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REGIOSELECTIVITY AND STEREOSELECTIVITY OF ELECTROPHILIC QUATERNIZATION OF SUBSTITUTED 2-ALLYL(2-CYCLOHEXEN-1-YL)THIONICOTINIC ACIDS TO THIAZOLO[3,2-a]PYRIDINIUM SALTS

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The electrophilic quaternization of substituted 2-allyl(2-cyclohexen-1-yl)-thionicotinic acids proceeds regioselectively and stereoselectively as a trans process with the formation of salts of 4a,10a-cis-4,4a-trans-1,2,3,4,4a,10a-hexahydrobenzothiazolo-[3,2-a]pyridinium acids. Trihalides of thiazolo[3,2-a]-pyridinium acids exist in equilibrium with their betaine form. The formation of betaines and reactions that proceed with a change in the anionic part of thiazolo[3,2-a]pyridinium salts have virtually no effect on the conformation of the heterocyclic cation.

The ability of heterocycles that contain an N=C–Y–CH–C=C fragment (Y = N, O, S, Se) to undergo quaternization under the influence of various electrophiles with the formation of rings makes it possible to obtain condensed heterocyclic systems in which pyridinium or pyrimidinium rings are annelated with imidazole, oxazole, thiazole, or selenazole rings and have a quaternary nitrogen atom as a nodal heteroatom [1-5]. The investigation of electrophilic quaternization makes it possible to isolate the general principles of the annelation of pyridines [1, 3, 4], pyrimidines [5], and 1,5-naphthyridines [6, 7] and to establish the stereostructures of quaternized condensed azines. The dependence of the three-dimensional structures of the reaction products on the structures of the starting compounds was established by comparison of the results of x-ray diffraction analysis with IR and PMR spectroscopic data.

We have observed that the electrophilic quaternization of hexahydrobenzothiazolo[3,2-a]-pyridinium salts proceeds stereoselectively as a trans process with the formation of cis-fused ring [7]. We assume that carbonium ions cannot act as intermediates in these reactions.

The aim of the present research was to develop methods for the synthesis of substituted 2-allyl(2-cyclohexen-1-yl)thionicotinic acids, to study the stereochemistry of their quaternization to thiazolo[3,2-a]pyridinium salts, and to establish the specific characteristics of the effect of the carboxy group on the structures and reactivities of the salts cited above.

2-Allyl(2-cyclohexen-1-yl)thionicotinic acids were obtained by alkylation of 6-methyl-3-carboxypyridine-2(1H)-thione with alkyl halides. Thus, the alkylation of I with alkyl halides IIa, b in DMF in the presence of an equimolar amount of a solution of KOH in water proceeds regioselectively exclusively at the sulfur atom with the formation of 2-alkenylthio-

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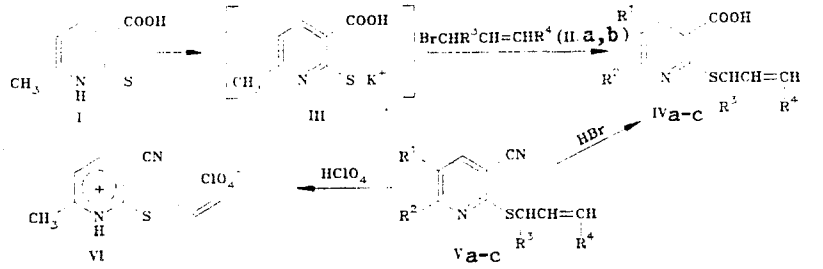
TABLE 1. Characteristics of Substituted 2-Allylthio(cyclohexenylthio)pyridines IVa-c and VI

