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REACTION OF 3-FORMYLCHROMONE WITH METHYL- AND METHYLENE-ACTIVE AZOCYCLES

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The reaction of 3-formylchromone with quaternary salts of nitrogen heterocycles containing active methyl or methylene groups was investigated. It is shown that the compounds obtained can be used in the synthesis of merocyanine dyes containing an o-hydroxybenzoyl substituent in the polymethine chain. Dicarbocyanines with such a substituent were not isolated, evidently because of the high electrophilicity of the polymethine chain and the ease of formation of a six-membered heteroring.

Aldehydes of the heterocyclic series are used in syntheses of polymethine dyes, where the polymethine chain is constructed through –CH= groups of a heteroring that is cleaved during the reaction [1-3]. Considering that the methods for the synthesis of meso-substituted dicarbocyanines – effective sensitizers [2] – have undergone little development, it seemed of interest to use 3-formylchromone for this purpose. Reactions involving the condensation or recyclization of this compound on reaction with nucleophilic agents, primarily with ketomethylene compounds, are known [4, 5]. The reaction of 3-formylchromone with quaternary salts of nitrogen heterocycles containing active methyl groups has not been described. 3-Formylchromone can be regarded as the cyclic ether of the enol form of a substituted malonaldehyde and, like the latter, it can therefore be used to construct the polymethine chain of meso-substituted dicarbocyanines and tetramethinemerocyanines. The fact that unsubstituted chromone itself reacts in the presence of bases with quaternary salts of nitrogen heterocycles with opening of the pyrone ring [6] also served as a basis for this assumption.

The condensation of 3-formylchromone with 2,3-dimethylbenzothiazolium and 1,2,3,3-tetramethylindolium salts and with N-ethyl-2-thioxo-4-thiazolidinone in acetic anhydride or in absolute alcohol in the presence of sodium acetate leads to the formation of II-V (see scheme on following page).

The IR spectra of these compounds do not contain a band of stretching vibrations of a formyl group (1700 cm^{-1}), but the frequency of the carbonyl group of the chromone ring (1650-1670 cm^{-1}) is retained (Table 1).

One might have expected that the $C_{(2)}$ atom and the carbon atom of the formyl group in the 3-formylchromone molecule would display increased reactivities. Calculations within the Hückel MO approximation, which correctly reflect the dependence of the distribution of the π-electron density on the topology of the conjugated system, show that relatively large posi-

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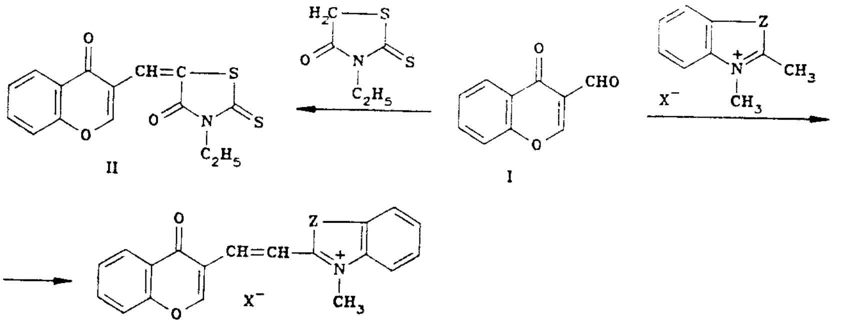

III Z=S, X=CH_3SO_4; IV Z=S, X=I; V Z=C$(CH_3)_2$, X=I

tive π charges are concentrated precisely on these atoms (Fig. 1a). On the basis of this one might assume that II-V are formed either by direct condensation at the formyl group or via the addition of the nucleophilic reagent at the $C_{(2)}$ atom of the pyrone ring with subsequent recyclization of the resulting adduct. The possibility of the latter mechanism was demonstrated in the case of reactions of 3-benzoylchromone with some cyclic ketomethylene compounds, as a result of which the corresponding 3-substituted flavones were obtained [7].

