SYNTHESIS OF TETRACARBOCYANINES BY THE SCISSION OF THE PYRYLIUM RING OF BENZOPYRYLOCYANINES

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Khimiya Geterotsiklicheskikh Soedinenii, Vol. 4, No. 3, pp. 459–462, 1968

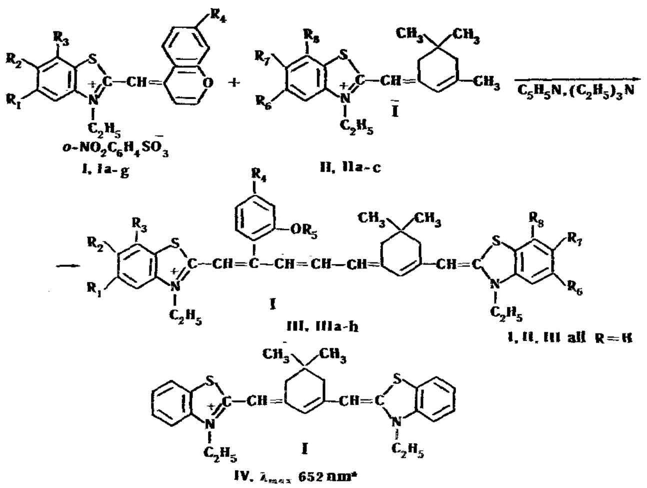
UDC 547.789.6'814.07:543.422.4

It has been shown that the reaction of monomethinecyanines containing 4-benzopyrylium residues with quaternary salts of derivatives of 2-[(1',5',5'-trimethylcyclohex-1'-en-3'-ylidene)-methyl]benzothiazole leads to the scission of the pyrylium ring and the addition of the quaternary salt to the position of scission. The reaction gives tetracarbocyanines containing an o-hydroxyphenyl or an o-acetoxyphenyl substituent in the polymethine chain in addition to a hydrocarbon ring.

Previously, one of us has described a reaction between unsymmetrical benzopyrylomonomethinecyanines of type I and compounds with active methyl or methylene groups [1, 2]. It was shown that if quaternary salts of 2-methyl-substituted nitrogen heterocycles were used as the nucleophilic components in this reaction, dicarbocyanines containing o-hydroxyphenyl groups as substituents in the polymethine chain were obtained [1]. The reaction of I with cyclic ketomethylene compounds forms tetramethinemerocyanines and the reaction with propenyl derivatives of quaternary salts of nitrogen heterocycle tricarbocyanines [2]. It appeared of interest to study the applicability of this reaction for the synthesis of dyes with longer polymethine chains, in partiuclar tetracarbocyanines. This deserved attention because dyes of this type are photosensitizers for photo emulsions in the IR region of the spectrum [3] and methods for their synthesis are inadequately developed.

In the present work we studied the reaction of monomethinecyanines of the type of I with quaternary salts of 2-[(1',5',5'-trimethylcyclohex-1'-en-3'-ylidene)methyl]benzothiazole of type II. As a result of the reaction, during which the pyrylium ring opened, thiatetracarbocyanines were formed with hydrocarbon residues and o-hydroxyphenyl substituents in the chromophore (III). The reaction took place when the reactants were heated briefly in the water bath in pyridine in the presence of an equimolecular amount of triethylamine. With an excess of triethylamine, in addition to the tetracarbocyanine, the dicarbocyanine IV was formed in considerable amount. In the performance of the reaction, the mixture had to be protected from sunlight, since the dyes formed are unstable to light. The reaction is best carried out in the presence of a small excess of acetic anhydride. In this case, the phenolic hydroxyl of the dye is acetylated, which is shown by the presence in the IR spectra of the compounds formed of a band characteristic for the carbonyl group (at 1760 cm^{-1}).

In the present work, in addition to I [4], the monomethinecyanines Ia–g given in Table 1 were synthesized by the condensation of 4-methoxybenzopyrylium salts with substituted 3-ethyl-2-methylbenzothiazolines. All these compounds dissolve in ethanol with an orange coloration.