Compound	Empirical formula	mp, °C (solvent)	IR spectrum, ν_{CO}, cm^{-1}	^1H NMR spectrum, δ, ppm, SSCC (J, Hz)	Yield, % (method)
IV	$C_{10}H_{11}NO_2S$	148...150 (acetone-hexane, 1:8)	1695	2,49 (3H, s CH_3); 3,78 (2H, d, SCH_2, ^3J=7 Hz); 5,06 (1H, dd, CH_2=C- cis ^3Jcis=10 Hz); 5,38 (1H, dd, CH_2=C-trans, ^3Jtrans, =17 Hz); 5,92 (1H, m, CH=C); 7,06 (1H, d, $C_{(5)}H$, ^3J=7,9 Hz); 8,09 (1H, d, $C_{(4)}H$, ^3J=7,9 Hz);	91 (A) 64 (B)
IV	$C_{13}H_{15}NO_2S$	141...143 (benzene)	1687	1,72, 2,02 [6H, m, $(CH_2)_3$]; 2,48 (3H, s, SCH_3); 4,63 (1H, m, SCH); 5,75, 5,84 (2H, m, CH=CH); 7,07 (1H, d, $C_{(5)}H$, ^3J=7,8 Hz); 8,08 (1H, d, $C_{(4)}H$, ^3J=7,8 Hz);	72 (A) 47 (B)
IV	$C_{13}H_{15}NO_2S$	206...208 (ethanol)	1692	1,82, 2,68 [8H, m, $(CH_2)_4$]; 3,82 (2H, dd, SCH_2, ^3J=6,8 Hz); 5,12 (1H, dd, CH_2=C-cis ^3Jcis =10 Hz); 5,24 (1H, dd, CH_2= =C-trans, ^3Jtrans, 18 Hz); 5,83 (1H, m, CH=C); 7,78 (1H, s, $C_{(4)}H$)	53 (B)
VI	$C_{10}H_{11}ClN_2O_4S$	78...80 (methanol)	2238 (C≡N)	2,48 (3H, s, CH_3); 3,74 (2H, d, SCH_2, ^3J=7 Hz); 5,10 (1H, dd, CH_2=C cis ^3Jcis=10 Hz); 5,32 (1H, dd, CH_2=C trans ^3Jtrans= =17 Hz); 5,98 (1H, m, CH=C); 7,11 (1H, d, $C_{(5)}H$, ^3J=8 Hz); 8,14 (1H, d, $C_{(4)}H$, ^3J=8 Hz)	87

pyridines IVa, b, c. The regioselectivity of the alkylation of I is determined by the formation of salt III, in which the sulfur atom is formally negatively charged, as in pyridine thiolates [8-10]. Since products of other transformations were not detected in the reaction mixture, it may be assumed that the reaction proceeds via an S_N2 mechanism.

As a result of a study of the quaternization of V under the influence of perchloric or hydrobromic acid we observed a second method for obtaining IV.



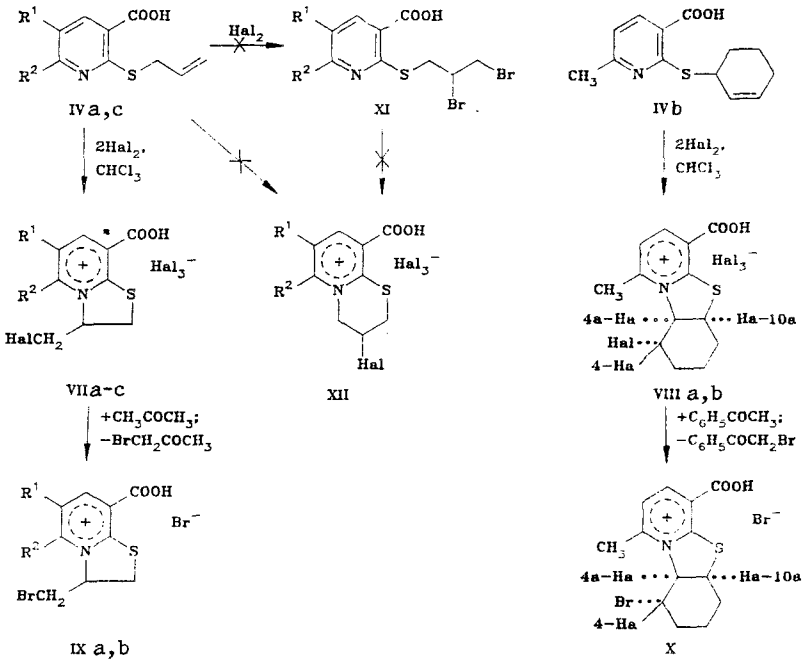
II a $R^3=R^4=H$; b $R^3-R^4=(CH_2)_3$; IV, V a $R^1=R^3=R^4=H$, $R^2=CH_3$; b $R^1=H$, $R^2=CH_3$, $R^3-R^4=(CH_2)_3$; c $R^1-R^2=(CH_2)_4$, $R^3=R^4=H$