Significant positive charge is concentrated in the 2 position of the chromone ring in the product of condensation of 3-formylchromone with a quaternary salt of 2-methylbenzothiazole (Fig. 1b), i.e., III-V should also be active with respect to nucleophiles. In fact, VI-IX are formed in the reaction of salts III and V with alcohol, dimethylamine, or 2,3-dimethylbenzothiazolium methylmetasulfate in acetonitrile in the presence of triethylamine.

A singlet of an H_c proton (6.26 and 5.91 ppm, respectively), as well as a doublet of one of the two methylidyne protons at 5.73 and 5.71 ppm, respectively, are observed in the PMR spectra of VI and VII. The doublet of the second proton evidently lies in the region of the complex multiplet of aromatic protons (6.8-8.0 ppm) (Table 1). The structures of VI-VIII are also confirmed by the electronic spectra, in which a virtually identical band, which is independent of fragment B, is observed (Table 1). It is natural to assume that fragment A, which is not conjugated with substituent B, is responsible for this absorption. The chromophore system of this part of the molecule is identical to that contained in XI, obtained by the reaction of chromone with a benzothiazolium salt [6]. In fact, the absorption maxima of the long-wave bands of XI and VI-VIII and the absorption maxima of IX and the product of the reaction of chromone with a 1,2,3,3-tetramethylindolium salt (476 nm in C_2H_5OH) are close (Table 1) [6].

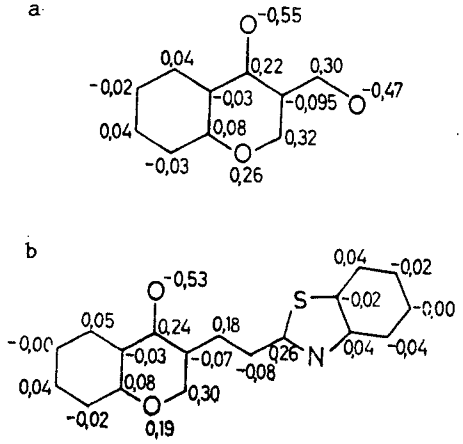

Fig. 1. π-Electron charges calculated within the Hückel MO approximation in: a) 3-formylchromone; b) 3-methyl-2-[(3-chromonyl)ethylidene]benzothiazolium methylmetasulfate.

TABLE 1. Characteristics of the Synthesized Compounds

Compound	Empirical formula	mp, °C (solvent)	IR spectrum, cm^{-1}			PMR spectrum, δ, ppm	UV spectrum, λ_{max} nm ($\varepsilon \cdot 10^{-4}$)	Yield, %
			C=O	C—O, C=C, C=N	C—N			
II	$C_{15}H_{11}NO_3S_2$	214...215 (benzene)	1700*, 1670	1630, 1600	1330	—	380 (2,8)	95
III	$C_{20}H_{17}NO_6S_2$	247 (absolute alcohol)	1650	1610, 1580	1300	—	375 (3,0)	93
IV	$C_{19}H_{14}INO_2S$	241 (CH_3NO_2)	1650	1620, 1580	1310	—	380 (2,9)	84
V	$C_{22}H_{20}INO_2$	235...238 (CH_3NO_2)	1670	1610, 1580	1300	—	390 (3,1)	78
VI	$C_{21}H_{19}NO_3S$	170...172 (ethanol)	1660	1610, 1590	1310	1,18 (3H, t, CH_3); 3,88 (2H, q, —CH_2—); 3,55 (3H, s, NCH_3); 5,73 (1H, d., H_a); 6,26 (1H, s, H_c); 7,0...8,0 (9H, arom and H_b, m.)	490 (3,0)	89
VII	$C_{21}H_{20}N_2O_2S$	169...171 (CH_3CN)	1630	1610, 1590	1320	2,38 [6H, s, $N(CH_3)_2$]; 3,50 (3H, s., NCH_3); 5,71 (1H, d., H_a); 5,91 (1H, s, H_c); 6,7...8,0 (9H, arom and H_b, m)	490 (5,0)	75
VIII	$C_{28}H_{22}N_2O_2S_2$	201...203	1630	1600, 1570	1320	—	492 (5,0)	79
IX	$C_{24}H_{25}NO_3$	130...132 (CH_3OH)	1660	1610, 1580	1330	1,11 (3H, t, CH_3); 1,55 and 1,59 [6H, two s $C(CH_3)_2$]; 3,26 (3H, s, NCH_3); 3,80 (2H, q, —CH_2—); 5,53 and 8,15 (2H, two d H_a & H_b); 6,5...7,8 (8H, arom and); 6,26 (1H, s. H_c)	466 (5,7)	74
XII	$C_{24}H_{20}N_2O_3S_3$	208...210 (pyridine)				—	580 (7,3)	58