Starting from these dyes and the quaternary salt II, and also its 5-methoxy (IIa), 6-methyl (IIb), and 6,7-tetramethylene (IIc) derivatives, the thiatetracarbocyanines (III, IIIa–h) (Table 2) have been synthesized by the scheme given above. It is interesting to note that the absorption maximum of the tetracarbocyanine III is displaced 25 nm to the long-wave region in comparison with the absorption maximum of the analogous tetracarbocyanine not containing an o-hy-

Table 1

Absorption Maxima of the Monomethinecyanines Ia–g

Compound	R$_1$	R$_2$	R$_3$	R$_4$	λ_{max}, nm
Ia	OCH$_3$	H	H	H	
Ib	H	CH$_3$	H	H	457
Ic	H	—CH$_2$—CH$_2$—CH$_2$—CH$_2$—		H	462
Id	H	H	H	CH$_3$	458
Ie	H	H	H	OCH$_3$	462
If	OCH$_3$	H	H	OCH$_3$	473
Ig	H	CH$_3$	H	CH$_3$	458

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*Here, and subsequently, the values of λ_{max} are given for alcohol solutions.

Table 2

The Tetracarbocyanines III, IIIa–h

Compound	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8	λ_{max}, nm
III	H	H	H	H	H	H	H	H	895
IIIa	H	H	H	H	H	OCH_3	H	H	905
IIIb	H	H	H	H	$COCH_3$	H	H	H	895
IIIc	OCH_3	H	H	H	$COCH_3$	H	H	H	904
IIId	OCH_3	H	H	H	$COCH_3$	OCH_3	H	H	912
IIIe	H	CH_3	H	H	$COCH_3$	H	CH_3	H	898
IIIf	H	$-CH_2-CH_2-CH_2-CH_2-$		H	$COCH_3$	H	$-CH_2-CH_2-CH_2-CH_2-$		906
IIIg	H	H	H	CH_3	$COCH_3$	H	H	H	898
IIIh	H	CH_3	H	CH_3	$COCH_3$	H	CH_3	H	906

Table 3

Monomethinecyanines Ia–g

Compound	Decomp. p., °C	Empirical formula	S, % found	S, % calculated	Yield, %
Ia	232	$C_{26}H_{22}N_2O_7S_2$	11.86, 11.80	11.90	32
Ib	241	$C_{26}H_{22}N_2O_6S_2$	12.40, 12.25	12.26	37
Ic	261	$C_{29}H_{26}N_2O_6S_2$	11.30, 11.31	11.21	45
Id	240	$C_{26}H_{22}N_2O_6S_2$	11.94, 12.07	12.26	46
Ie	213	$C_{26}H_{22}N_2O_7S_2$	11.63, 11.57	11.90	22
If	238	$C_{27}H_{24}N_2O_8S_2$	11.42, 11.38	11.27	30
Ig	262	$C_{27}H_{24}N_2O_6S_2$	11.72, 11.70	11.94	22

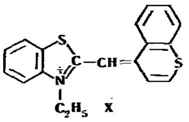
Table 4

Thiatetracarbocyanines IIIa–h

Compound	Decomp. p., °C	Empirical formula	Found, %	Calculated, %	Yield, %
IIIa	190	$C_{32}H_{41}IN_2O_2S_2$	S 8.46; 8.50	S 8.42	26
IIIb	188	$C_{40}H_{41}IN_2O_2S_2$	S 8.45; 8.61	S 8.29	20
IIIc	192	$C_{42}H_{45}IN_2O_4S_2$	S 8.00; 8.07 I 15.65; 15.69	S 7.98 I 15.84	16
IIId	190	$C_{42}H_{45}IN_2O_4S_2$	S 7.99; 8.01	S 7.69	24
IIIe	188	$C_{42}H_{45}IN_2O_2S_2$	S 7.84; 7.70	S 8.00	22
IIIf	194	$C_{48}H_{53}IN_2O_2S_2$	S 7.21; 7.24	S 7.27	34
IIIg	192	$C_{41}H_{43}IN_2O_2S_2$	S 7.98; 8.07	S 8.14	25
IIIh	197	$C_{43}H_{47}IN_2O_2S_2$	S 7.72; 7.69	S 7.86	27

droxyphenyl substituent in the chromophore, while this group in the meso position of a thiacarbocyanine does not affect its coloration [5] and in position 9 of a thiadicarbocyanine shifts the absorption maximum in the long-wave direction by only 14 nm [1].

It was noted previously that benzothiapyrylomonomethinecyanines (for example, V) react with a greater difficulty than their oxygen analogs with compounds having active methyl groups. The monomethinecyanine V does not react at all with compounds of type II under the conditions given above. The lower electron affinity of V as compared with I was difficult to predict beforehand.



