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# HALOGEN-CONTAINING SPIRO COMPOUNDS BASED ON A 4-VINYLOXYETHYL-1,4-PERHYDROTHIAZINE 1-OXIDE

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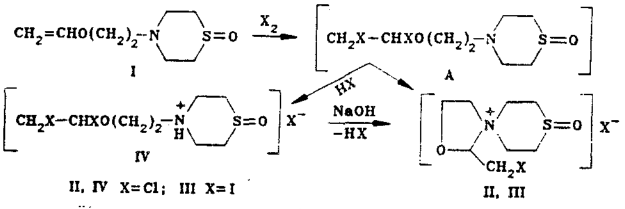
Depending on the nature of the halogen and the polarity of the solvent, the chlorination and iodination of 4-vinyloxyethyl-1,4-perhydrothiazine 1-oxide leads to new heterocyclic tertiary or quaternary ammonium salts, including halogen-containing spiro compounds.

It is known that the halogenation of vinyl ethers and their analogs is complicated by side processes involving heterocyclization [1] and polymerization [2, p. 138], which are sometimes accompanied by explosions [3].

For the first time we have accomplished [4, p. 118] the chlorination and iodination of 4-vinyloxyethyl-1,4-perhydrothiazine 1-oxide (I), which is readily obtained on the basis of the new accessible divinyl sulfoxide [5; 6, p. 141].



Spiro bicyclic ammonium salt II was obtained in 70-75% yields in the chlorination of thiazine oxide I in benzene (10-20°C) and dichloroethane and $CCl_4$ (−30 to +20°C). The corresponding quaternary ammonium salt III was isolated in quantitative yield in the iodination of perhydrothiazine oxide I in both polar (methanol, ethanol) and nonpolar ($CCl_4$, benzene) solvents. The synthesis of salts II and III is possible by halocyclization of the initially formed intermediate A with participation of the nitrogen atom and the highly active halogen in the α position with respect to the oxygen atom of the halo ether group. Hydrochloride IV was obtained in 57% yield in the chlorination of thiazine oxide I in methanol (20-25°C). Simultaneously with chlorination at the multiple carbon—carbon bond of thiazine oxide I, the hydrogen chloride formed as a result of side processes, despite drying of the chlorine used, enters into the reaction.

The compositions and structures of the synthesized compounds are confirmed by the results of elementary analysis, IR spectroscopy, and mass spectrometry. The reaction of IV with triethylamine leads to the formation of triethylamine hydrochloride.

The multiplicity of the signals in the $^{13}C$ NMR spectrum of IV makes it possible to unambiguously identify the signal of the $\underline{C}HCl$ methylidyne carbon (62.95 ppm). The shift of the $O\underline{C}H_2$ carbon atom is 58.18 ppm, while the shift of the $N^+\underline{C}H_2$ (acyclic) carbon atom is 47.4 ppm. The assignment of the signals of the perhydrothiazine oxide ring in IV can be made on the basis of the shifts of the α-carbon atoms of 1-methylpiperidine (57.2 ppm) and thiocyclohexane 1-oxide (48.2 ppm) [7] taking into account the effect of protonation of the nitrogen atom, which gives rise to a shift to strong field of the resonance signals of the α-carbon

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atom of 1.5 ppm and of the β-carbon atom of ≤5.5 ppm: the shifts of the $N^+\underline{C}H_2$ and $S\underline{C}H_2$ ring carbon atoms should have values of ~55.7 and 42.7 ppm, respectively. The signals at 54.34 ppm and 41.34 or 41.23 ppm in the $^{13}C$ NMR spectrum of IV correspond to these values. The shift of the $Cl\underline{C}H_2$ grouping is 41.23 or 41.34 ppm. The PMR spectra of salts II-IV at 3.4-4.1 ppm are in agreement with the data in [8] for series of 4,4-dialkyl-1,4-perhydrothiazinium 1-oxide salts, which also contain a perhydrothiazinium oxide group.

In the potentiometric titration of IV with a 0.1 N solution of NaOH in methanol the HCl is titrated with the subsequent formation of salt II. At the same time, as one should have expected, the back titration of product II with a 0.1 N solution of $HClO_4$ in methanol does not take place (a titration curve is not observed); this indicates the absence of basic properties for it and the presence of a quaternized nitrogen atom in this molecule. On the basis of this it may be assumed that cyclization at the nitrogen atom with the formation of product II occurs after tying up of the HCl in IV with alkali.

The ionic structure of II-IV was confirmed by volumetric titration [9, 10] with a solution of $Hg(NO_3)_2$ (with diphenylcarbazone as the indicator).

## EXPERIMENTAL

The IR spectra of the compounds (KBr pellets) were recorded with a UR-20 spectrometer. The PMR spectra of solutions of the compounds in $D_2O$ or DMSO were obtained with a Jeol PX-90Q spectrometer relative to sodium 4,4-dimethyl-4-silapentanesulfonate (for III) or tetramethylsilane (TMS) (for IV). The mass spectra were obtained with a 4MKh-1203 spectrometer. A pH-meter-340 was used for potentiometric titration with calomel and glass electrodes. The calomel reference electrode was filled with a saturated methanol solution of KCl.