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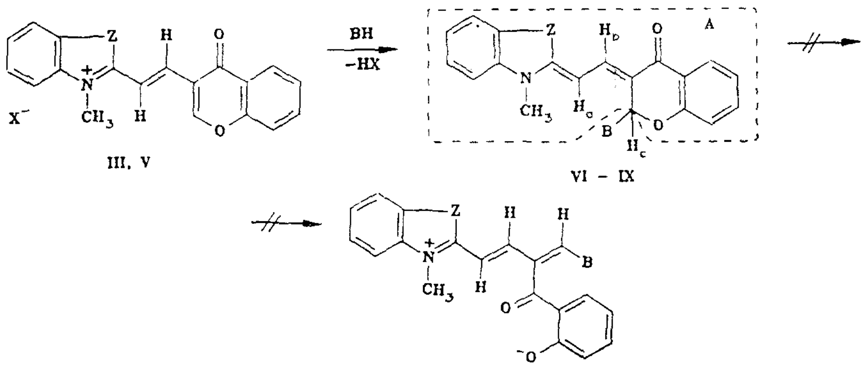
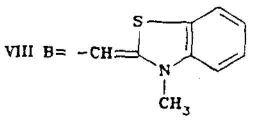
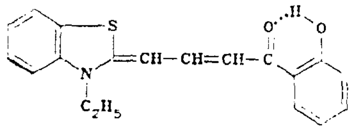
*The $\nu_{C=O}$ frequency of the rhodanine component.



VI, IX B=OC$_2$H$_5$, VII B=N(CH$_3$)$_2$; VI—VIII Z=S, IX Z=C(CH$_3$)$_2$;



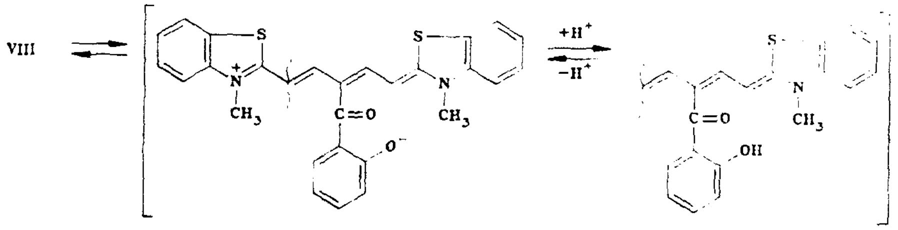
The addition of alcohols and amines to III and V is reversible, which is indicated by the development of the maximum at 380 nm that is characteristic for III when solutions of adducts VI and VII in acetonitrile are acidified. The usual protonation with the formation of the corresponding benzothiazolium dication [λ_{max} 470 nm (CH$_3$CN)] probably occurs when a solution of VIII is acidified.



XI

λ_{max} 503 nm (in C$_2$H$_5$OH)

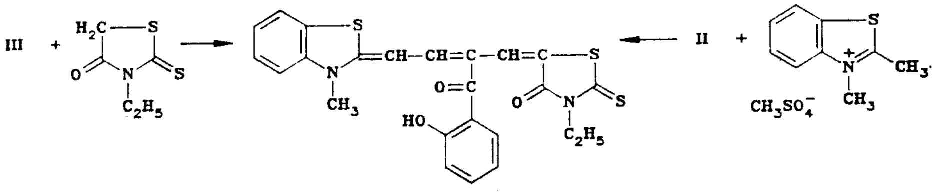
If the addition of a nucleophile to III and V were accompanied by opening of the pyran ring with the formation of betaines of the X type, they would have different electronic spectra, depending on the nucleophile. At the same time, in the case of VIII the existence of an equilibrium between cyclic and open-chain forms VIIIa, b is possible under certain conditions.



