I-V and 3 mmole of triethylsilane. At the end of the reaction the precipitated crystals of thiacyclohexanes VI-X were separated (see Table 1).

Reaction of Thiopyran I with Perchloric Acid and Triethylsilane. A 0.65-g (5.6 mmole) sample of triethylsilane and 0.5 ml (8.4 mmole) of $HClO_4$ were added successively to a suspension of 0.5 g (1.4 mmole) of thiopyran I in 15 ml of glacial acetic acid. At the end of the reaction (as monitored by thin-layer chromatography on Silufol) the precipitated crystals of the known thiacyclohexane VI were separated. The product, with mp 116-117°C (from ethanol) [1], was obtained in 78% yield.

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CONDENSED HETEROCYCLES WITH A THIAZOLE RING.

4.* THIAZOLO[3',4':1,2]PYRIMIDO[6,5-b]QUINOLINES

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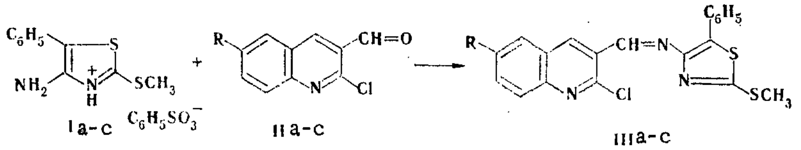
UDC 547.837.2'789.5.6.67.07:543.422

Derivatives of a new heterocyclic system that are suitable for the synthesis of dyes were obtained by condensation of 4-amino-2-methylthiazolium salts with 2-chloro-3-formylquinolines.

In an investigation of the possibility of the use of condensed heterocycles with a thiazole ring in the synthesis of dyes we studied the reaction of 4-amino-2-methylthio-5-phenylthiazoliumbenzenesulfonate (I) with 2-chloro-3-formylquinolines IIa-c.

We found that condensation products IIIa-c are readily formed when this reaction is carried out in acetic acid or dimethylformamide (DMF) at room temperature:



Absorption bands of N-H and C=O bonds at 3200-3400 and 1610-1750 cm^{-1} are absent in the IR spectra of the condensation products; thus the reaction leads to condensation rather than hetarylation of I, in which 2-methylthio-5-phenyl-4-(6-R-3-formyl-2-quinolyl)aminothiazole hydrochlorides (IV) or 4-amino-2-methylthio-5-phenyl-3-(6-R-3-formyl-2-quinolyl)thiazolium chlorides (V), which have similar elementary analysis data, might have been formed. The synthesized III do not form the corresponding monomethylidynecyanine and nullomethylidynemerocyanine dyes upon condensation with 2-methyl-3-ethylbenzothiazolium tosylate, and this constitutes evidence in favor of a structure of the III type for the condensation products, since it is known that quaternary salts of 4-amino-2-methylthio-5-phenylthiazole [2] and 2-methylthio-3-hetarylthiazolium salts [3] react under the same conditions. It should be noted that

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*See [1] for Communication 3.

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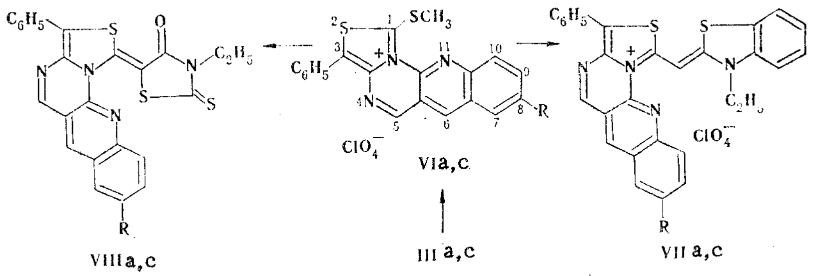
TABLE 1. PMR Spectra of Salts VIa-c

Compound	R	Chemical shift, ppm				
		R	S—CH₃	Ar—H	6-H	5-H
VIa	H	—	2,63	7,0—8,0	8,63	8,77
VIb	CH_3	2,20	2,63	7,0—7,8	8,55	8,75
VIc	OCH_3	3,66	2,63	7,0—7,5	8,50	8,75

azomethines IIIa-c, despite the presence of an equimolar amount of benzenesulfonic acid in the solution, are isolated in the base form.



New compounds VIa-c, the structure of which is also confirmed by the results of elementary analysis and data from the PMR spectra (Table 1), are formed when IIIa-c are heated in acetic acid (at 90-110°C) when the condensation of salt I with 2-chloro-3-formylquinolines IIa-c is carried out under these conditions.

The resulting derivatives of a new heterocyclic system undergo cyanine condensation in the usual way to give dyes (VIIa,c and VIIIa, c for example). The synthesized dyes are 20 and 50 nm more highly colored, respectively, than the analogous thiazolo[3,4-a]pyrimidine derivatives [1, 4]. Only one band is observed in the visible part of the absorption spectra of solutions of dyes of the VII type, whereas a second band also appears in the spectra of nullomethylidynemerocyanines VIII in the form of an inflection on the long-wave slope, and two bands of comparable intensity are observed in the case of the corresponding thiazolopyrimidine derivatives. These regularities can evidently be explained by a decrease in the effective length in the dyes [5] of the thiazolopyrimidoquinoline ring as compared with the effective length of the thiazolopyrimidine ring due to a decrease in the participation of the heteroring π electrons in conjugation with the chromophore as a result of annelation of a quinoline ring with it.