(2-Chloromethyl-1,3-oxazolidine)-3,4'-spiro-(1',4'-perhydrothiazinium-1'-oxide) Chloride (II). Dried gaseous chlorine was passed at 20°C (or at −20°C to −30°C) for 0.25 to 0.5 h through a solution of 1 g (5 mmole) of thiazine oxide I in 20 ml of freshly distilled $CCl_4$ until the mixture was saturated. The resulting white precipitate was washed with $CCl_4$, separated, and dried in vacuo to give 0.96 g (70.2%) of white powdery II, which was unstable and darkened in air and had mp 70-72°C. IR spectrum: 690, 710 (C—S, C—Cl), 1030, 1060 (S=O), 2500-3000 $cm^{-1}$ ($N^+$). PMR spectrum: 3.4-4.1 ppm (m, $OCH_2$, $N^+CH_2$, $CH_2S{=}O$, CH, $CH_2Cl$). Found, %: C 14.2; $Cl^-$ 13.6; N 5.4; S 12.5. $C_8H_{15}Cl_2NO_2S$. Calculated, %: C 13.6; $Cl^-$ 13.6; N 5.4; S 12.3.

(2-Iodomethyl-1,3-oxazolidine)-3,4'-spiro-(1',4'-perhydrothiazinium-1'-oxide) Iodide (III). A solution of 1.27 g (5 mmole) of iodine in alcohol was added dropwise at 20-25°C to a solution of 1 g (5 mmole) of thiazine oxide I in 20 ml of anhydrous methanol. After the formation of a white precipitate, the solvent was removed by distillation, and the product was dried in vacuo to give 2.28 g (97.4%) of salt III with mp 155-158°C. IR spectrum: 600 (C—I), 625, 635 (C—S), 1025, 1060 (S=O), 1399-1450 and 2905-3000 $cm^{-1}$ ($N^+$). An absorption band corresponding to an NH group was absent. Mass spectrum (m/z): 189 $(M - 2I)^+$, 254 $(I_2)^+$. Found, %: I 28.2; $I^-$ 29.5; N 3.1; S 7.2. $C_8H_{15}I_2NO_2S$. Calculated, %: I 28.6; $I^-$ 28.6; N 3.2; S 7.2.

4-[(1',2'-Dichloro)ethoxy]ethyl-1,4-perhydrothiazinium 1-Oxide Chloride (IV). Dried (over concentrated $H_2SO_4$) gaseous chlorine was passed at room temperature (or at −5°C to −15°C) for 0.3-1 h through a solution of 1 g (5 mmole) of thiazine oxide I in 20 ml of anhydrous methanol, after which the solvent was removed by distillation, and the residue was dried in vacuo to give 0.89 g (57.1%) of salt IV with mp 170°C (dec.). IR spectrum: 655, 770, 790 (C—S, C—Cl), 1035, 1050 (S=O), 2565, 2640-2660 $cm^{-1}$ ($N^+H$). PMR spectrum ($D_2O$): 3.4-4.0 (m, $CH_2Cl$, $OCH_2$, $CH_2N$, $CH_2S{=}O$), 5.53 ppm (dd, OCHCl). $^{13}C$ NMR spectrum: 41.23, 41.34 ($\underline{C}H_2Cl$, $\underline{C}H_2S{=}O$ in a ring), 47.40 ($N^+\underline{C}H_2$ acyclic), 54.34 ($N^+\underline{C}H_2$ in a ring), 58.18 ($O\underline{C}H_2$), 62.95 ppm (CHCl). Found, %: Cl 36.1; N 4.5; S 11.8. $C_8H_{16}Cl_3NO_2S$. Calculated, %: Cl 35.9; N 4.7; S 10.8.

Triethylamine hydrochloride ($Et_3N \cdot HCl$), with mp 254°C (see [11, p. 828]), was isolated when thiazine oxide IV was mixed with a stoichiometric amount of $Et_3N$. No melting-point depression was observed for a mixture of this product with specially obtained triethylamine hydrochloride.

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# CONDENSED HETEROCYCLES WITH A THIAZOLE RING.

## 15.* DYES BASED ON THIAZOLO[3,4-b][1,2,4]TRIAZINE

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27'651:543.422.6

Unsymmetrical tri- and pentamethinecyanine dyes with a thiazolo[3,4-b][1,2,4]triazine ring were synthesized. The electron-density distribution on the atoms of the dyes in the ground, first, and second excited states was calculated by a quantum-chemical method. It was established that the first two electron transitions are localized on the same atoms of the dyes and that charge transfer to the triazine fragment of the molecule is realized upon excitation. The degree of participation of the heterocyclic ring in the first electron transition, which is responsible for the color of the dye, decreases with an increase in the length of the polymethine chain.

It was recently shown [1] in an investigation of the absorption spectra of a series of symmetrical dyes — thiazolo[3,4-b][1,2,4]triazine derivatives — that significant interaction of the first two π-electron transitions localized on the atoms of the polymethine chain and the terminal heteroresidues is observed in their molecules. However, in this case the symmetrical dyes of this type must be strictly regarded as cyanines that contain a system of three interacting chromophones. The analysis of the spectra of such dyes is not always unequivocal [2].

For a detailed and more accurate elucidation of the nature of the absorption bands of cyanines that contain a thiazolotriazine ring it seemed of interest to synthesize the corresponding unsymmetrical dyes with different chain lengths and to investigate the absorption spectra of solutions of them.

For this, tri- and pentamethinecyanines Vb, c were obtained by the reaction of acetanilidovinyl derivative I [1] with 2-methyl-3-ethylbenzothiazolium p-toluenesulfonate (II) and ethoxybutadienyl derivative III with 6-methyl-2,3,8-triphenylthiazolo[3,4-b][1,2,4]triazinium perchlorate (IV). (See first scheme on following page.)

In Table 1 the spectral characteristics of the synthesized compounds are compared with the analogous data for monomethinecyanine Va [3]. It is apparent from Fig. 1 that two bands

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*See [1] for Communication 14.

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