It was established that heating Va with perchloric acid in acetic acid leads only to protonation of pyridine and the formation of perchlorate VI and not to the corresponding thiazolo[3,2-a]pyridinium salt. Heating Va-c in the presence of hydrobromic acid leads to hydrolysis of the cyano group and the formation of substituted 2-alkenylthionicotinic acids IVa-c. However, the yields of nicotinic acids IVa-c obtained by this method are considerably lower.

The results of physicochemical analysis confirm the structures of IV and VI (Table 1). An absorption band of a carboxy group at 1687-1695 cm^{-1} is present in the IR spectra of acids IVa-c. The absorption band of the CN group of VI is shifted to the high-frequency region to 2238 cm^{-1} and has a lower intensity than in the case of starting Va [4]; this is associated with delocalization of the positive charge in the pyridinium ring.

Compounds IVa-c react readily at room temperature with bromine or iodine in dry chloroform to give thiazolo[3,2-a]pyridinium trihalides VII and VIII in 79-95% yields. In contrast to triiodides VIIb and VIIIb, tribromides VIIa, c and VIIIa react with acetone or acetophenone to give monobromides IXa, b and X and bromo ketones. The use of IX and X as catalysts for the bromination of methyl alkyl (aryl) ketones increases the yields of the final products substantially. Thus, bromoacetophenone was obtained in 78% yield in the bromination of acetophenone in methanol in the presence of catalytic amounts of bromide X.

The reactions of IVa-c with halogens proceed regioselectively with the formation of thiazolo[3,2-a]pyridinium salts VII and VIII and not thiazino[3,2-a]pyridinium salts XII or adducts of addition of halogen to the allyl double bond XI. The regiospecificity and stereospecificity of the quaternization reactions are confirmed by the data from IR and ^{1}H NMR spectroscopy of VII-X (Table 2). On passing from IV to salts VII-X in the ^{1}H NMR spectra of the salts one observes a shift of the signals of the protons of the pyridine ring and of the alkyl substituents bonded to it to weak field (for IVa and VIIa $\Delta\delta$ = 0.63-0.71 ppm and $\Delta\delta$ = 0.46 ppm, respectively), which constitutes evidence for delocalization of the positive charge in the pyridinium ring.



VII a Hal = Br, R^1=H, R^2=CH_3; b Hal=I, R^1=H, R^2=CH_3; c Hal=Br, R^1,R^2=$(CH_2)_4$;
VIII a Hal=Br; b Hal=I; IX a R^1=H, R^2=CH_3; b R^1, R^2=$(CH_2)_4$

We made stereochemical correlations of this reaction on the basis of ^{1}H NMR spectroscopic data and a comparison of them with previously obtained data from ^{1}H NMR spectra and x-ray diffraction analysis of thiazolo[3,2-a]pyridinium salts [3, 6, 7]. The signals of the protons of the HalCHCHCHS fragment of VIII and X show up at 4.64-4.73, 6.03-6.11, and 4.75-4.79 ppm, respectively. The signal of the 4a-H_a proton shows up in the form of a quartet with spin-spin coupling constant (SSCC) $^3J_{cis}$ = 5.5-5.8 Hz and $^3J_{trans}$ = 10.1-10.2 Hz. The assignment of the SSCC in the group of HalCHCHCHS protons was made on the basis of double NMR experiments with VIII and X. In the case of irradiation at the frequency of the 10a-H_a proton the components of the quartet of the signal of the 4a-H_a proton contract to a doublet with a greater SSCC, whereas in the case of irradiation at the frequency of the 4-H_a proton they contract to a doublet with a smaller SSCC. Consequently, the 4a-H_a and 10a-H_a protons have SSCC ^3J = 5.5-5.8 Hz, and the 4-H_a and 4a-H_a protons have SSCC ^3J = 10.1-10.2 Hz. The calculated (from the Karplus–Conroy equation [11]) dihedral angles $\varphi_{4a\text{-}H_a,10a\text{-}H_a}$ = 48-50° and $\varphi_{4a\text{-}H_a,4\text{-}H_a}$ = 149° of VIII and X (Table 2) correlate well with the experimentally found angles in the previously described hexahydrobenzothiazolo[3,2-a]pyridinium salts [3, 6, 7] and provide evidence that the 4a-H_a and 10a-H_a protons are cis-diaxially oriented, while the 4-H_a and 4a-H_a protons are trans-diaxially oriented.

