height of 3 cm. The silica gel was washed with toluene and then with acetone. The tertiary alcohol (IVa) was concentrated in the acetone fraction. After the acetone had been distilled off, 0.35 g (8%) of (IVa) was obtained.

B. In portions, 8.24 g (0.045 mole) of anhydrous cadmium chloride and 60 ml of benzene were added to 14.49 g (0.09 mole) of butylmagnesium bromide in 80 ml of ether, and then the ether was distilled off and the mixture was boiled for 2 h. The resulting diethylcadmium was treated with 5 ml of acetone, and then 3.5 g (0.015 mole) of the acid chloride (I) in 50 ml of benzene was added dropwise. The resulting mixture was stirred at 22°C for 3 h 30 min. Then it was worked up by method A. The ketones obtained by method A and B did not differ according to their spectral characteristics and melting points.

<u>2-Alkylbenzo[b]thiophenes (VII)</u>. Dropwise 10.2 g (0.2 mole) of hydrazone hydrate was added to 0.049 mole of one of the ketones (IIIa and b) in 70 ml of diethyleneglycol, and the mixture was heated to 140°C over 1 h 30 min with the simultaneous elimination of water by distillation. After this, 5.6 g (0.1 mole) of potassium hydroxide was added and the mixture was heated to 180°C for 2 h and was then cooled to room temperature and treated with 300 ml of water. The resulting mixture was extracted three times with hexane, and the hexane was distilled off. The reaction product obtained was reduced with hydriodic acid as described previously [1] (see Table 1).

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MESOIONIC COMPOUNDS WITH A BRIDGE NITROGEN ATOM.

9.* IMIDAZO[1,2-c]THIAZOLES

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5-Methylthio-2-oxo-2,3-dihydro-1H-imidazo[1,2-c]thiazolium salts readily react with 3-ethylrhodanine, p-dimethylaminobenzaldehyde, and 3-ethyl-2-methylbenzothiazolium tosylate with the formation of polymethine dyes, including dyes with a mesoionic structure. Reaction with acetic anhydride has given acetyl-substituted imidazothiazolium 2-oxides.

New derivatives (Ia-c) of a little-studied heterocyclic system — imidazo[1,2-c]thiazole — have been synthesized previously [2]. It appeared of interest to investigate the chemical reactions of these compounds.



Ia $R=H, b R=CH_3, c R=C_6H_5$

^{*}For communication 8, see [1].

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| Com- | mp °C | Found, % | | | Propriet of formula | Calculated, % | | | Yield, |
|--|---|----------|--|--|--|---------------|--|--|--|
| | | Сі | N | s | | Cl | N | s | 70 |
| IIb IIc IIIa IIIb IIIc IVa IVb IVc VI VII VII VII IX | 300-302 290-291 230-231 230-232 218-220 301-303 297-300 246-247 231-233 215-216 202-203 | | $ \begin{array}{c} 10,9\\ 9,2\\ 10,5\\ 10,2\\ 9,0\\ 8,9\\ 8,2\\ 7,4\\ -\\ 10,3\\ 8,2\\ 7,4 \end{array} $ | $\begin{array}{c} 24,7\\21,3\\16,3\\15,8\\13,2\\-\\-\\13,1\\16,5\\18,6\\16,7\\\end{array}$ | $\begin{array}{c} C_{17}H_{18}N_3O_2S_3\\ C_{22}H_{17}N_3O_2S_3\\ C_{21}H_{17}N_3OS_2\\ C_{22}H_{19}N_3OS_2\\ C_{27}H_{21}N_3OS_2\\ C_{21}H_{18}CIN_3O_5S_2\\ C_{22}H_{20}CIN_3O_5S_2\\ C_{22}H_{22}CIN_3O_5S_2\\ C_{21}H_{22}CIN_3O_5S_2\\ C_{21}H_{20}CIN_3O_5S_2\\ C_{21}H_{19}N_3OS_2\\ C_{21}H_{19}N_3OS_2\\ C_{16}H_{14}N_2O_3S_2\\ C_{16}H_{16}N_3O_5S_2\\ \end{array}$ | | $ \begin{array}{c} 10,8\\9,3\\10,7\\10,4\\9,0\\8,5\\8,3\\7,4\\-\\10,7\\8,1\\7,4\end{array} $ | 24,7 21,3 16,4 15,8 13,7 | 89 69 76 83 85 64 72 71 61 97 71 79 |

