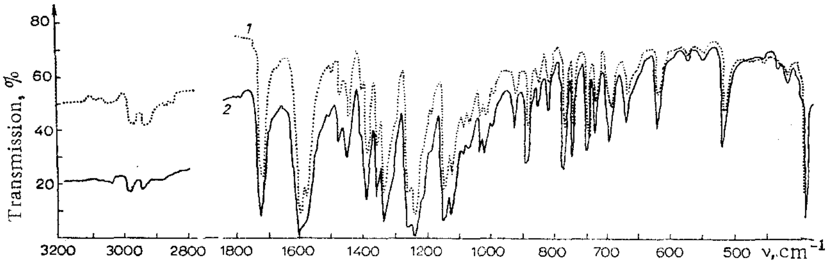

Fig. 1. IR spectrum of 3-ethyl-5-(α-phenyl-γ-ethoxyallylidene)-rhodanine (VIa) obtained: 1) from 3-ethylrhodanine and VII; 2) from 3-ethylrhodanine and I.

Thus a yellow compound with mp 108° and λ_{max} 410 nm was isolated in all cases in the condensation of I containing benzothiazolium, 4,5-diphenylthiazolium, 5-phenylbenzoxazolium, 5,6-dimethylbenzothiazolium,5-methoxybenzothiazolium, 2-quinolinylium, and 4-quinolinylium residues with 3-ethylrhodanine. There is a band at 1714 cm^{-1} in the IR spectra of the compound, which attests to the presence in the product of a C=O bond related to the rhodanine ring [6]. The analytical data for this product made it possible to assign the VIa structure to it. The formation of VIa can apparently be explained by the fact that substitution of the heterocyclic residue of salt I by a ketomethylene residue occurs during the reaction between I and 3-ethylrhodanine, and thus the phenyl group is found in the α position of the polymethine ring.

We also studied the condensation of benzoylacetaldehyde tetraethylacetal (VII) [7] with 3-ethylrhodanine in acetic anhydride. One might have expected the formation of VIa or the isomeric product with a phenyl group attached to the γ-carbon atom in this case. However, the identical melting points, the identical character of the IR spectra (Fig. 1), and the absence of a melting-point depression in mixtures with VIa made it possible to assign the VIa structure to the product obtained from VII and 3-ethylrhodanine.

The condensation of I with other ketomethylene compounds proceeds similarly: 3-substituted rhodanines, 3-ethyloxazolidinethione, and 1-phenylthiohydantoin give VIb-g (Table 2).

Pyrazolones proved to be an exception in this reaction, since γ-phenyl-substituted tetramethylidynemerocyanine dyes (VIIIa-g) (Table 3) formed readily in the condensation of them with I in absolute alcohols in the presence of triethylamine.

We were able to obtain tetramethylidynemerocyanine dyes V by reaction of I with 3-ethylrhodanine in absolute methanol in the presence of sodium methoxide. An α-phenyl-substituted tetramethylidynemerocyanine dye (IX) was obtained by the reaction of VIa with 2-methyl-3-ethylbenzothiazolium tosylate in absolute methanol in the presence of triethylamine. In addition to IX, we isolated, as an impurity, a product with mp 183° and λ_{max} 668 nm, which corresponds to a β-phenyl-substituted thiadicarbocyanine dye (compare this with IIIa).

A β-phenyl-substituted tetramethylidynehemicyanine dye (X) was obtained in the reaction of salt I (Z_1 = 3-ethylbenzothiazolium) with aniline in alcohol.

EXPERIMENTAL

3,3'-Diethyl-9-phenylthiadicarbocyanine Iodide (IIIa). A mixture of 0.23 g (0.5 mmole) of 2-(δ-ethoxy-β-phenylbutadienyl)-3-ethylbenzothiazolium iodide, 0.15 g (0.5 mmole) of 2-methyl-3-ethylbenzothiazolium iodide, 4 ml of absolute ethanol, and 0.3 ml of triethylamine was refluxed for 15 min, and the resulting crystals were removed by filtration and washed with alcohol to give 0.24 g (80%) of a product with mp 183° (from ethanol) and λ_{max} 668 nm (mp 184-185°, λ_{max} 667 nm [5]).

3,3'-Diethyl-4',5',9-triphenylthiathiazolodicarbocyanine Perchlorate (IIIb). A mixture of 0.23 g (0.5 mmole) of 2-(δ-ethoxy-β-phenylbutadienyl)-3-ethylbenzothiazolium iodide, 0.27 g (0.5 mmole) of 2-methyl-3-ethyl-4,5-diphenylthiazolium iodide, 3 ml of chloroform, and 0.4 ml of triethylamine was held at room temperature for 3 h. The dye was precipitated by the addition of ether and converted to 0.3 g of the perchlorate (Table 1). Compounds IIIc-j (Table 1) were similarly obtained.

