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REACTIONS OF POLYHALOGENOPYRIDINES. 15.* REACTION OF ISOMERIC TETRACHLOROCYANOPYRIDINES AND PENTACHLOROPYRIDINE WITH POTASSIUM ISOPROPYLTRITHIOCARBONATE

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The reaction of isomeric tetrachlorocyanopyridines and pentachloropyridine with potassium isopropyltrithiocarbonate was investigated. It was found that the structure and composition of the reaction products depend both on the initial polychloropyridines and on the solvent in which the process is carried out. The intramolecular transformations of the isopropyltrithiocarbonate derivatives of tetrachloro-2-cyanopyridine in acetonitrile solution lead to 1,3-dithiolo[4,5-c]pyridines. In other cases heterocyclization was not observed. If the reactions were conducted in ethanol (except with tetrachloro-3-cyanopyridine) thioalkylation of the pyridine ring occurred.

In previous communications we examined the synthesis of 1,3-dithiolo[4,5-*c*]pyridines based on the reactions of 2-substituted tetrachloropyridines with the N,N-dialkyldithiocarbamates of alkali metals. In a continuation of investigations into methods for the annellation of sulfur-containing heterocycles to the pyridine ring we studied the reactions of a series of polychloropyridines [tetrachloro-2-cyanopyridine (Ia), tetrachloro-4-cyanopyridine (Ib), tetrachloro-3-cyanopyridine (Ic), and pentachloropyridine (Id)] with potassium isopropyltrithiocarbonate (II).

The reaction conditions and the monitoring methods were similar to those described earlier [1]. In the reaction of the cyanopyridine (Ia) with (II) in acetone only compound (III), i.e., the product from disubstitution of the pyridine ring at positions 3 and 4 by two isopropyltrithiocarbonate fragments (Scheme 1), was obtained. Attempts to detect the monosubstituted derivative (IV) in the reaction mixture were unsuccessful. Chromatographic control of the reaction showed that the disubstituted derivative (III) is formed immediately after the trithiocarbonate (II) is added to an excess of the initial compound (Ia) (without any intermediate products) and is the main component of the reaction mixture [together with the pyridine (Ia)]. Thus, the introduction of one isopropyltrithiocarbonate fragment at position 4 of the pyridine ring substantially accelerates the substitution of the next chlorine atom, situated at position 3. As a result the first stage of substitution becomes the rate-controlling stage of the whole process. No new cyclic derivatives of (III) were subsequently detected when a solution of compound (III) in acetone was heated.

In order to determine the conditions securing heterocyclization of the isopropyltrithiocarbonate derivatives of (Ia) we investigated the reaction of compounds (Ia, II) in other solvents. In ethanol the only reaction product was the 4-isopropylthio derivative (V), while in acetonitrile it was a mixture of four compounds, which were separated and isolated in the individual state by column chromatography. The chromatographically most mobile component of the reaction mixture was a reddish liquid, which represented the S,S-diisopropyl trithiocarbonate (VI). [^{1}H NMR spectrum (deuterochloroform, δ, ppm): 1.41 (6H, dd, Me); 4.05 (1H, m, CH). ^{13}C NMR spectrum: 21.3, 21.5 (Me); 43.4, 43.7 (CH_2); 214.3 (C=S).] The yellow solid (VII), identical with our previously described 4,7-dichloro-6-cyano-1,3-dithiolo[4,5-*c*]pyridine-2-thione [1], was then obtained.

*For Communication 14, see [1].