TABLE 1. Characteristics of the Compounds Synthesized

It has been found that, like ordinary quaternary salts, the 2-methylthiazolium perchlorates (Ia-c) readily react with the nucleophilic reagents used for the synthesis of polymethine dyes. Thus, for example, with 3-ethylrhodanine they form the nulmethinemerocyanines (IIb and c) (Table 1).



However, in the production of monomethinecyanines by the reaction of the imidazothiazoles (Ia-c) with 3-ethyl-2-methylbenzothiazolium tosylate in ethanol in the presence of triethylamines, non-salt-like deeply colored dyes (Table 2) were unexpectedly obtained. Judging from the results of elementary analysis, it is obvious that, in addition to the methylthio group a molecule of perchloric acid is split out in this reaction with the formation of the mesoionic monomethinecyanines (IIIa-c).



In actual fact, the action of perchloric acid on these dyes formed the perchlorates (IVac), which had higher colors than the initial oxides (IIIa-c). The absorption maxima of solutions of compounds (IVa-c) were close to the analogous characteristics of the monomethinecyanine (V) (452 nm) [3], which confirmed the structure of the products obtained (III, IV).



It can be seen from a comparison of the characteristics of the electronic spectra of solutions of the compounds synthesized that the introduction into position 3 of the imidazothiazole nucleus of a methyl or a phenyl group (compounds b and c, respectively), led to a slight bathochromic shift of the long-wave absorption band. This effect can apparently be explained by the steric and electronic influence of the substituents. It must be mentioned that although in dyes of type (III, IV) the chromophore responsible for the color is the same, compounds (IIIa-c) absorb in a considerably longer-wave region of the spectrum ($\Delta\lambda_{max} = 42-46$ nm). This deepening of the absorption on passing from cationic dyes to mesoionic dyes obviously has the same nature as for mesoionic heterocycles such as the (3-thiazolo[3,2-a]pyridinio)oxides [4].

| | DMFA | | | | | СН₃СООН | | | | |
|----------|---------------|--|----------------|--|---------------|----------------------------------|---------------|---|--|--|
| R | com- pound | λ_{\max} , nm (log ϵ) | com- pound | λ_{\max} , nm (log ϵ) | com- pound | λ _{max} , nm (log ε) | com- pound | λ_{\max} , nm (log ε) | | |
| H CH3 | IIЪ | 488 (4,44) | III a III b | 496 (4,43) 500 (4,45) | IV a IV b | 450 (4,73) 456 (4,70) | Ia Ib | 278, 348 277 (4,10), 349 (407) | | |
| C_6H_5 | llc | 490 (4,45) | IIIc | 500 (4,41) | IVc | 458 (4,73) | Ic | 276 (4,07), 351 (3.07) | | |
| | | | VII | 464 (4,49) | VI | 516 (4,61) | VIII IX | 320 (3,97) 320 (3,96) 350 (3,95) | | |

TABLE 2. Parameters of the Electronic Absorption Spectra of Solutions of Imidazo[1,2-c]thiazole Derivatives

Further investigations showed that the imidazothiazole (Ia) reacts not only with nucleophiles but also with the electrophilic agents used for the synthesis of dyes. Thus, for example, with p-dimethylaminobenzaldehyde the benzylidene derivative (VI) was obtained.



Under the action of bases on the perchlorate (VI), as in the case of the salts (IVa-c), again a molecule of perchloric acid was readily split out with the formation of the oxide (VII). However, in contrast to the monomethinecyanines, the color did not deepen on passing to the mesoionic dye (VII) but lightened (52 nm), since under these conditions in the chromophore of the molecule of a mesoionic compound the conjugation of the p-dimethylaminophenyl residue with the carbonyl group of the imidazothiazole is disturbed.