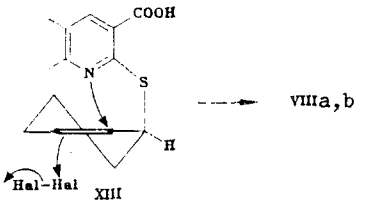
TABLE 2. Characteristics of Thiazolo[3,2-*a*]pyridinium Salts VIIa-c, VIIIa, b, IXa, b, X, and XVI

Compound	Empirical formula	mp, °C (solvent)	IR spectrum, ν, cm^{-1}	^1H NMR spectrum, δ, ppm SSCC (J, Hz)	Calc. dihedral angle, φ°	Yield, %
VIIa	$C_{10}H_{11}Br_4NO_2S$	150 (dec.)	1704	2,95 (3H, s, CH_3); 3,77, 3,90 (2H, m, $BrCH_2$); 3,99 (2H, m, SCH_2); 6,06 (1H, m, NCH); 7,77 (1H, d, $C_{(6)}H$, ^3J=8,2 Hz); 8,72 (1H, d, $C_{(7)}H$)	—	95
VIIb	$C_{10}H_{11}I_4NO_2S$	190...195 (nitromethane)	1702	2,92 (3H, s, CH_3); 3,68, 3,82 (2H, m, CH_2); 3,93 (2H, m, SCH_2); 6,02 (1H, m, NCH); 7,78 (1H, d, $C_{(6)}H$, ^3J=8,1 Hz); 8,70 (1H, d, $C_{(7)}H$)	—	88
VIIc	$C_{13}H_{15}Br_4NO_2S$	155...157 (dec.)	1682	1,76 [4H, m, $(CH_2)_2$]; 2,86 (2H, m, $C_{(6)}$—CH_2); 3,22 (2H, m, $C_{(5)}$—CH_2); 3,72, 3,82 (2H, m, $BrCH_2$); 3,93 (2H, m, SCH_2); 6,10 (1H, m, NCH); 8,68 (1H, s, $C_{(7)}H$)	—	85
VIIIa	$C_{13}H_{15}Br_4NO_2S$	143...145 dec.	1700	1,73, 2,06, 2,28 [6H, m, $(CH_2)_3$]; 3,20 (3H, s, CH_3); 4,72 (1H, m, BrCH); 4,78 (1H, m, SCH); 6,11 (1H, q, $^3J_{4a\text{-}H_a,\ 10a\text{-}H_a}$ =5,7 Hz, $^3J_{4a\text{-}H_a,\ 4\text{-}H_a}$ =10,2 Hz); 7,79 (1H, d, $C_{(7)}H$, ^3J=8,2 Hz); 8,73 (1H, d, $C_{(8)}H$)	49 (4a-H_a, 10a-H_a); 149 (4a-H_a, 4-H_a)	79
VIIIb	$C_{13}H_{15}I_4NO_2S$	195...196 (nitromethane)	1700	1,58, 1,80, 2,05...2,36 [6H, m, $(CH_2)_3$]; 3,22 (3H, s, CH_3); 4,64 (1H, m, ICH); 4,75 (1H, m, SCH); 6,03 (1H, q, $^3J_{4a\text{-}H_a,\ 10a\text{-}H_a}$ =5,5 Hz, $^3J_{4a\text{-}H_a,\ 4\text{-}H_a}$ = =10,2 Hz); 7,77 (1H, d, $C_{(7)}H$, ^3J=8,2 Hz); 8,72 (1H, d, $C_{(8)}H$)	50 (4a-H_a, 10a-H_a); 149 (4a-H_a, 4-H_a)	83
IXa	$C_{10}H_{11}Br_2NO_2S$	320...322 (dec.) (nitromethane)	1705	2,96 (3H, s, CH_3); 3,77, 3,93 (2H, m, $BrCH_2$); 4,00 (2H, m, SCH_2); 6,06 (1H, m, NCH); 7,78 (1H, d, $C_{(6)}H$, ^3J=8,2 Hz; 8,72 (1H, d, $C_{(7)}H$)	—	90
IXb	$C_{13}H_{15}Br_2NO_2S$	241...243 (ethanol)	1692	1,76 [4H, m, $C(H_2)_2$]; 2,85 (2H, m, $C_{(6)}$—CH_2); 3,20 (2H, m, $C_{(5)}CH_2$); 3,74, 3,80 (2H, m, $BrCH_2$); 3,95 (2H, m, SCH_2); 6,08 (1H, m, NCH); 8,62 (1H, s, $C_{(7)}H$)	—	87
X	$C_{13}H_{15}Br_2NO_2S$	193..195 (acetonitrile)	1704	1,76, 2,07, 2,27 [6H, m, $(CH_2)_3$]; 3,12 (3H, s, CH_3); 4,73 (1H, m, BrCH); 4,79 (1H, m, SCH); 6,10 (1H, q, NCH, $^3J_{4a\text{-}H_a,\ 10a\text{-}H_a}$ =5,8 Hz, $^3J_{4a\text{-}H_a,\ 4\text{-}H_a}$ = =10,1 Hz); 7,78 (1H, d, $C_{(7)}H$, ^3J=8,2 Hz); 8,72 (1H, d, $C_{(8)}H$)	48 (4a-H_a, 10a-H_a); 149 (4a-H_a, 4-H_a)	98
XVI	$C_{10}H_{11}ClBr_2NO_6S$	207...208 (nitromethane)	1725	2,97 (3H, s, CH_3); 3,75, 3,90 (2H, m, $BrCH_2$); 4,04 (2H, m, SCH_2); 6,02 (1H, m, NCH); 7,77 (1H, d, $C_{(6)}H$, ^3J=8,2 Hz); 8,72 (1H, d, $C_{(7)}H$)		82

