STEREOCHEMISTRY OF ELECTROPHILIC ANNELATION OF 2-ALLYL- (AND 2-CYCLOHEXEN-1-YL)THIO-1,5-NAPHTHYRIDINES TO THIAZOLO]3,2-a]-1,5-NAPHTHYRIDINIUM SALTS

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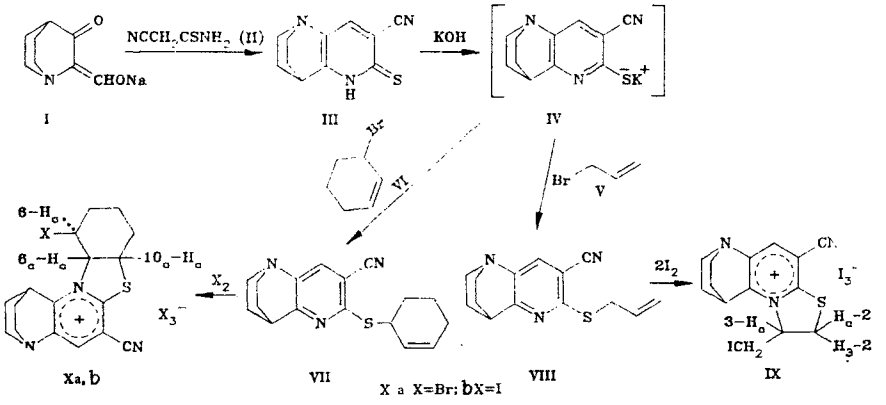
Methods have been developed for the synthesis of 3-cyano-5,8-ethano-5,6,7,8-tetrahydro-1,5-naphthyridine-2(1H)-thione and 2-allyl- (and 2-cyclohexen-1-yl)thio-1,5-naphthyridines, and their structures have been studied. X-ray diffraction examination has shown that these compounds contain a disordered contact between the free electron pair of the pyridine nitrogen and the π-bond of the allyl grouping, so that they react stereoselectively with halogens to give thiazolo[3,2-a]-1,5-naphthyridinium salts.

We have shown previously [1, 2] that electrophilic quaternization of 2-allyl- (and 2-cyclohexen-1-yl)thio- (and seleno)pyridines to give thiazolo- (and selenazolo)[3,2-a]pyridinium salts proceeds stereoselectively as the trans-reaction. It was assumed that the high stereoselectivity of the reaction was favored in the transition state by donor-acceptor interactions between the p-orbital of the pyridine nitrogen, the π-bond of the allyl system, and the positively charged dipole of the halogen molecule.

We now report the preparation of 2-allyl- (and 2-cyclohexen-1-yl)thio-3-cyano-5,8-ethano-5,6,7,8-tetrahydro-1,5-naphthyridine and -3-cyano-2(1H)-quinuclidino[3,2-b]pyridinethione, and discuss the stereochemical features of their quaternization to thiazolo[3,2-a]-1,5-naphthyridinium salts.

Condensation of the sodium salt of 2-formyl-3-quinuclidone (I) with cyanothiacetamide in ethanol in the presence of acetic acid afforded 1,5-naphthyridine-2(1H)-thione (III). The reaction was regioselective, no other reaction products being found, owing to the electrophilicity of the sp^2-hybridized carbon atoms in the NaO–CH=C–C=O chain in these compounds.



Reaction of the 1,5-napthyridine-2(1H)-thione (III) with the unsaturated haloalkanes (V) and (VI) in DMF in the presence of KOH gave 2-allylthio- and 2-(2-cyclohexen-1-yl)thio-1,5-naphthyridines (VII) and (VIII), respectively. The alkylation was regioselective, apparently owing to the involvement of the anion of the potassium salt (IV) formed in the reaction, in which the sulfur atom bears a formal negative charge, as in morpholinium 5-acetyl-1,4-dihydro-

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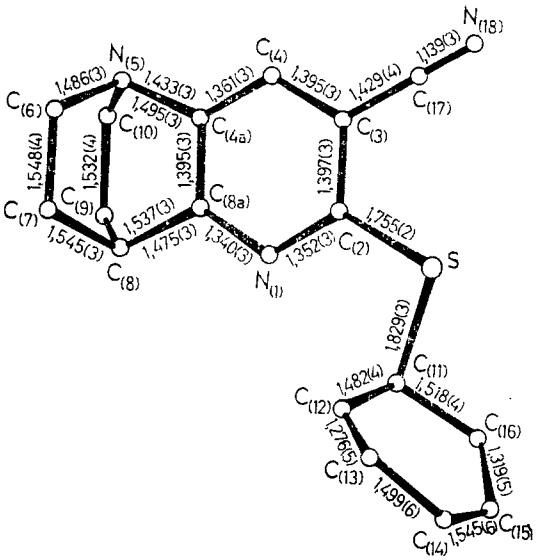


Fig. 1. Projection of the molecule of (VII) on to its mean plane, with bond lengths.