EXPERIMENTAL

The IR spectra of the compounds (in KBr pellets) were obtained with a UR-10 spectrometer. The electronic spectra of solutions of the compounds in DMF were recorded with SF-8 and SF-10 spectrophotometers. The PMR spectra of solutions of CF_3COOH were obtained with a Tesla BS-467 spectrometer (60 MHz) with hexamethyldisiloxane as the internal standard. Data on the properties of the synthesized compounds are presented in Table 2.

2-Methylthio-5-phenyl-4-(6-R-2-chloroquinolyl-3-methylene)aminothiazoles (IIIa-c). A 1-mmole sample of the corresponding chloroformylquinoline IIa-c was added to a solution of 0.38 g (1 mmole) of benzenesulfonate I in 3 ml of acetic acid, and the mixture was allowed to stand at 15-25°C for 30 min. The resulting precipitate was removed by filtration and washed with alcohol.

8-R-1-Methylthio-3-phenylthiazolo[3',4':1,2]pyrimido[6,5-b]quinolinium Perchlorates (VIa-c). A) A 1-mmole sample of the corresponding azomethine IIIa-c was dissolved in 3 ml of acetic acid by heating to 90-110°C, after which the solution was heated for 1 h. A solution of perchloric acid or sodium perchlorate was then added, and the mixture was cooled. The reaction product was removed by filtration and crystallized.

B) A mixture of 0.38 g (1 mmole) of salt I, 1 mmole of the corresponding quinoline II, and 3 ml of acetic acid was heated at 90-110°C for 1 h, after which perchloric acid or sodium perchlorate was added. The reaction product was removed by filtration and crystallized.

TABLE 2. Properties of the Synthesized Compounds

Compound	mp,* °C	λ_{max}, nm (lg ε)	Found, %		Empirical formula	Calc., %		Yield, %
			Cl(N)	S		Cl(N)	S	
IIIa	295—296	305 (3,37), 400 (3,06)	(10,4)	16,3	$C_{20}H_{14}ClN_3S_2$	(10,6)	16,1	64
IIIb	281—282	305 (3,44), 400 (3,10)	8,8	15,2	$C_{21}H_{16}ClN_3S_2$	8,6	15,6	75
IIIc	283—285	305 (3,42), 400 (3,12)	8,2	15,0	$C_{21}H_{16}ClN_3OS_2$	8,3	15,0	50
VIa	273—275		7,8	14,0	$C_{20}H_{14}ClN_3O_4S_2$	7,7	13,9	65
VIb	276—277		7,4	13,7	$C_{21}H_{16}ClN_3O_4S_2$	7,6	13,5	53
VIc	268—269		7,1	12,6	$C_{21}H_{16}ClN_3O_5S_2$	7,2	13,1	57
VIIa	256—259	514 (3,62)	6,4	10,8	$C_{29}H_{21}ClN_4O_4S_2$	6,2	11,2	87
VIIc	265—267	514 (3,57)	5,7	10,2	$C_{30}H_{23}ClN_4O_5S_2$	5,7	10,3	67
VIIIa	303—305	498 (3,39)	(12,0)	20,3	$C_{24}H_{16}N_4OS_3$	(11,9)	20,3	92
VIIIc	313—315	496 (3,40)	(11,5)	19,1	$C_{25}H_{18}N_4O_2S_3$	(11,2)	19,1	80

*Compounds VI, VII, and VIII were crystallized from alcohol—DMF.

8-R-3-Phenyl-1-[(3-ethylbenzothiazolin-2-ylidenes)methyl]thiazolo[3,4':1,2]pyrimido[6,5-b]quinolinium Perchlorates (VIIa, c). A mixture of 0.35 g (1 mmole) of 2-methyl-3-ethylbenzothiazolium tosylate, 1 mmole of the corresponding perchlorate VI, 10 ml of absolute alcohol, and 2 ml of DMF was heated until the components had dissolved, after which 0.1 g (1 mmole) of triethylamine was added, and the precipitated dye was removed by filtration and crystallized.

2-Thioxo-3-ethyl-5-(1H-8-R-3-phenylthiazolo[3',4':1,2]pyrimido[6, 5-b]quinol-1-ylidene)-thiazolidin-4-one (VIIIa, c). A mixture of 0.16 g (1 mmole) of 3-ethylrhodanine, 1 mmole of the corresponding perchlorate VI, and 10 ml of absolute alcohol was heated to the boiling point, and 0.1 g (1 mmole) of triethylamine was added. The precipitated dye was removed by filtration and crystallized.

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THERMOLYSIS AND MASS SPECTROMETRY OF meso-SUBSTITUTED THIACARBOCYANINES

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The pathways of fragmentation of thiacarbocyanine dyes with various electron-donor substituents in the meso position of the polymethine chain under the influence of high temperatures and electron impact were investigated. The results of thermolysis of the dyes are compared with the results of quantum-chemical calculations of the labilities of the bonds in the molecules.

We have previously shown [1] by means of gas-chromatographic analysis of the volatile products of the pyrolysis of 3,3'-dialkylthiacarbocyanine halides that in the molecules of these dyes processes involving thermal heterolytic dissociation of the C—C bonds of the external polymethine chain may compete with dealkylation. It seemed of interest to ascertain what effect substituents in the 9 position of the polymethine chain have on the character of the thermal fragmentation of thiacarbocyanines. In this connection, in the present research we investigated the pathways of the thermal transformations of meso-substituted thiacarbocyanine

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