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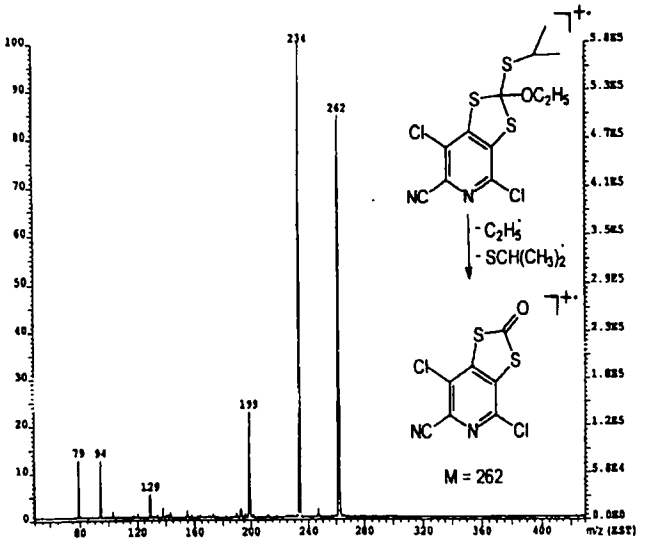


Fig. 1. Collision-activation spectrum of the $[M\text{-}C_2H_5, \text{-}SCH(CH_3)_2]^+$ ion (*m/z* 262) of compound (IX).

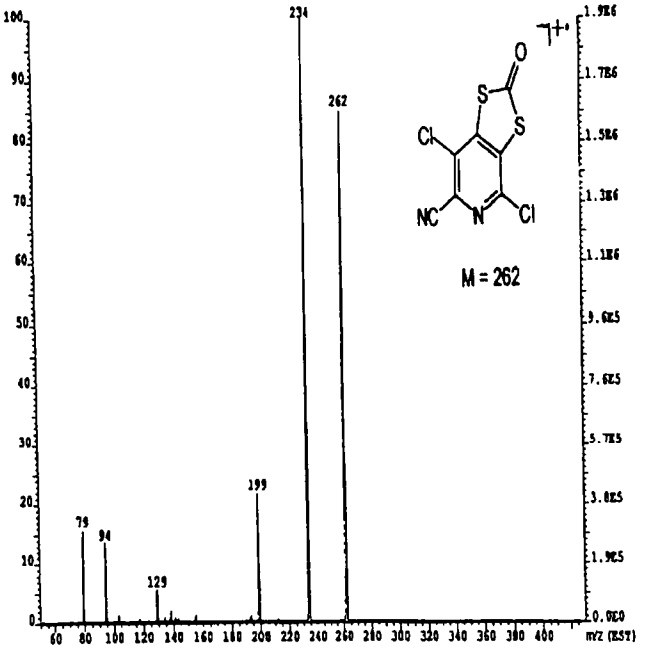
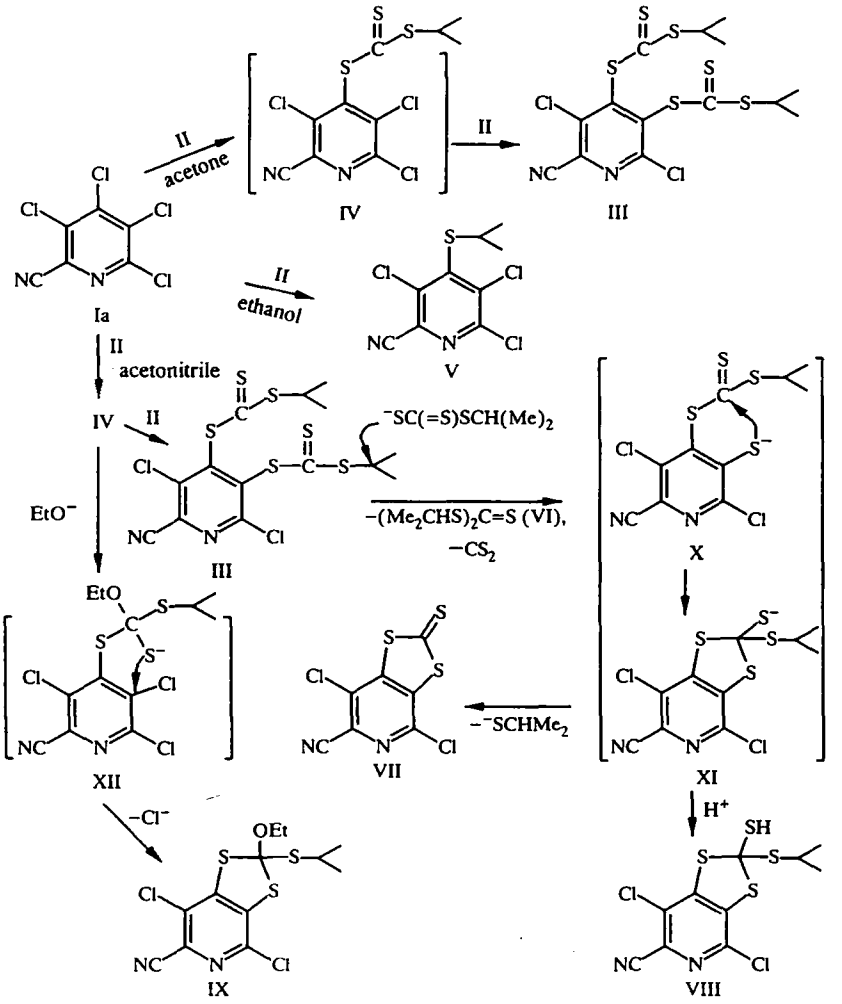