6-methyl-4-(2-nitrophenyl)-3-cyanopyridyl-2-thiolate and other pyridinethiolates [3, 4]. The reaction involves bimolecular nucleophilic substitution. Thus, the corresponding allyl compounds undergo various rearrangements (allyl, 3,3-sigmatropic, etc.)P [5]. In these reactions, however, the sole products are 2-allylthio- and 2-(2-cyclohexen-1-yl)thiopyridines.

The IR spectra of (VII) and (VIII) show characteristic absorption for CN and C=C at 2228-2230 and 1645-1646 cm^{-1}, respectively. The PMR spectra of these compounds contain signals for the protons of the quinuclidine and pyridine fragments and the allyl and cyclohexenyl substituents (Table 1).

In order to confirm the structures of (III), (VII), and (VIII), and to establish the stereochemical features of this electrophilic quaternization, an x-ray diffraction study of (VII) was carried out. It was found to be 2-(2-cyclohexen-1-yl)thio-3-cyano-5,8-ethano-5,6,-7,8-tetrahydro-1,5-naphthyridine (Fig. 1, and Tables 2 and 3).

The molecule of (VII) is found to contain a virtually planar (to within 0.016(1) Å) fragment which incorporates the pyridine heterocycle and the adjacent atoms S, $N_{(5)}$, $C_{(8)}$, $C_{(17)}$, $N_{(18)}$ (plane 1). The planar fragments $N_{(5)}C_{(6)}C_{(7)}C_{(8)}$ (plane 2) and $N_{(5)}C_{(10)}C_{(9)}C_{(8)}$ (plane 3) form dihedral angles with plane 1 of 120.2 and 59.6°, respectively (the dihedral angle between planes 2 and 3 is 60.5°, Fig. 2). Hence, the quinuclidine heterocycle possesses approximately the characteristic C_{3v} symmetry.

The $C_{(2)}$–S bond length of 1.755(2) Å is normal for the $C_{(sp^2)}$–S bond [6], is the same as the C–S bond length in the related pyridyl-1-thio-β-D-glucopyranoside (1.759(3) Å) [7], and indicates the absence of conjugation between the lone pair of the sulfur and the heterocycle. The S–$C_{(11)}$ bond length (1.829(3) Å) is close to the standard value for S–$C_{(sp^2)}$ (1.817 Å [8], and is slightly greater than in the glucopyranoside (1.793(3) Å) [7].

The bond lengths in the pyridine heterocycle have the usual values, and are the same as in unsubstituted pyridine [9] and the glucopyranoside.

The cisoid disposition of the $N_{(1)}$–$C_{(2)}$ and S–$C_{(11)}$ bonds in the $N_{(1)}C_{(2)}SC_{(11)}$ fragment ($N_{(1)}C_{(2)}SC_{(11)}$ torsion angle 2.9°) results in the nonvalent contacts $N_{(1)}\ldots C_{(12)}$, 3.246(4) Å and $N_{(1)}\ldots C_{(11)}$ 2.883(4) Å, which are comparable with the sum of the van der Waals radii of N and C (3.25 Å [10]). In fact, the dihedral angle between the plane of the pyridine heterocycle and the planar fragment $C_{(11)}$, $C_{(12)}$, $C_{(13)}$, $C_{(14)}$ (maximum departure of the atoms from the mean plane, 0.096(8) Å), is 72.9°, i.e., close to the value of 90° which is favored for this interaction.