The reaction of the salt (Ia) with acetic anhydride in the presence of triethylamine took place somewhat unexpectedly. According to the results of elementary analysis, the compound formed was not salt-like. The PMR spectrum of the product isolated showed the signals of the protons of two nonequivalent acetyl groups and of a methylthio group, and a multiplet of aromatic protons with chemical shifts (δ , ppm) of, respectively: 2.23 (3H); 2.30 (3H); 2.57 (3H); and 6.7-7.2 (5H). Only the bands of the stretching vibrations of C=C-O, C=N, and C=O bonds were found in the IR spectrum (1580, 1615, 1680, 1695 cm⁻¹). These results permit us to propose structure (VIII) for the compound formed, i.e., apparently, under the action of triethylamine on the salt (Ia) a molecule of perchloric acid is split out and acetylation of the mesoionic compound formed takes place at the nucleophilic center - the carbon atom in position 3 - together with replacement of the atom in position 1. The hypothesis put forward was confirmed by the fact when a substituent was present in position 3 of the imidazothiazole molecule only the monoacetylation product was formed. For example, from salt (Ic) was obtained the Nacetyl derivative (IX), the PMR spectrum of which showed the signals of the protons of two methyl groups and a multiplet of the protons of phenyl groups with chemical shifts of, respectively (ppm); 2.30 (3H); 2.43 (3H); and 6.9-7.3 (10H), while the IR spectrum contained the absorption bands of the stretching vibrations of only one carbonyl group (1680 cm^{-1}).



VIII $R^1 = COCH_3$, IX $R^1 = C_6H_5$

We may note that the protons of the phenyl group present in position 7 of compounds (VIII) and (IX), unlike the protons of the phenyl groups of the initial salts (Ia, c), are non-equivalent, and the corresponding signals are located in a fairly wide range of values of chemical shifts (~ 0.5 ppm) and not in the form of a singlet as for the perchlorates (Ia, c). This fact can be explained, on the one hand, by hindered rotation of the phenyl group about the C-C bond, which is due to the neighboring substituent present in position 1, and, on the other hand, by the anisotropy of the magnetic field caused by the electron pairs of the C=O group, which is an additional confirmation of the structures of the acetylated mesoionic compounds (VIII) and (IX).

As in the case of substituted mesoionic thiazolopyridines and thiazoloquinolines of types (X) and (XI) [4], which are structural analogs of the oxides (VIII) and (IX), the replacement of an acetyl group by a phenyl group leads to a considerable deepening of the coloration (Table 2).



X $R^1 = COCH_3$; XI $R^1 = C_6H_5$

EXPERIMENTAL

Electronic spectra were obtained on SF-8 and SF-10 spectrophotometers, PMR spectra on a Tesla BS-467 spectrometer (60 MHz, internal standard HMDS) in CF_3COOH , and IR spectra on a UR-10 spectrophotometer in KBr tablets.

<u>3-Ethyl-5-(3-methyl-2-oxo-7-phenyl-2,3-dihydro-1H,5H-imidazo[1,2-c]thiazol-5-ylidene)-2-thioxothiazolidin-4-one (IIb).</u> A mixture of 0.37 g (1 mmole) of the perchlorate (Ib), 0.16 g (1 mmole) of 3-ethylrhodanine, and 6 ml of absolute ethanol was heated until the solid components had dissolved, and then 0.1 g (1 mmole) of triethylamine was added. The dye that precipitated was filtered off and crystallized from a mixture of acetic acid, ethanol, and DMFA (3:1:1). Yield 0.35 g. Information on the properties of the compound synthesized is given in Table 1.

<u>3-Ethyl-5-(2-oxo-3,7-diphenyl-2,3-dihydro-1H,5H-imidazo[1,2-c]thiazol-5-ylidine)-2-thioxo-</u> thiazolidin-4-one (IIc). This was obtained in a similar manner to the preceding compound from the salt (Ic), the product being crystallized from acetonitrile.