Fig. 2. Collision-activation spectrum of the M^+ ion (*m/z* 262) of 4,7-dichloro-6-cyano-1,3-dithiolo[4,5-*c*]pyridin-2-one [1].

Apart from this bicyclic compound the reaction mixture also contained two other derivatives (VIII, IX) substituted at position 2 in the dithiole ring of 1,3-dithiolo[4,5-*c*]pyridine. The probable mechanisms of the formation of compounds (V-IX) are shown in Scheme 1. Whereas in ethanol position 4 of the pyridine ring in the polychloropyridine (Ia) is initially substituted by the isopropyltrithiocarbonate group with the formation of the intermediate (IV), followed by the loss of a CS_2 molecule as a result of intramolecular redistribution of the bonds [1], in acetone the initial compound (Ia) is disubstituted by isopropyltrithiocarbonate fragments at positions 3 and 4 of the pyridine ring without further transformations of compound (III), and in acetonitrile solution further heterocyclization of both monosubstituted and disubstituted derivatives (IV, III) occurs. According to the proposed mechanism, the reaction of the isopropyltrithiocarbonate anion with one of the sulfur-containing substituents at position 3 or 4 of the pyridine ring of compound (III) takes place initially through the removal of the isopropyl

group with the formation of S,S'-diisopropyl trithiocarbonate (VI) and the subsequent loss of a carbon disulfide molecule. As a result the intermediates (X) appear in the reaction medium. Intramolecular reactions of the latter can lead the heterocyclic thiolate (XI), which is converted either into the thiol (VIII) (during acidification) or into the thiocarbonyl derivative (VII) (with the elimination of the isopropanethiolate anion). Highly unexpected for us was the isolation of compound (IX), containing an ethoxy group at position 2 of the 1,3-dithiole ring, from the reaction mixture (albeit with a yield of only 5-6%). Analysis of the initial potassium isopropyltrithiocarbonate (II) by ^{1}H NMR showed the presence of a small amount (about 5%) of potassium ethoxide, remaining from the synthesis of the reagent. It can be supposed that the formation of compound (IX) from the monosubstituted derivative (IV) results from its reaction with the ethoxide anion through the intermediate (XII) followed by heterocyclization of the latter.