Compounds (VII) and (VIII) react stereoselectively with halogens in chloroform to give the salts (IX) and (X). This is confirmed by comparison of the IR and PMR spectra with the physicochemical data for previously-obtained thiazolo[3,2-a]thiazolium salts [1, 2]. Comparison of the IR spectra of salts (IX) and (X) with those of (VII) and (VIII) shows that the CN

TABLE 1. Characteristics of 1,5-Naphthyridines (III), (VII-IX), and (Xa, b)

Compound	Empirical formula	mp, °C	IR spectrum, $\nu_{C=N}$, cm^{-1}†	PMR spectrum (in DMSO-D_6), δ, ppm (J, Hz)	Calculated dihedral angle φ, deg	Yield, %
III	$C_{11}H_{11}N_3S$	234...235	2230	1,54, 1,88 (4H, m, 7-CH_2, 9-CH_2); 2,50‡, 3,18 (4H, m, 6-CH_2, 10-CH_2); 3,20 (1H, m, 8-H); 7,54 (1H, s, 4-H)	—	65
VII	$C_{17}H_{19}N_3S$	131...133	2228	1,68, 2,06 [10H, m, $(CH_2)_3$, 7-CH_2, 9-CH_2]; 2,68, 3,20 (4H, m 6-CH_2, 10-CH_2); 3,33 (1H, m, 8-H); 4,78 (1H, m, SCH); 5,85, 5,94 (2H, m, CH=CH); 7,47 (1H, s, 4-CH)	—	80
VIII	$C_{14}H_{15}N_3S$	66...67	2230	1,65, 2,03 (4H, m, 7-CH_2, 9-CH_2); 2,64, 3,17 (4H, m, 6-CH_2, 10-CH_2); 3,24 (1H, m, 8-H); 3,75 (2H, d, SCH_2, ^3J=7); 5,19 (1H, d.d. CH_2=CH, $^3J_{cis}$=10); 5,32 (1H, d, q. CH_2=CH, $^3J_{trans}$=17,5); 5,98 (1H, m, $CH=CH_2$); 7,48 (1H, s, 4-H)	—	88
IX	$C_{14}H_{15}I_4N_3S$	179...182	2248	1,70, 2,12 (4H, m, 7-CH_2, 9-CH_2); 2,60‡, 3,22 (4H, m, 6-CH_2, 10-CH_2); 3,48 (1H, q, J_{CH}, ^2J=11,3, ^3J=3); 3,69 (1H, q, J_{CH}, ^2J=11,3, ^3J=9,5); 4,04 (1H, d, 2-H_a, ^2J=12,5); 4,25 (1H, q, 2-H_a, ^2J=12,5, ^3J=8,2); 3,79 (1H, quint, 5-H); 6,2 (1H, sext, 3-H_a); 8,66 (1H, s, 9-H)	$\varphi_{CH,\ 3\text{-}H_a}$=69; $\varphi_{CH,\ 3\text{-}H_a}$=145; $\varphi_{2\text{-}H_a,\ 3\text{-}H_a}$=138	87
Xa	$C_{17}H_{19}Br_4N_3S$	147...148	2249	1,78, 2,09, 2,40 [10H, m, $(CH_2)_3$, 3-CH_2, 4a-CH_2]; 2,63, 3,30 (4H, m, 2-CH_2, 1a-CH_2); 3,96 (1H, m, 4-H); 4,84 (1H, m, 6-H_a); 5,08 (1H, m, 10a-H_a); 6,33 (1H, d.d, 6a-H_a, $^3J_{6a\text{-}H_a,\ 10a\text{-}H_a}$=5,5, $^3J_{6a\text{-}H_a,\ 6\text{-}H_a}$=9,8); 8,67 (1H, s, 12-H)	$\varphi_{6a\text{-}H_a,\ 10a\text{-}H_a}$=50; $\varphi_{6a\text{-}H_a,\ 6\text{-}H_a}$=147	70
Xb	$C_{17}H_{19}I_4N_3S$	166...168	2244	1,78, 2,07, 2,38‡ [10H, m, $(CH_2)_3$, 3-CH_2, 4a-CH_2]; 2,62, 2,27 (4H, m, 2-CH_2, 1a-CH_2); 3,94 (1H, quint, 4-H); 4,79 (1H, m 6-H_a); 5,03 (1H, m, 10a-H_a); 6,28 (1H, d.d, 6a-H_a, $^3J_{6a\text{-}H_a,\ 10a\text{-}H_a}$=5,1; $^3J_{6a\text{-}H_a,\ 6\text{-}H_a}$=10,5); 8,68 (1H, s, 12-H)	$\varphi_{6a\text{-}H_a,\ 10a\text{-}H_a}$=53; $\varphi_{6a\text{-}H_a,\ 6\text{-}H_a}$=151	82

*Compounds (III), (IX), and (Xb) were crystallized from nitromethane, and (VII) and (VIII) from hexane. (Xa) was not crystallized, since it decomposed on heating in solvents.
†For (VII): $\nu_{C=C}$ absorption at 1645 cm^{-1}; for (VIII): $\nu_{C=C}$ absorption at 1646 cm^{-1}.
‡Partially overlapping the signals for the DMSO protons.