TABLE 3. ^{1}H NMR Spectra of Betaines XIVa-c and XVa, b

Compound	Chemical shift, δ, ppm			$\Delta\delta_{VII, VIII-XIV, XV}$, ppm		
		$C_{(6)}H(C_{(8)}H)$, d	$C_{(7)}H(C_{(9)}H)$, d	Δδ NCH	$\Delta\delta_{C_{(6)}H(C_{(8)}H)}$	$\Delta\delta_{C_{(7)}H(C_{(9)}H)}$
XIVa	6,28, m	8,44	8,88	0,22	0,67	0,16
XIVb	6,19, m	8,40	8,82	0,17	0,62	0,10
XIVc	6,30, m	—	8,80	0,20	—	0,12
XVa	6,22, q	8,01	8,78	0,11	0,22	0,05
XVb	6,09, q	7,97	8,74	0,06	0,20	0,02

Thus, the results of physicochemical analysis provide evidence for the high regioselectivity and stereoselectivity of the reactions involving quaternization of IV to salts VII-X. It is most probable that this selectivity is achieved in transition state XIII through transoid apical overlapping of the donor (the pyridine nitrogen atom) and the acceptor (the halogen molecule) with the π electrons of the allyl fragment. Lateral overlapping of the donor and the acceptor with the π electrons of the allyl fragment can be excluded, since the hydrogen atoms of the CH=CH group of the IVb molecule are coplanar, and the stereochemistry of the reaction products would differ from that examined above.