Scheme 1



Whereas the protons of the two isopropyl groups of compound (III) appear in the PMR spectra in the form of only two overall signals [a doublet at 1.43 (Me) and a CH multiplet at 4.08 ppm], the ^{13}C NMR spectrum contains a pair of signals for the carbon atoms of the two isopropyltrithiocarbonate groups in the regions of 21.5, 44.1-44.3, and 213.8-215.3 ppm, belonging to the methyl, methine, and thiocarbonyl groups respectively. The chemical shifts of the pyridine carbon atoms have values similar to those obtained previously for the analogous bisethylxanthate derivatives [1], and their assignment does not therefore give rise to difficulty. The isopropyl group directly attached to the pyridine ring [compound (V)] gives two signals each in the NMR spectra: in the PMR spectra a doublet for the methyl protons at 1.33 and a quartet for the CH protons at 3.88 ppm; in the ^{13}C NMR spectrum signals at 23.3 (Me) and 40.8 ppm (CH). The localization of the S-alkyl substituent at position 4 was determined from the substantial downfield shift of the signals for the $C_{(3)}$, $C_{(4)}$, and $C_{(5)}$ atoms of the initial (Ia), which is typical of the trifluoromethyl analog of compound (V) [5]. From the chemical shifts of the pyridine carbon atoms in tetra-

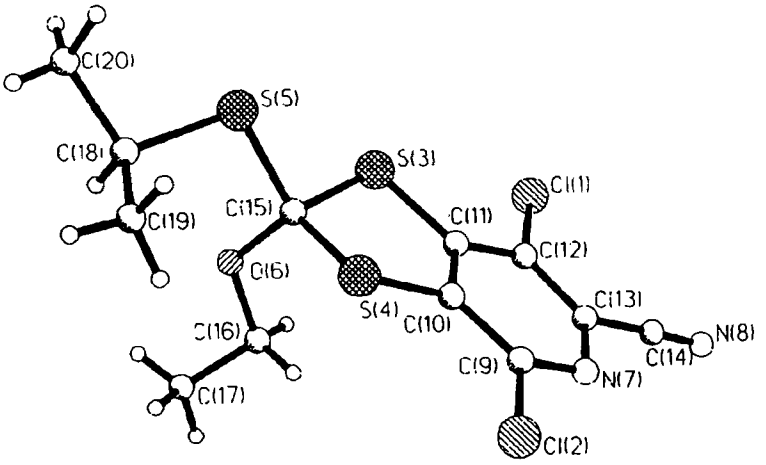


Fig. 3. Molecular structure of 4,7-dichloro-2-isopropylthio-6-cyano-2-ethoxy-1,3-dithiolo[4,5-*c*]pyridine (IX).

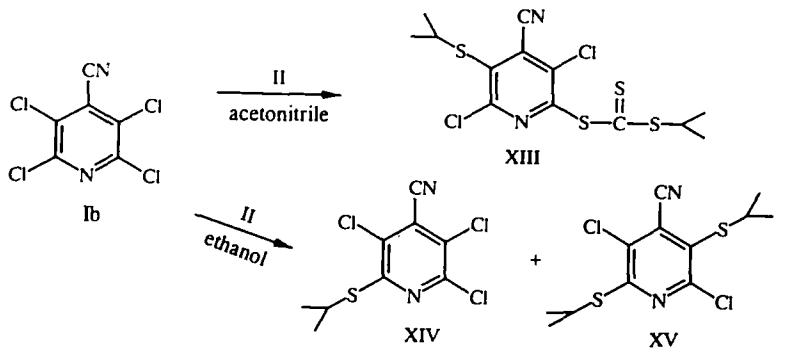
chloro-2-cyanopyridine (Ia) [6] we calculated the effects of substitution of the chlorine atom by the isopropylthio group in compound (V): $C_{(2)}$ +1.3; $C_{(3)}$ +5.5; $C_{(4)}$ +5.4; $C_{(5)}$ +6.4; $C_{(6)}$ +1.1 ppm. The derivatives of 1,3-dithiolo[4,5-*c*]pyridine (VIII, IX) have fairly similar chemical shifts for the pyridine carbon atoms. (The latter can be assigned easily by means of the data in [1].) The ^{13}C NMR spectra of these compounds contain signals for the quaternary carbon atoms of the 1,3-dithiole ring at 84.2 (VIII) and 111.6 ppm (IX), for the isopropyl group in the region of 23.6-24.3 (Me) and 39.3-41.0 ppm (CH), and for the ethoxy group of (IX) at 14.3 (Me) and 63.6 ppm (CH_2). The protons of the S-isopropyl substituents were detected in the PMR spectra of both dithiolopyridines (VIII) and (IX), and the protons of the ethoxy group were also detected in the latter.