TABLE 2. Valence Angles (ω) in (VII)

Angle	ω°
$C_{(2)}SC_{(11)}$	102,7(1)
$C_{(2)}N_{(1)}C_{(8a)}$	117,0(2)
$N_{(1)}C_{(2)}C_{(3)}$	122,2(2)
$N_{(1)}C_{(2)}S$	119,2(2)
$SC_{(2)}C_{(3)}$	118,5(2)
$C_{(2)}C_{(3)}C_{(4)}$	119,6(2)
$C_{(2)}C_{(3)}C_{(17)}$	119,6(2)
$C_{(4)}C_{(3)}C_{(17)}$	120,8(2)
$C_{(3)}C_{(4)}C_{(4a)}$	118,0(2)
$C_{(4)}C_{(4a)}N_{(5)}$	125,1(2)
$C_{(4)}C_{(4a)}C_{(8a)}$	119,6(2)
$N_{(5)}C_{(4a)}C_{(8a)}$	115,3(2)
$C_{(4a)}N_{(5)}C_{(6)}$	106,6(2)
$C_{(4a)}N_{(5)}C_{(10)}$	106,7(2)
$C_{(6)}N_{(5)}C_{(10)}$	108,6(2)
$N_{(5)}C_{(6)}C_{(7)}$	111,7(2)
$C_{(6)}C_{(7)}C_{(8)}$	108,6(2)
$C_{(7)}C_{(8)}C_{(8a)}$	106,9(2)
$C_{(7)}C_{(8)}C_{(9)}$	107,8(2)
$C_{(8a)}C_{(8)}C_{(9)}$	106,6(2)
$C_{(8)}C_{(8a)}N_{(1)}$	123,1(2)
$C_{(8)}C_{(8a)}C_{(4a)}$	113,3(2)
$C_{(4a)}C_{(8a)}N_{(1)}$	123,6(3)
$C_{(8)}C_{(9)}C_{(10)}$	108,4(3)
$C_{(9)}C_{(10)}N_{(5)}$	112,5(2)
$SC_{(11)}C_{(12)}$	111,8(2)
$SC_{(11)}C_{(16)}$	106,7(2)
$C_{(12)}C_{(11)}C_{(16)}$	112,7(2)
$C_{(11)}C_{(12)}C_{(13)}$	121,4(4)
$C_{(12)}C_{(13)}C_{(14)}$	126,3(4)
$C_{(13)}C_{(14)}C_{(15)}$	109,7(3)
$C_{(14)}C_{(15)}C_{(16)}$	121,4(3)
$C_{(15)}C_{(16)}C_{(11)}$	122,5(3)
$C_{(3)}C_{(17)}N_{(18)}$	177,5(3)

