ELECTROPHILIC TRANS QUATERNIZATION OF SUBSTITUTED 2-[2-
CYCLOHEXEN-I-YLTHIO(SELENO)PYRIDINES TO 4a, 10-a-cis-4,4a-
trans-1,2,3,4,4a,10a-HEXAHYDROBENZOTHIAZOLO(SELENAZOLO)-
[3,2-a]PYRIDINIUM SALTS


It was established that the electrophilic quaternization of substituted 2-[2-
cyclohexen-1-ythio(seleno)]pyridines is a stereoselective process and pro-
cceeds as trans quaternization with the formation of 4a,10a-cis-4,4a-trans-
1,2,3,4,4a,10a-hexahydrobenzothiazolo(selenazo)[3,2-a]pyridinium salts.

The study of the mechanism and stereochemistry of electrophilic heterocyclization -
quaternization - was associated with its extensive use as a general method in the synthesis
of various heterocycles [1-6]. Thus, this reaction was used in the synthesis of annelated
pyridinium salts. Imidazo-, oxazolo-, thiazolo-, and selenazo[3,2-a]pyridinium salts, re-
spectively, were obtained in the bromination or iodination of 2-N-, O-, S', and Se-allylpy-
ridines [7, 8]. However, the use of 2-N-, O-, S', and Se-allylpyridines in electrophilic
quaternization did not make it possible to form a judgment regarding the stereochemistry of
this reaction and its mechanism. In order to develop stereochemical concepts of the investi-
gated reaction we synthesized a number of substituted 2-[2-
cyclohexen-1-ythio(seleno)]pyri-
dines, studied their reaction with various electrophilic reagents, and investigated the
structures of the annelated pyridinium salts obtained.

Substituted 2(1H)-pyridinethiones and -selenones Ia-c [9, 10] and 3-bromo-1-cyclohexene
(II) were convenient and accessible reagents for the synthesis of IIIa-c; the alkylation of
pyridines Ia-c with 3-bromo-1-cyclohexene (II) in DMF in the presence of an equimolar amount
of KOH proceeds regioselectively exclusively at the sulfur or selenium atom with the forma-
tion of 2-[2-cyclohexen-1-ythio(seleno)]pyridinium salts IIIa-c.

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The results of elementary analysis and the IR and PMR spectroscopic data do not contradict the structures of the IIIa-c obtained (Table 1).

The reactions of 2-[2-cyclohexen-1-ylthio(seleno)]pyridines III with electrophilic reagents (bromine, iodine, perchloric acid) proceed in different directions depending on the nature of the electrophile. The reaction of IIIb with perchloric acid in acetic acid at 25°C proceeds with the formation of pyridinium perchlorate IV rather than a benzothiazolo[3,2-a]pyridinium salt. This reaction pathway is associated with the rather high basicity of pyridine. Benzothiazolo(selenazolo)[3,2-a]pyridinium trihalides Vla-d are formed in high yields in the reaction of IIIa-c with a twofold excess of bromine or iodine in chloroform; triiodides VIb-d are always formed regardless of the amount of iodine introduced into the reaction. The starting IIIa-c remain unchanged when there is insufficient iodine. Quaternized azine VIa was also obtained in the bromination of perchlorate IV in acetic acid at 25°C. The direction of this reaction depends on the temperature of the reaction mixture and excludes the possibility of the occurrence of such quaternizations via a nucleophilic mechanism through intermediate VII. The bromination of IV in acetic acid at 70-80°C leads to benzothiazolo[3,2-a]pyridinium perchlorate VIII.

A decrease in the intensity of the absorption band of the CN group and its shift to the high-frequency region to 2234-2239 cm\(^{-1}\) occur in the IR spectra on passing from IIIa-c to Vla-d and VIII; this is associated with delocalization of the positive charge in the pyridine fragment of the molecules of these compounds. Delocalization of the positive charge in the pyridine fragment of Vla-d and VIII leads to an increase in the polarization of the pyridine protons and the protons of the alkyl substitutents bonded to the pyridine ring; a shift of the signals of these protons in the PMR spectra of Vla-d and VIII to weak field is observed. Thus, for IIIa and Vla the differences in the chemical shifts of the protons of the R, CH\(_3\), and pyridine CH groups are, respectively, 0.29, 0.61, and 0.78 ppm. The protons of the 6-CH\(_3\) group of Vla-d and VIII are more polarized than the protons of the 8-CH\(_3\) group. Signals of protons of the benzothia(selenazolo)zo fragment are also present in the PMR spectra of Vla-d and VIII. Multiplets of protons of YCH and HalCH groups appear at 4.98-5.20 and 4.77-4.92 ppm, respectively. The signal of the proton of the NCH group of the NCH group of Vla-d and VIII shows up in the form of a double doublet at 6.02-6.17 ppm with \(3J_{\text{cis}} = 4.7-5.2\) Hz and \(3J_{\text{trans}} = 9.9-10.6\) Hz. This multiplicity of the signal of the proton of the NCH group in the series of these compounds is a consequence of the high stereoselectivity of the quaternization of azines IIIa-c to Vla-d and VIII. The assignment of the spin-spin coupling constants (SSCC) to the group of YCH\(_3\)CH\(_3\)Hal protons was made on the basis of double-resonance experiments in the spectra of Vla-d and VIII. Irradiation at the frequency of the proton of the CHHal group contracts