Mass-spectrometric analysis of compound (IX) showed that its molecular ion M^+ is unstable and dissociates in a number of directions. One of the most stable is the ion with *m/z* 262. High-resolution mass spectrometry showed that this fragment is formed during the removal of the isopropylthio and ethyl radicals from M^+ (calculated 261.88290, found 261.88274). In order to determine its structure we obtained its collision-activation spectrum (Fig. 1). Comparison with the collision-activation spectrum of the molecular ion of 4,7-dichloro-6-cyano-1,3-dithiolo[4,5-*c*]pyridin-2-one [1] (Fig. 2) shows that they are fully identical, demonstrating that these compounds have identical structures. Thus, the structure assigned to compound (IX) is supported by experiment.

The structure of the molecules of compound (IX) was proved finally by x-ray crystallographic analysis. The general appearance of the molecule of (IX) is shown in Fig. 3, and the bond lengths and angles are given in Table 2. The five-membered dithiole fragment of the molecule is not planar but is bent along the S···S line by 26.8° toward the substituent at the $C_{(15)}$ atom. The plane of the EtO group is orthogonal to the plane of the three $S_{(3)}$, $C_{(15)}$, and $S_{(4)}$ atoms and has a bisector orientation in relation to it — the $C_{(16)}O_{(6)}C_{(15)}S_{(4)}$ torsion angle is 64.1°. The orientation of the $SCH(Me)_2$ group in relation to the dithiole ring is characterized by the following torsion angles: $C_{(18)}S_{(5)}C_{(15)}S_{(4)}$ −86.3°, $C_{(15)}S_{(5)}C_{(18)}C_{(20)}$ 187.7°.

As seen in the case of the reaction of compound (Ia) and isopropyltrithiocarbonate (II), the reaction in acetonitrile promoted heterocyclization, whereas the S-alkyl derivatives were obtained in ethanol. This is of interest as a method for the thioalkylation of polychloropyridines. The next experiments with the polychloropyridines (Ib-d) were conducted in acetonitrile in order to secure the maximum probability of cyclization or in ethanol in order to develop a method for S-alkylation. In the case of tetrachloro-4-cyanopyridine (Ib) in acetonitrile disubstitution by the isopropyltrithiocarbonate fragments occurs first at positions 2 and 5 of the pyridine ring with the subsequent loss of a carbon disulfide molecule and the formation of compound (XIII). In ethanol two compounds were obtained, i.e., the 2-isopropylthio- and 2,5-bisisopropylthio derivatives (XIV) and (XV) (Scheme 2). Their NMR spectra revealed respectively one and two isopropylthio groups directly attached to the pyridine ring. The signals of the pyridine carbon atoms were assigned by means of the long-range spin—spin coupling constants that we discovered between the methine protons of the isopropylthio groups and the carbon atoms in contact with them in the proton-coupled ^{13}C NMR spectra. This coupling shows up in the form of doublets with $^3J_{C(2)-H}$ = 1.85 Hz at 158.7 ppm ($C_{(2)}$) for (XIV) and $^3J_{C(2)-H}$ = 3.30 Hz and $^3J_{C(5)-H}$ = 1.45 Hz at 160.5 ppm ($C_{(2)}$) and 127.2 ppm ($C_{(5)}$) for (XV).