absorption of the salts is shifted towards higher frequencies (2244-2249 cm^{-1}), and the intensity is considerably reduced (Table 1). This is due to delocalization of the positive charge in the pyridine ring, reduction in the π-electron density therein, and consequently a decrease in the extent of conjugation in the CN group. Delocalization of the positive charge in the pyridine ring results in an increase in the polarization of the 4-H and 12-H protons, which is accompanied by a shift of their signals to lower field by $\Delta\delta$ = 1.18-1.21 and $\Delta\delta$ = 0.55-0.63 ppm, respectively, as compared with (VII) and (VIII). The signals for the thiazole ring protons in (IX) constitute an ABB'XX'-system [11], the signals for the protons of the ICH_2 group being seen as two quadruplets at 3.48 and 3.69 ppm with coupling constants ^2J = 11.3, ^3J = 3,and ^3J = 9.5 Hz. This multiplicity for the protons corresponds to the geminal cis- and trans-arrangement of the ICH_2 protons with those of the NCH group. This is in good agreement with the values for the dihedral angles calculated from the Karplus–Conroy equation [11], namely $\varphi_{H_{cis},\,3\text{-}H}$ 68° and $\varphi_{H_{trans},\,3\text{-}H}$ 145°. The signals for the SCH_2 protons are seen as a quadruplet and doublet at δ 4.25 and 4.04 ppm, with coupling constants ^2J = 12.5 and ^3J = 8.2 Hz, respectively. The multiplicity of the SCH_2 protons suggests the geminal and trans-diaxial disposition of the 2-H_a and 3-H_a protons, with a torsion angle $\varphi_{2\text{-}H_a,\,3\text{-}H_a}$ of 138°. The signal for the 3-H_a proton is seen as a sextet at 6.2 ppm. The multiplicity of the signals, their coupling constants, and the calculated values for the dihedral angles show that the 3-H_a proton is oriented axially, and that the ICH_2 group is equatorial. The correctness of the assignments of the coupling constants for the protons of the thiazole ring in (IX) has been confirmed by double NMR. Irradiation at the frequency of the 3-H_a proton resulted in the quadruplets for the 2-H_a and CH_2 protons merging into doublets. Hence, the values for the dihedral angles, the construction of a model of (IX), and comparison of these data with the PMR data and x-ray diffraction analysis of previously-obtained dihydrothiazolo[3,2-a]-pyridines [1, 2] show that the CH_2 group of the thiazole stands out from the plane of all the remaining four atoms, and bearing in mind that the annelated pyridinium ring is planar, that the thiazole ring has the twist conformation.

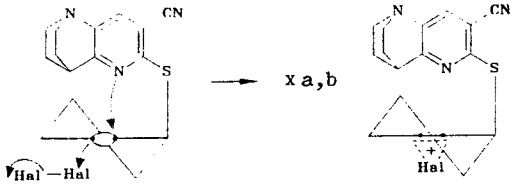
The signals for the protons of the HalCHCHCHS fragment in (Xa, b) are seen at 4.79-4.84, 6.28-6.33, and 5.03-5.08 ppm, respectively. The signal for the 6a-H_a proton occurs as a quadruplet with coupling constants $^3J_{cis}$ = 5.1-5.5 and $^3J_{trans}$= 9.8-10.5 Hz. Assignment of the

TABLE 3. Coordinates ($\times 10^5$ for S, $\times 10^4$ for N and C, $\times 10^3$ for hydrogen atoms) and Isotropic Equivalent Thermal Parameters for Nonhydrogen Atoms (isotropic for hydrogen atoms)

Atom	x	y	z	B_{equ}^{iso}, Å^2
S	35996(5)	3857(1)	64116(5)	5,51(2)
$N_{(1)}$	2163(1)	5158(3)	5500(1)	3,91(6)
$N_{(5)}$	1008(1)	5856(3)	3527(1)	4,9(1)
$N_{(18)}$	4228(2)	2725(4)	5059(2)	8,2(1)
$C_{(2)}$	2830(2)	4421(3)	5547(2)	3,9(1)
$C_{(3)}$	2937(2)	4108(3)	4929(2)	4,3(1)
$C_{(4)}$	2343(2)	4568(4)	4237(2)	4,5(1)
$C_{(4a)}$	1673(2)	5311(3)	4192(2)	3,8(1)
$C_{(6)}$	189(2)	5286(4)	3445(2)	5,6(1)
$C_{(7)}$	50(2)	5590(4)	4123(2)	5,3(1)
$C_{(8)}$	833(2)	6373(4)	4691(2)	4,2(1)
$C_{(8a)}$	1598(2)	5578(3)	4828(2)	3,6(1)
$C_{(9)}$	898(2)	7681(4)	4326(2)	5,6(1)
$C_{(10)}$	1001(2)	7332(4)	3642(2)	5,8(1)
$C_{(11)}$	3176(2)	4443(4)	7025(2)	5,4(1)
$C_{(12)}$	2473(3)	3578(5)	6987(2)	7,8(1)
$C_{(13)}$	2589(5)	2751(8)	7499(3)	16,2(2)
$C_{(14)}$	3260(4)	2844(7)	8286(3)	11,2(2)
$C_{(15)}$	3898(4)	3973(8)	8371(3)	11,2(2)
$C_{(16)}$	3926(3)	4504(7)	7793(2)	9,3(2)
$C_{(17)}$	3663(2)	3341(4)	5016(2)	5,7(1)
$H_{(4)}$	238(2)	455(4)	376(2)	6,6(9)
$H_{(6.1)}$	−29(2)	557(3)	299(2)	5,9(8)
$H_{(6.2)}$	19(2)	438(4)	328(2)	7(1)
$H_{(7.1)}$	−7(2)	464(4)	428(2)	8(1)
$H_{(7.2)}$	−46(2)	611(3)	402(2)	6,4(9)
$H_{(8)}$	77(2)	656(3)	514(1)	4,3(7)
$H_{(9.1)}$	49(2)	815(3)	425(1)	4,3(7)
$H_{(9.2)}$	147(2)	809(4)	471(2)	6,8(9)
$H_{(10.1)}$	166(2)	780(3)	367(2)	5,3(8)
$H_{(10.2)}$	51(2)	775(4)	317(2)	9(1)
$H_{(11)}$	287(2)	541(4)	684(2)	8(1)