 $\frac{\{3-R-5-[(3-Ethyl-3H-benzothiazolin-2-ylidene)methyl]7-phenylimidazo[1,2-c]thiazolio\}-2-oxides (IIIa-c). A mixture of 2 mmole of the appropriate salt (Ia-c) and 0.7 g (2 mmole) of 3-ethyl-2-methylbenzothiazolium tosylate was dissolved with heating in 10 ml of absolute ethanol, and then 0.4 g (4 mmole) of triethylamine was added. The dye that deposited was filtered off and crystallized from ethanol.$

 $\frac{3-R-5-[(3-Ethyl-3H-benzothiazolin-2-ylidene)-methyl]-2-oxo-7-phenyl-2,3-dihydro-1H-imid$ azo[1,2-c]thiazolium Perchlorates (IVa-c). These were obtained by the action of an excess of72% perchloric acid on a solution of the appropriate oxide (IIIa-c) in ethanol and were crystallized with the addition of 2-3 drops of perchloric acid from mixtures of methanol and DMFA:(IVa, b) (4:1) or DMFA:(IVc) (1:1),

3-(p-Dimethylaminobenzylidene)-5-methyl-2-oxo-2,3-dihydro-lH-imidazo[1,2-c]thiazolium Perchlorate (VI). A mixture of 0.36 g (1 mmole) of the perchlorate (Ia), 0.15 g (1 mmole) of pdimethylaminobenzaldehyde, and 6 ml of acetic anhydride was heated for 10 min. The dye that deposited was filtered off and crystallized from ethanol with the addition of 2-3 drops of 72% perchloric acid. Yield 0.3 g.

{3-(p-Dimethylaminobenzylidene)-5-methylthio-7-phenyl-3H-imidazo[1,2-c]thiazolio}-2-oxide (VII). This was obtained by the addition of triethylamine to an ethanolic solution of the preceding compound. It was crystallized from ethanol.

 $\frac{\{1,3-\text{Diacetyl-5-methylthio-7-phenyl-lH-imidazo[1,2-c]thiazolio}-2-oxide (VIII).}{\text{of 0.36 g (1 mmole) of the perchlorate (Ia) in 6 ml of acetic anhydride was heated to the boil, and 0.1 g (1 mmole) of triethylamine was added. The product that deposited was filtered off and crystallized from acetic anhydride. Yield 0.25 g.$

 $\{1-\text{Acetyl-5-methylthio-3,7-diphenyl-1H-imidazo[1,2-c]thiazolio}\}-2-oxide (IX).$ A solution of 0.43 g (1 mmole) of the perchlorate (Ic) in 5 ml of acetic anhydride was boiled for 10 min and then 0.1 g (1 mmole) of triethylamine was added. The resulting product was filtered off and crystallized from acetic anhydride. Yield 0.3 g.

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SYNTHESIS AND TRANSFORMATIONS OF S- AND N-SUBSTITUTED

2-MERCAPTOBENZOTHIAZOLES

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2-Mercaptobenzothiazole reacts with alkyl halides and hydrazine hydrate in the thiol form, and with formaldehyde in the thione form. The alkylation of 2-mercaptobenzothiazolidin-3-yl-methanol has been performed with sulfoalkyl halides and with propan-1,3-sultone. A number of new 2-hydrazinobenzothiazoles derivatives have been synthesized.

The existence of 2-mercaptobenzothiazole (I) in the thiol and thione tautomeric forms [1] explains its capacity for forming derivatives substituted at the sulfur or the nitrogen atoms. The aim of the present investigation was to find luster-imparting additives for the electrolytic deposition of metals, in connection with which methods have been developed for obtaining some derivatives of the thiazole (I) of various types and studying their reactivities.