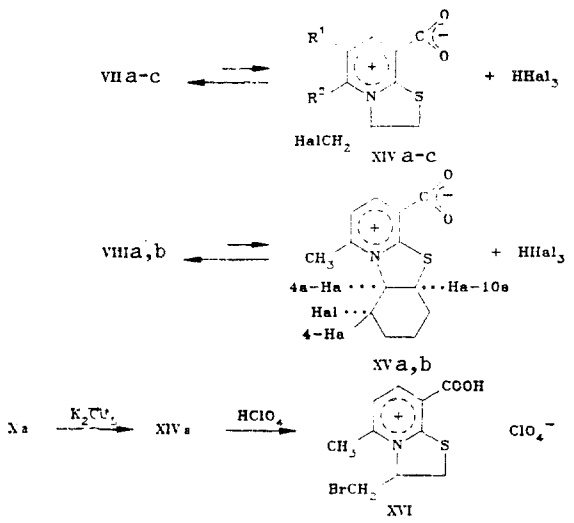


The cleavage of the old bonds and the formation of the new bonds in transition state XIII are evidently accomplished synchronously; the 4a-H_a and 10a-H_a atoms in the VIIIa, b molecules are cis-diaxially oriented, while the 4-H_a and 4a-H_a atoms are trans-diaxially oriented. The cis and trans systems of the hydrogen atoms in the HalCHCHCHS fragment of the VIII and X molecules are a consequence of the trans-diapical N...CH=CH...Hal_2 contact and the strict orientation of the hydrogen atom of the SCH fragment (pseudoaxially relative to the planar part of cyclohexene) in transition state XIII. Electrophilic synchronous addition Ad_E3 is represented in the literature [12, 13] as an unlikely process; however, examples of trimolecular anti addition are known [14]. In this case electrophilic trans quaternization differs from Ad_E3 reactions in that the two reaction centers – the donor and the unsaturated hydrocarbon – enter into one molecule as its fragments, and the existence of transition state XIII therefore has much greater probability than the transition state in Ad_E3 reactions; in this case the realization of the transition state is determined by the electronic nature of the donor and acceptor. The high stereoselectivities of the reactions presented above, as well as the experimentally observed intramolecular contact of the pyridine nitrogen atom with the π electrons of the cyclohexene fragment in 2-(cyclohexen-1-yl)thio-1,5-naphthyridines [6], make it possible to a certain extent to exclude the formation of the bromonium or iodonium complex that is characteristic for electrophilic addition to unsaturated hydrocarbons [15].

The difference between trihalides VII and VIII and their cyanide analogs [6] consists in the fact that they exist in equilibrium with betaines XIV in solutions in d_6-DMSO.

According to ^{1}H NMR spectroscopic data, the VII, VIII ⇄ XIV, X equilibria at 25°C are shifted to favor trihalides VII and VIII, and the ratio of the components was determined as 4-5:1 (see top of following page).

The equilibria under consideration are observed only in the case of trihalides VIIa-c and VIIIa, b; according to ^{1}H NMR spectroscopic data, monohalides IX and X do not give betaines under normal conditions in solutions in d_6-DMSO. The formation of betaines XIV and XV from salts VII and VIII occurs due to bonding of the proton of the carboxy group; conse-



XIV a Hal=Br, R^1=H, R^2=CH_3; b Hal=I, R^1=H, R^2=CH_3; c Hal=Br, R^1,R^2=$(CH_2)_4$;
XV a Hal=Br; b Hal=I