coupling constants in the protons of the HalCHCHCHS group was made from the results of double NMR on (Xa, b). Irradiation at the frequency of the 6a-H_a protons resulted in the components of the quadruplet for the 6a-H_a with the greater coupling constant narrowing. The components of the quadruplet for the NCH group with the smaller coupling constant merged into a doublet on irradiation at the frequency of the 10a-H_a proton. Consequently, the 6a-H_a and 10a-H_a protons have coupling constants ^3J = 5.1-5.5 Hz, and the 6-H_a and 6a-H_a protons ^3J = 9.8-10.5 Hz. The dihedral angles $\varphi_{6a\text{-}H_a,\,10a\text{-}H_a}$ = 50...53° and $\varphi_{6a\text{-}H_a,\,6\text{-}H_a}$ = 147...151° calculated for (Xa) and (Xb) from equation [1] correlate well with the experimentally determined angles in previously described hexahydrobenzothiazolo(and selenazolo)[3,2-a]pyridinium salts [1], and show that the 6a-H_a and 10a-H_a protons are cis-diaxial, and the 6-H_b and 6a-H_a protons trans-diaxial.

These physicochemical findings show that the quaternization of (VII) and (VIII) to the salts (IX) and (X) is highly stereoselective. The stereoselectivity factors are built into the starting materials (VII) and (VIII). The observed disordered apical contact of the lone pair of the pyridine nitrogen with the π-electrons of the cyclohexane fragment is enhanced when an acceptor (a halogen molecule) is introduced into the reaction mixture, and in the transition state this disordering disappears. The donor and acceptor groups are in the trans-axial positions relative to the plane of the cyclohexene ring, and show partial apical overlap with the π-electrons of the C=C bond in (XI). Lateral overlapping may be excluded, since the hydrogen atoms of the CH=CH group are coplanar, and the stereochemistry of the reaction products would be other than that described above.



XI Hal = Br, I XII

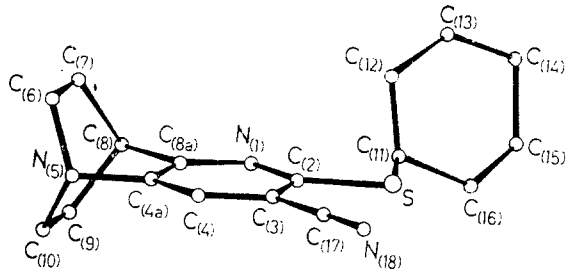


Fig. 2. Mutual orientation of the cyclic fragments in (VII) (projection obtained by rotating Fig. 1 by 70° around the line passing through the centers of bonds $C_{(2)}$–$C_{(3)}$ and $C_{(8a)}$–$C_{(4a)}$, and by 30° around the normal and mean planes of the molecule).

Bond rupture and the formation of new bonds in the transition state (XI) probably occur synchronously, atoms 6-H_a and 6a-H_a adopting the trans-diaxial positions. The high stereoselectivity of the reactions described above and the previously-described analogous quaternizations [1, 2] apparently to some extent enables the formation in these reactions of the complex (XII), which is characteristic of electrophilic addition to unsaturated hydrocarbons, to be avoided [12].