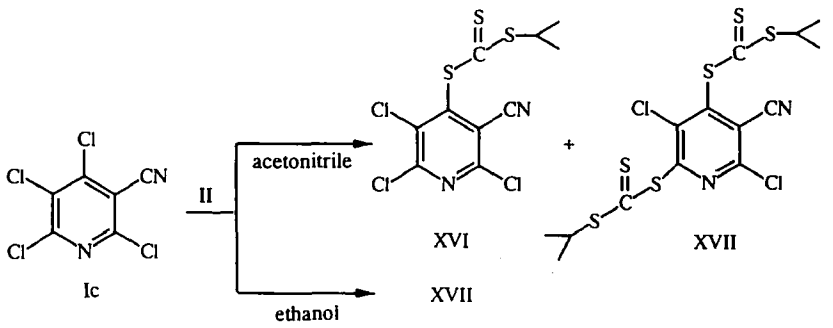
Scheme 2



As a result the effects of substitution of the chlorine atom at position 2 by an isopropylthio group in relation to the chemical shifts of the carbon atoms of the initial compound (Ib) were calculated: $C_{(2)}$ +11.5; $C_{(3)}$ −2.6; $C_{(4)}$ +0.3; $C_{(5)}$ −9.2; $C_{(6)}$ 0 ppm. The following increments were obtained during substitution of the second chlorine atom at position 5: $C_{(2)}$ +1.8; $C_{(3)}$ −0.4; $C_{(4)}$ +3.2; $C_{(5)}$ +4.4; $C_{(6)}$ +7.0 ppm. In the light of the presented data it was possible to assign the signals of the pyridine carbon atoms in compound (XIII). In its spectrum, although it contained the signals of the isopropylthio and isopropyltrithiocarbonate groups, substantial differences were found in the chemical shifts of the heterocyclic carbon atoms compared with the ethylthio and ethylxanthate analogs [1]. (This applies particularly to the signal of $C_{(5)}$.) The substantial downfield shift of this signal can only be explained by the presence of the isopropyl group at position 5. We note that compound (XIII) does not undergo subsequent cyclizations during heating, i.e., analogies with the N,N-dialkyldithiocarbamate derivatives of pyridine (Ib) were not found in this case [2].

During the reaction of the initial compound (Ic) with the reagent (II) in acetonitrile 4-mono- and 4,6-disubstitution of the pyridine ring by the isopropyltrithiocarbonate substituent occur with the formation of compounds (XVI, XVII), while in ethanol only the disubstitution product (XVII) was isolated (Scheme 3). As expected, the isopropyltrithiocarbonates (XVI, XVII) do not undergo further cyclizations when heated in a solvent.

Scheme 3



The ^{1}H and ^{13}C NMR spectra of compounds (XVI, XVII) contain the signals of one and two isopropyltrithiocarbonate groups respectively (Table 1), as seen in the latter case from the presence of two signals for the thiocarbonyl carbon atoms. The signals of the pyridine carbon atoms were assigned by analogy with the corresponding S-ethylxanthate derivatives (Ic), the NMR spectra of which were described in the previous communication [1]. The effects of substitution of one chlorine atom at position 4 by the isopropyltrithiocarbonyl group in compound (XVI) in relation to the chemical shifts of the initial compound (Ic) [4] are as follows: $C_{(2)}$ +1.1; $C_{(3)}$ +5.1; $C_{(4)}$ −1.0; $C_{(5)}$ +6.4; $C_{(6)}$ +2.0 ppm. Substitution of the second atom at position 2 leads to the following effects $C_{(2)}$ +0.4; $C_{(3)}$ +0.6; $C_{(4)}$ −0.9; $C_{(5)}$ +4.0; $C_{(6)}$ +4.6 ppm. Comparative analysis of these increments and of previously obtained data [1] confirms the conclusion about the analogous effects of the S-alkyldithiocarbonate and alkyltrithiocarbonate substituents at equivalent positions of polychloropyridines.

TABLE 1. Spectral Characteristics of Compounds (III, V, VIII, IX, XIII-XIX)