quently, trihalide anions are stronger bases than halide anions, and the hydrogen trihalide acids formed are weaker than the hydrohalic acids. A weak-field shift of the signals of the protons of the pyridine ring and the NCH group occurs in the ^{1}H NMR spectra in the formation of betaines XIV and XV: $\Delta\delta_{C(6)H(C(8)H)}$ = 0.20-0.67, $\Delta\delta_{C(7)H(C(9)H)}$ = 0.02-0.16, and $\Delta\delta_{NCH}$ = 0.06-0.22 ppm (Table 3). The chemical shifts of the signals of the protons of the alkyl groups bonded with the benzothiazolo[3,2-a]pyridinium system remain unchanged; the SSCC and, consequently, the conformations of the heterorings do not change. The $C_{(6)}H$ or $C_{(8)}H$ protons are subject to the greatest deshielding and polarization in the formation of betaines. According to ^{1}H NMR spectroscopic data, complete conversion to betaine XIV occurs when potassium carbonate is added to a solution of IXa in d_6-DMSO. We were unable to obtain and isolate in its individual state betaine XIVa by treatment of bromide IXa with potassium carbonate in absolute ethanol or ether because of the hygroscopicity of the desired product. However, perchlorate XVI is formed in high yield when a solution of betaine XIVa in ethanol is treated with perchloric acid.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The ^{1}H NMR spectra of solutions in d_6-DMSO were obtained with a Bruker WM-250 spectrometer (250 MHz) with tetramethylsilane (TMS) as the internal standard. The course of the reactions and the individuality of the compounds obtained were monitored by TLC on Silufol UV-254 plates in an acetone–hexane system (3:5).

Compound I was obtained by the method in [16], while Va-c were obtained by the methods in [3, 4]. The results of elementary analysis of the compounds obtained for C, H, N, Hal, and S were in agreement with the calculated values.

Substituted 2-Allyl(2-cyclohexen-1-yl)thionicotinic Acids IVa, b. A) A 5.6-ml sample of a 10% solution of KOH in water and 10 ml of the corresponding bromoalkene II were added dropwise successively to a solution of 10 mmole of I in 15-20 ml of methanol, and the reaction mixture was stirred for 1 h. It was then diluted with 15-20 ml of water, and the precipitate was separated.

B) A solution of 5 mmole of the corresponding V in 12 ml of 48% hydrobromic acid was refluxed for 2 h, after which it was cooled to 25°C and made alkaline with 10 ml of a 15% solution of sodium carbonate, and the precipitate was separated. Data on Iva-c obtained by methods A and B are presented in Table 1.

2-Allylthio-6-methyl-3-cyanopyridinium Perchlorate (VI). A 2.5-mmole sample of Va was added to a solution of 1.2 g of 50% $HClO_4$ and 3.4 g of acetic anhydride in 8 ml of acetic acid, and the solution was stirred for 1 h at 25°C. It was then filtered through a fluted filter, and the filtrate was cooled to −4°C and diluted with 15 ml of ether. The resulting precipitate was removed by filtration and washed with ether (Table 1).

Substituted Thiazolo[3,2-a]pyridinium Trihalides VII and VIII. A solution of 6 mmole of the halogen in 10-20 ml of chloroform was added with stirring at 25°C to a solution of 3 mmole of the corresponding IV in 10 ml of dry chloroform, after which the mixture was stirred for another 30 min, and the precipitate was separated. Data on VII and VIII are presented in Table 2.

Substituted Thiazolo[3,2-a]pyridinium Bromides IX and X. A 1-ml sample of acetone or acetophenone was added to a suspension of 2 mmole of the corresponding thiazolo[3,2-a]pyridinium tribromide VIIa, c or VIIIa in 5 ml of chloroform, after which the mixture was stirred for 30 min, and the precipitate was separated (Table 2).

Phenacyl Bromide. A solution of 20 mmole of acetophenone and 0.02 g of X in 10 ml of methanol was brominated with 20 mmole of Br_2 with stirring at 25°C for 15 min. The colorless solution was maintained at −4°C for 12 h, and the resulting precipitate was removed by filtration and washed with 5 ml of 50% methanol. The yield was 3.1 g (78%), and the product had mp 51°C.

3-Bromomethyl-5-methyl-8-carboxy-2,3-dihydrothiazolo[3,2-a]pyridinium Perchlorate (XVI). A suspension of 5 mmole of IX and 2.5 mmole of potassium carbonate in 15 ml of absolute ethanol was stirred for 1.5 h at 25°C, after which the solution was filtered through a fluted filter, and 2 ml of 70% perchloric acid was added to the filtrate. The reaction mixture was maintained at −4°C for 3 h, after which it was diluted with 10 ml of ether, and the precipitate was removed by filtration (Table 2).

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