EXPERIMENTAL

The IR spectra of the compounds were obtained on a UR-20 in KBr disks. PMR spectra were recorded on a Bruker WM-250 (250 MHz) in DMSO-D_6, internal standard TMS.

The crystals of (VII) were monoclinic: a = 17,609(4), b = 10.001(3), c = 20.477(3), β = 117.46(1)°, V = 3200.2 Å^3, d_{calc} = 1.23 g/cm^3, Z = 8, space group C 2/sec. The cell parameters and the intensities of 1688 independent reflections with $F^2 > 5\sigma$ were measured at room temperature on an Enraf-Nonius CAD-4 automatic four-circle diffractometer (λMo_{K_a}, graphite monochromator, scanning rate ratio $\omega:\theta$ = 1.2:1.2; θ_{max} = 56°). The structure was calculated directly. Nonhydrogen atoms were refined by full-matrix least squares in anisotropic approximation. Some of the hydrogen atoms were located from the Fourier difference synthesis, and refined isotropically (the H atoms at $C_{(12)}$, $C_{(13)}$, $C_{(14)}$, $C_{(15)}$, and $C_{(16)}$ were not seen). The cyclohexene ring was disordered at two positions of similar population density, differing in rotation by ~180° around the axis $C_{(11)}$–$C_{(14)}$, in consequence of which the double bond occupies positions $C_{(12)}$–$C_{(13)}$ and $C_{(15)}$–$C_{(16)}$. There is also the alternative possibility that the disordering occurs with retention of the double bond at $C_{(12)}$–$C_{(13)}$, but with disordering of $C_{(15)}$ and $C_{(16)}$ at two positions, with the result that the $C_{(15)}$–$C_{(16)}$ bond is effectively shortened. Unfortunately, the impossibility of locating the hydrogen atoms of the cyclohexene ring, and observed the thermal parameters of the ring atoms make it impossible to assign any preference to either of these two types of disordering. The final values of the divergence factors were R = 0.053 and R_w = 0.078. All calculations were carried out on a PDP-11/23 computer using the SDP-PLUS programs [13]. The coordinates and isotropic equivalent thermal parameters are shown in Table 3.

The properties of (III) and (VII-X) are given in Table 1. The elemental analyses for C, H, Hal, N and S were in agreement with the calculated values.

3-Cyano-5,8-ethano-5,6,7,8-tetrahydro-1,5-naphthyridine-2(1H)-thione (III). A mixture of 6.7 g (38 mmole) of the salt (I) (obtained in the usual way [14] from quinuclidone, ethyl formate, and sodium in ether) and 3.8 g (38 mmole) of cyanothioacetamide (II) in 40 ml of ethanol as brought to the boil, treated with 1.5 ml of acetic acid, and filtered through a fluted filter paper. The filtrate was boiled for 30 min, whereupon a solid began to separate. The mixture was cooled, and kept at −5°C for 5 h. The solid was filtered off, washed with ethanol and hexane, and recrystallized from nitromethane to give the naphthyridinethione (III).

2-Allylthio-3-cyano-5,8-ethanol-5,6,7,8-tetrahydro-1,5-naphthyridine (VIII). To a suspension of 0.87 g (4 mmole) of the naphthyridine (III) in 10 ml of DMF were added successively with stirring 2.2 ml of 10% KOH and 0.34 ml (4 mmole) of allyl bromide (V). The mixture was stirred for 20 min, diluted with 10 ml of water, and kept at −5°C for 12 h. The precipitated (VIII) was filtered off, washed with water, air-dried, and recrystallized to give the naphthyridine (VIII).

3-Cyano-2-(2-cyclohexene-1-ylthio)-5,8-ethano-5,6,7,8-tetrahydro-1.5-naphthyridine (VII) was obtained as for (VIII).

Thiazolo[3,2-a]-1,5-naphthyridinium Trihalides (IX), (Xa, b). General Method. To a solution of 5 mmole of the naphthyridine (VII or VIII) in 10 ml of chloroform was added dropwise with stirring at 25°C a solution of 10 mmole of the halogen in 20-60 ml of chloroform, over 10-15 min. The mixture was kept for 12 h at −5°C, and the solid which separated was filtered off and washed with chloroform. Compounds (IX) and (Xb) were recrystallized from nitromethane. The tribromide (Xa) was not crystallized in view of its instability, and was analyzed as quickly as possible.

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