VIII a VIII b

Thus, in the reaction of methylmetasulfate III with a 2,3-dimethylbenzothiazolium salt in acetonitrile in the presence of 0.2 mole of triethylamine per mole of the salt the mixture takes on a persistent blue coloration with an absorption maximum at 634 nm that is evidently due to the formation in solution of dye VIIIb. An attempt to isolate the compound led to cyclic adduct VIII. The instability of polymethine compounds formed in the reaction of vinylogs of furfural with amines is also evidently due to the ease of formation of a six-membered ring [1].

According to theoretical concepts [8], the alternation of charges in the polymethine chain of unsymmetrical cyanine dyes is decreased. On the basis of this one should expect that merocyanine dye XII, the electrophilicity of the polymethine chain of which is decreased, would be the product of addition of ketomethylene compounds to 3-methyl-2-[(3-chromonyl)ethylidene]benzothiazolium methylmetasulfate (III).



XII

Bands that indicate the absence of the cyclic form are not observed in the absorption spectrum of this compound at 490-500 nm. The structure of tetramethinemerocyanine XII was confirmed by alternative synthesis: The dye obtained in the reaction of II with 2,3-dimethylbenzothiazolium methylmetasulfate has the same absorption maximum and does not depress the melting point of the compound obtained from benzothiazolium salt III.

EXPERIMENTAL

The PMR spectra were obtained with a Bruker WP-200 SY spectrometer (200 MHz) with tetramethylsilane (TMS) as the internal standard. The electronic spectra were recorded with an SF-20 spectrophotometer. The IR spectra were recorded with a UR-10 spectrometer (KBr).

The quantum-chemical calculations were carried out within the Hückel MO approximation with parameters for the atoms and bonds borrowed from [9].

The results of elementary analysis for C, H, N, S, and Hal were in agreement with the calculated values.

3-Ethyl-5-[(3-chromonyl)methine]thiazoline-2-thion-4-one (II). A mixture of 0.32 g (2 mmoles) of N-ethyl-2-thioxo-4-thiazolidinone, 0.35 g (2 mmoles) of 3-formylchromone, and 10 mg of anhydrous sodium acetate was heated to the boiling point for 10 min in 10 ml of absolute alcohol. The yellow precipitate that formed from the hot solution was removed by filtration and washed with absolute alcohol and ether.

3-Methyl-2-[(3-chromonyl)ethylidene]benzothiazolium Methylmetasulfate (III). A mixture of 0.55 g (2 mmoles) of 2,3-dimethylbenzothiazolium methylmetasulfate, 0.4 g (2.3 mmoles) of 3-formylchromone, and 0.03 g of anhydrous sodium acetate was refluxed in 5 ml of absolute alcohol for 10 min. The precipitate that separated after cooling was removed by filtration and washed with absolute alcohol.

3-Methyl-2-[(3-chromonyl)ethylidene]benzothiazolium Iodide (IV). A mixture of 0.29 g (1 mmole) of 2,3-dimethylbenzothiazolium iodide and 0.174 g (1 mmole) of 3-formylchromone was refluxed in 3 ml of acetic anhydride for 10 min. After cooling, the resulting precipitate was removed by filtration and washed with glacial acetic acid.

1,3,3-Trimethyl-2-[(3-chromonyl)ethylidene]indolium Iodide (V). This compound was similarly obtained from 1,2,3,3-tetramethyl-3H-indolium iodide and 3-formylchromone.

2,3-Dihydro-2-ethoxy-3-{2-[3-methyl-2(3H)-benzothiazolylidene]ethylidene}-4H-1-benzopyran-4-one (VI). An 0.1-ml sample of triethylamine was added to a hot solution of 0.215 g (0.5 mmole) of salt III in 10 ml of absolute alcohol, and the mixture was refluxed for 5 min. The precipitate that separated after cooling was removed by filtration and washed with alcohol.