V

EXPERIMENTAL

The monomethinecyanines (Ia-g) were obtained by the following procedure. The derivatives of 3-ethyl-2-methylenebenzothiazoline were obtained by the general method [6], i.e., by the treatment with caustic soda of the corresponding quaternary salt in aqueous acetone. The product obtained by the dilution of the filtrate with water was washed with ice water. They were white amorphous substances.

A solution of 0.01 mole of the corresponding 3-ethyl-2-methylenebenzothiazole in 3 ml of glacial acetic acid was added to a solution of 0.012 mole of 4-methoxybenzopyrylium o-nitrobenzene sulfonate [7], or its 7-methyl or 7-methoxy derivative (the latter were obtained by the addition of methyl o-nitrobenzenesulfonate to, respectively, 7-methyl- and 7-methoxychromones [8]) in 15 ml of acetic anhydride. The mixture was heated at 100° C for 1 hr, and the product that precipitated on cooling was filtered off and crystallized. If the dye did not precipitate, the mixture was diluted with ether, and the product was triturated with 15 ml of ethanol and filtered. Table 3 gives the yields, decomposition points, and analytical results for the monomethinecyanides Ia-g. Compound Ic was crystallized from glacial acetic acid, Ia and Ig from a mixture of ethanol and nitromethane, and the other substances from ethanol.

2-[(1',5',5'-Trimethylcyclohex-1'-en-3'-ylidene)methyl]-6,7-tetramethylenebenzothiazole IIc) was obtained in a similar manner to II [9]. A mixture of 10 g (0.025 mole) of the ethyl tosylate of 2-methyl-6,7-tetramethylenebenzothiazole and 6.9 g (0.05 mole) of isophorone was heated at 150—155° C for 17 hr. The reaction mixture was poured into 220 ml of water and extracted with ether (3 x 200 ml). To the aqueous solution was added a solution of 8 g of potassium iodide in 15 ml of water. After standing for 3 hr at 0° C, the precipitate was filtered off, washed with 10 ml of ice water, and crystallized from methanol. Yield 2.7 g (23%), decomp. p. 230—231° C. Found, %: S 6.49, 6.52. Calculated for $C_{23}H_{30}INS$, %: S 6.68.

2-[(1',5',5'-Trimethylcyclohex-1'-en-3'-ylidene)methyl]-5-methoxybenzothiazole ethiodide (IIa) and 2-[(1',5',5'-trimethylcyclohex-1'-en-3'-ylidene)methyl]-6-methylbenzothiazole ethiodide (IIb) were obtained by heating the ethyl tosylates of the corresponding 5-methoxy- and 6-methylbenzothiazoles with isophorone at 135—140° C for 16 hr. The products were isolated in a similar manner to IIc. The yield of IIa was 20%, decomp. p. 231—232° C. The yield of IIb was 16%, decomp. p. 229—230° C. For IIa, found, %: S 6.91, 6.87. Calculated for $C_{20}H_{26}INOS$; %: S 7.03.

3,3'-Diethyl-9,11-(β, β-dimethyltrimethylene)-15-(o-hydroxyphenyl)thiatetracarbocyanine iodide (III). A mixture of 0.508 g of I 0.425 g of II, 0.1 g of triethylamine, and 10 ml of pyridine was heated at 100° C for 5 min. The cooled solution was poured into a mixture of 50 ml of ice water and 50 ml of ether. The solution was decanted off and the viscous oil that had separated was repeatedly washed with ether and water. The solidifying substance was filtered off, washed on the sintered glass filter with 5 ml of cold ethanol, and dissolved in 50 ml of methanol heated to the boil. The solution was filtered, the filtrate was treated with a methanolic solution of potassium iodide, and the mixture was cooled in ice. The dye was filtered off and was washed with methanol, water, methanol, and ether. Green microcrystalline product with a metallic luster. Yield 0.4 g (52%), decomp. p. 196° C. Found, %: S 8.33, 8.43. Calculated for $C_{38}H_{39}IN_2OS_2$, %: S 8.77.

The other thiatetracarbocyanines were synthesized analogously, except that in the preparation of IIIb—h 0.15 ml of acetic anhydride was added to the mixture (see Table 4).

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3 May 1966

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