3-Ethyl-5-(α-phenyl-γ-ethoxyallylidene)rhodanine (VIa). A. A mixture of 0.23 g (0.5 mmole) of 2-(δ-ethoxy-β-phenylbutadienyl)-3-ethylbenzothiazolium iodide, 0.08 g (0.5 mmole) of 3-ethylrhodanine, 4 ml of absolute ethanol, and 0.16 ml of triethylamine was refluxed for 1 min. The crystals were removed by filtration and washed with alcohol, and dissolved in benzene. The benzene solution was chromatographed on aluminum oxide to give 0.13 g of product (Table 2). The other VI were similarly obtained (Table 2).

B. A mixture of 0.3 g (2 mmole) of 3-ethylrhodanine, 0.6 g (2 mmole) of benzoylacetaldehyde tetraethylacetal (VII), and 5 ml of acetic anhydride was heated at 130° for 4 h. The acetic anhydride was removed by vacuum distillation, and alcohol was added to the residue. The crystals were removed by filtration and washed with alcohol to give 0.44 g (71%) of a product that was identical to that described above in method A.

1-Phenyl-3-methyl-4-(3'-ethyl-2'-benzothiazolinylidene-2'-phenylbutenylidene)-5-pyrazolone (VIIIa). A mixture of 0.46 g (1 mmole) of 2-(δ-ethoxy-β-phenylbutadienyl)-3-ethylbenzothiazolium iodide, 0.17 g (1 mmole) of 3-methyl-1-phenyl-5-pyrazolone, 4 ml of absolute ethanol, and 0.32 ml of triethylamine was held at room temperature, and the resulting crystals were removed by filtration and washed with alcohol to give 0.18 g of product (Table 3). The other VIII were similarly obtained (Table 3).

3-Ethyl-5-(3'-ethyl-2'-benzothiazolinylidene-γ-phenylbutenylidene)thiazolidine-2-thion-4-one (Va). A mixture of 0.23 g (0.5 mmole) of 2-(δ-ethoxy-β-phenylbutadienyl)-3-ethylbenzothiazolium iodide, 0.08 g (0.5 mmole) of 3-ethylrhodanine, 2 ml of absolute methanol, and 0.3 g of sodium methoxide was refluxed for 1 h, and the resulting crystals were removed by filtration and washed with alcohol to give 0.15 g (65%) of blue needles with mp 182° (from ethanol) and λ_{max} 630 nm (log ε 4.89). Found: N 6.3%. $C_{24}H_{22}N_2OS_3$. Calculated: N 6.2%.

3-Ethyl-5-(3'-ethyl-4',5'-diphenyl-2'-thiazolinylidene-γ-phenylbutenylidene)thiazolidine-2-thion-4-one (Vb). This compound was similarly obtained in 50% yield as blue plates with mp 211° (from ethanol) and λ_{max} 660 nm (log ε 5.21). Found: N 4.9%. $C_{38}H_{28}N_2OS_2$. Calculated: N 5%.

3-Ethyl-5-(1'-ethyl-2'-dihydroquinolinylidene-γ-phenylbutenylidene)thiazolidine-2-thion-4-one (Vc). This compound was similarly obtained in 59% yield as blue needles with mp 193° (from ethanol) and λ_{max} 640 and 690 nm (log ε 4.57 and 4.89). Found: N 6.2%. $C_{26}H_{24}N_2OS_2$. Calculated: N 6.3%.

3-Ethyl-5-(3'-ethyl-2'-benzothiazolinylidene-α-phenylbutenylidene)thiazolidine-2-thion-4-one (IX). A mixture of 0.18 g (0.5 mmole) of 2-methyl-3-ethylbenzothiazolium tosylate, 0.16 g (0.5 mmole) of VIa, 3 ml of absolute methanol, and 0.2 ml of triethylamine was refluxed for 1 h. The methanol was removed by distillation, and the residue was dissolved in benzene. The benzene solution was filtered to remove the undissolved solids, and the filtrate was chromatographed on aluminum oxide to give 0.17 g (68%) of IX as blue prisms with mp 197° (from alcohol) and λ_{max} 630 nm (log ε 5.1). Found: N 6.3%. $C_{24}H_{22}N_2OS_3$. Calculated: N 6.2%. The insoluble residue was crystallized from alcohol to give 0.05 g (16%) of a substance with mp 183° and λ_{max} 668 nm (log ε 5.40), which were in agreement with the physical constants obtained for IIIa.

2-(δ-Anilino-β-phenylbutadienyl)-3-ethylbenzothiazolium Perchlorate (X). A 0.23-g (0.5 mmole) sample of 2-(δ-ethoxy-β-phenylbutadienyl)-3-ethylbenzothiazolium iodide was dissolved by warming in 5 ml of absolute ethanol, 0.4 ml of aniline was added, and the mixture was refluxed for 2 h. The dye was precipitated by the addition of ether and converted to 0.15 g (62%) of the perchlorate as red prisms with mp 209-210° (from ethanol) and λ_{max} 534 nm (log ε 4.84) (in chloroform). Found: N 5.8%. $C_{25}H_{23}ClN_2O_4S$. Calculated: N 5.8%.

The IR spectra of KBr pellets of the crystalline samples were recorded with a UR-10 spectrophotometer. The electronic spectra of 10^{-4} -$5 \cdot 10^{-5}$ M ethanol solutions were recorded with an SF-10 spectrophotometer.

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