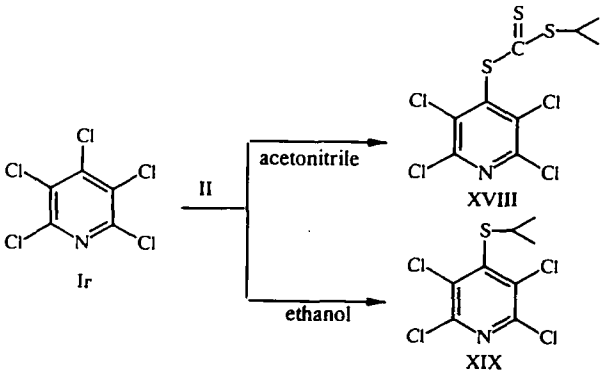
Compound	^{13}C NMR spectra, δ, ppm						^{1}H NMR spectra, δ, ppm
	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	other C atoms	
III	155,3	139,6	151,3	139,8	133,6	21,5, 21,6 (Me); 44,1, 44,3 (CH); 113,3 (CN); 213,8, 215,3 (C=S)	1,43 (6H, d, Me); 4,08 (1H, q, CH)
V	149,8	141,0	149,4	140,2	130,4	23,3 (Me); 40,8 (CH); 114,3 (CN)	1,33 (6H, d, *J* = 6,7 Hz, Me); 3,88 (1H, q, CH)
VIII	151,0	128,1	140,7	140,3	127,0	24,3 (Me); 41,0 (CH); 84,2 (quat. C at.); 113,4 (CN)	1,41 (6H, d, *J* = 6,9 Hz, Me); 3,53 (1H, q, CH)
IX	149,6	127,4	139,9	139,1	126,3	14,3, 23,6 (Me); 39,3 (CH); 63,6 (CH_2); 111,6 (quat. C at.); 113,5 (CN)	1,25 (3H, t, Me); 1,39 (6H, d, Me); 3,49 (1H, q, CH); 3,71 (2H, q, CH_2)
XIII	155,5	131,3	131,5	136,8	154,5	21,6 (Me); 43,8, 44,3 (CH); 111,8 (CN); 213,8 (C=S)	1,44 (6H, m, Me); 4,11 (1H, q, CH)
XIV	158,7	129,4	125,8	129,4	147,2	22,4 (Me); 36,9 (CH); 111,5 (CN)	1,44 (6H, d, Me); 3,95 (1H, q, Me)
XV	160,5	129,0	120,0	127,2	154,2	22,4, 23,1 (Me); 36,8, 40,9 (CH); 112,8 (CN)	1,34 (6H, d, *J* = 6,7 Hz, Me); 1,45 (6H, d, *J* = 6,8 Hz, Me); 3,61 (1H, q, CH); 3,99 (1H, q, CH)
XVI	150,0	116,8	147,1	135,6	153,0	21,6 (Me); 44,6 (CH); 211,7 (C=S)	1,43 (6H, d, Me); 4,12 (H, q, CH)
XVII	150,4	117,4	146,2	139,6	157,6	21,4 (Me); 43,7 (CH); 212,0, 213,3 (C=S)	1,42 (6H, d, Me); 4,10 (1H, q, CH)
XVIII	146,8	135,6	143,4	135,6	146,8	21,7 (Me); 44,0 (CH); 213,2 (C=S)	1,42 (6H, d, *J* = 6,9 Hz, Me); 4,09 (1H, q, CH)
XIX	146,3	134,7	148,6	134,7	146,3	23,3 (Me); 40,5 (CH)	1,31 (6H, d, *J* = 6,6 Hz, Me); 3,83 (1H, q, CH)

The reaction of the pentachloropyridine (Id) with the reagent (II) in acetonitrile solution gave the product from substitution at position 4 of the pyridine ring by the isopropyltrithiocarbonate fragment, i.e., compound (XVIII), while the reaction in ethanol gave the 4-isopropylthio derivative of tetrachloropyridine (XIX) (Scheme 4). The localization of the sulfur-containing substituents in the pyridine ring of compounds (XVII, XIX) was established from the data of the ^{13}C NMR spectra, in which three signals were observed for the carbon atoms characteristic of 4-substituted tetrachloropyridines [2-4]. The signal of the thiocarbonyl carbon atom in the spectrum of the derivative (XIX) at 213.2 ppm in the presence of the signals of the isopropyl group confirms the presence of the isopropyltrithiocarbonate fragment in the molecules of this compound. The effects of substitution of the chlorine atom at position 4 of the pyridine ring by one isopropyltrithiocarbonate group [in compound (XVIII)] or isopropylthio group [in compound (XIX)] are as follows: $C_{(2)}$, $C_{(6)}$ +0.6; $C_{(3)}$, $C_{(5)}$ +5.9; $C_{(4)}$ −0.7 ppm and $C_{(2)}$, $C_{(6)}$ +0.1; $C_{(3)}$, $C_{(5)}$ +5.0; $C_{(4)}$ +3.9 ppm respectively in relation to the chemical shifts of the initial pentachloropyridine (Id) [6].