The thiazole (I) reacts with formalin in the thione form, giving rise to 2-thioxobenzothiazolidin-3-yl-methanol (II) [1], which is alkylated by sulfoalkyl halides or propan-1,3-sultone in the presence of caustic potash to form salts of the (2-thioxobenzothiazolidin-3-ylmethoxy)alkanesulfonic acids (III-V) (Table 1).

| Com- | mp °C | Found, % | | | Empirica1 | Calculated, % | | | Yield, |
|--|---|---|---|--|--|--|---|--|---|
| pound | | с | н | s | formula | с | н | s | <i></i> |
| III IV V VII VIII IX XI XIII XIV XVI XVI | $\begin{array}{c} 210-212^{a}\\ 240a\\ 271a\\ 125-127\\ 92-94\\ 208a\\ 71-72\\ 159-160\\ 193-194b\\ 144-145\\ 216-217c\\ 191-192\\ 285a\\ 101-102\\ 76-79\\ 141-142\\ 171-172d\\ \end{array}$ | $\begin{array}{c} 35,2\\ 36,5\\ 36,8\\ 47,7\\ 52,8\\ 34,9\\ 50,2\\ 45,3\\ 56,1\\ 60,0\\ 66,2\\ 62,8\\ 34,2\\ 55,0\\ 54,6\\ 62,7\\ 54,8\\ \end{array}$ | $\begin{array}{c} 3.1 \\ 3.2 \\ 3.5 \\ 4.9 \\ 6.1 \\ 3.0 \\ 4.0 \\ 4.7 \\ 5.8 \\ 4.3 \\ 5.8 \\ 4.8 \\ 4.8 \\ 4.9 \\ 4.7 \\ 2.9 \end{array}$ | 25,4 29,4 27,0 39,3 33,0 28,3 27,1 27,0 16,5 14,4 12,6 11,3 22,8 14,3 14,3 13,7 18,4 | $\begin{array}{c} C_{11}H_{12}KNO_5S_3\\ C_{10}H_{10}NNaO_5S_3\\ C_{11}H_{12}KNO_4S_3\\ C_{13}H_{16}N_2S_4\\ C_{17}H_{24}N_2S_4\\ C_{10}H_{10}KNO_4S_3\\ C_{10}H_9NO_2S_2\\ C_9H_9N_3S\\ C_{11}H_{12}N_3S\\ C_{14}H_{11}N_3S\\ C_{15}H_{13}N_3OS\\ C_8H_8N_2NaO_3S_2\\ C_{10}H_{10}N_4S\\ C_{10}H_{11}N_3OS\\ C_{12}H_{11}N_3S\\ C_{12}H_{11}N_3S\\ C_{12}H_{11}N_3S\\ C_{12}H_{11}N_3S\\ C_{12}H_{11}N_3S\\ C_{12}H_{11}N_3S\\ C_{12}H_{10}N_3S\\ C_{12}H_{10}N_3S\\ \end{array}$ | $\begin{array}{c} 35.4\\ 36,7\\ 37,0\\ 53,1\\ 35,0\\ 50,2\\ 45,2\\ 60,2\\ 66,2\\ 60,2\\ 66,4\\ 34,1\\ 55,0\\ 54,5\\ 62,8\\ 54,9\\ 54,9\end{array}$ | 3,2 3,1 3,4 4,9 3,8 3,8 4,7 6,0 4,4 6,0 4,6 2,9 4,6 5,0 4,8 2,9 4,6 2,9 4,8 2,9 4,6 4,6 2,9 4,6 4,6 4,6 2,9 4,6 4,6 4,6 4,6 2,9 4,6 | $\begin{array}{c} 25.8\\ 29,4\\ 26,9\\ 39,0\\ 33,3\\ 28,0\\ 26,8\\ 16,7\\ 14,6\\ 12,7\\ 11,1\\ 22,8\\ 14,7\\ 14,5\\ 14,0\\ 18,3\\ \end{array}$ | $\begin{array}{c} 48\\ 92\\ 60\\ 88\\ 51\\ 54\\ 61\\ 73\\ 71\\ 72\\ 84\\ 78\\ 58\\ 56\\ 77\\ 52\\ 86\\ \end{array}$ |

TABLE 1. Characteristics of the Compounds (III-V), (VII-XI), and (XIII-XXI)

^a Melts with decomposition. ^b According to [4], mp 194-195°C. ^c According to [4], mp 221-222°C. ^d According to [2], mp 174.5-177°C.

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