2,3-Dihydro-2-dimethylamino-3-{2-[3-methyl-2(3H)-benzothiazolylidene]ethylidene}-4H-1-benzopyran-4-one (VII). This compound was similarly obtained from 0.5 mmole of salt III and 1 ml of a 15% solution of dimethylamine in benzene.

2,3-Dihydro-2-{[3-methyl-2(3H)-benzothiazolylidene]methylene}-3-{2-[3-methyl-2(3H)-benzothiazolidene]ethylidene}-4H-1-benzopyran-4-one (VIII). This compound was obtained in the same way as VI from 0.5 mmole of salt III and 0.5 mmole of 2,3-dimethylbenzothiazolium methylmetasulfate by heating for 20 min in 5 ml of acetonitrile.

2,3-Dihydro-2-ethoxy-3-[2-(1,3,3-trimethyl-1,2-dihydro-3H-indolinylidene)ethylidene]-4H-1-benzopyran-4-one (IX). An 0.1-ml sample of triethylamine was added to a hot solution of 0.23 g (0.5 mmole) of salt V in 10 ml of absolute alcohol, and the mixture was refluxed for 10 min. The solution was then evaporated in vacuo to a volume of 3 ml, and the residue was diluted with water. The resulting precipitate was removed by filtration and washed with water.

3-Ethyl-5-{2-(2-hydroxybenzoyl)-4-[3-methyl-2(3H)-benzothiazolylidene]buten-2-ylidene}thiazolidine-2-thion-4-one (XII). A. A 0.1-ml sample of ethyldicyclohexylamine was added to a mixture of 0.16 g (0.5 mmole) of II and 0.14 g (0.5 mmole) of 2,3-dimethylbenzothiazolium methylmetasulfate in 30 ml of acetonitrile, and the solution was heated to the boiling point. Pyridine (2 ml) was then added, and the mixtue was refluxed for 30 min. The resulting precipitate was removed by filtration and washed with acetonitrile.

B. A mixture of 0.215 g (0.5 mmole) of salt III and 0.08 g (0.5 mmole) of N-ethyl-2-thioxo-4-thiazolidinone was dissolved by heating in a mixture of 10 ml of acetonitrile and 1 ml of pyridine. The precipitate that formed after the addition of 0.1 ml of triethylamine was removed by filtration and washed with acetonitrile.

No melting-point depression was observed for a mixture of the products obtained by methods A and B.

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CONDENSED HETEROCYCLES WITH A THIAZOLE RING.
18.* PYRIDO(QUINOLINO)THIAZOLOPYRAZINES

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Derivatives of new condensed heterocyclic systems – pyrido- and quinolino[1',2':3,2]thiazolo[4,5-b]pyrazines – were synthesized by condensation of 2,3-dichloropyrazine with 2-mercaptopyridine and 2-mercaptoquinolines.

Derivatives of new heterocyclic systems – azino[1',2':3,2]thiazolo[4,5-b]quinoxalinium salts [2], which can be used in the synthesis of cyanine dyes – are formed in the condensation of 2,3-dichloroquinoxaline with 2-mercaptopyridine and 2-mercapto-4-R-quinolines. Since it was found that, as compared with known analogs [3], the absorption maxima in the electronic spectra of such dyes are shifted to the red part of the spectrum, it seemed of interest to make a more detailed study of the dependence of the color indices of the new type of cyanines on the structure of the terminal heteroresidue.

In order to obtain new condensed heterocyclic systems with a nodal nitrogen atom that contain a thiazolo azinium fragment, we studied the reaction of 2,3-dichloropyrazine with 2-mercaptopyridine and 2-mercapto-4-R-quinolines and observed that perchlorates I and IIa, b, respectively, are readily formed when the reaction is carried out in acetic acid (see scheme on following page).

Signals that are characteristic only for condensed heterocycles that contain a quaternary nitrogen atom are observed in the PMR spectra of these compounds. As expected, the signal of the proton in the 9 position shows up at weakest field in the spectrum of salt I (10 ppm, α-pyridinium proton). However, the signal of the proton in the 1 position is observed at even

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*See [1] for Communicaton 17.

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