These values of the increments agree with data obtained for the analogous derivatives (Ia-c) and can, consequently, help to establish the structure of the newly synthesized analogs.

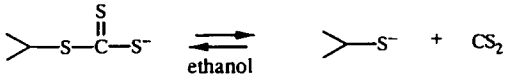
Analysis of the mass spectra of the isopropyltrithiocarbonate derivatives (XIII, XVI-XVIII) shows that the $[M-Cl]^+$ fragment is the heaviest and strongest. Its formation in the presence of the labile alkyltrithiocarbonate groups can be explained by the analogous intramolecular cyclization previously described [1] for the related ethylxanthates, where the sulfur atom of the thiocarbonyl group attacks the *ortho* position of the pyridine ring with the elimination of a chlorine atom.

Scheme 4



In the course of the experiments it was found that compounds (Ia, b, d) [with the exception of compound (Ic), the chlorine atoms of which at positions 4 and 6 are the most reactive in this series of polychloropyridines in nucleophilic substitution reactions on account of the concerted effect of the cyano group and the pyridine nitrogen atom on the redistribution of electron density in the pyridine ring] react with potassium isopropyltrithiocarbonate in ethanol with the formation of only alkylthio derivatives. In other solvents (acetonitrile, acetone) the substituent is the isopropyltrithiocarbonate fragment. Experiment shows that two nucleophilic agents (isopropyltrithiocarbonate and isopropanethiolate anions) may be present in the ethanol solution, and the latter is clearly a stronger nucleophile. The formation of the isopropanethiolate anion can be represented as the result of dissociation of the isopropyltrithiocarbonate anion in ethanol, where the equilibrium of the process is displaced to the left to a significant degree (Scheme 5). The most reactive tetrachloro-3-cyanopyridine (Ic) reacts directly with isopropyl trithiocarbonate; here the introduction of one substituent does not hinder the entry of the second (as noted above). The less active polychloropyridines only react with the isopropanethiolate anion, and the rate-controlling stage of the process as a whole is probably the formation of this anion.

Scheme 5



Thus, a method of thioalkylation using the salts of alkyltrithiocarbonic acids was found and made it possible to introduce, for example, an isopropylthio group into the molecules of polychloropyridines regioselectively and with high yields. In addition, it was found that heterocyclizations similar to those established for ethyldithiocarbonate (ethylxanthate) derivatives occur during the reaction of tetrachloro-2-cyanopyridine (Ia) with potassium isopropyltrithiocarbonate (II).

EXPERIMENTAL

The NMR spectra were recorded in deuterochloroform solutions on a Bruker AC-200 instrument at 50 MHz (^{13}C) with TMS as internal standard. The electron-impact mass spectra were obtained on a Varian MAT-44S instrument (source temperature 170°C). The collision-activation mass spectra were obtained on a VG 70-250 SEQ instrument (source temperature 250°C). Direct injection into the ion source with 70-eV ionizing electrons was used. The temperature of the samples was kept at the minimum level in order to prevent thermolysis. Argon was used in the collision chamber, and its pressure was chosen so as to reduce the signal of the investigated ion by 20%. The collision energy was 100 eV. The reactions were monitored by TLC on Silufol UV-254 plates with various mixtures of hexane and benzene as eluant.

The crystals of compound (IX) belong to the monoclinic system. The principal crystallographic data were as follows: a = 9.989(2), b = 19.598(4), c = 8648(2) Å, β = 79.34(3)°, V = 1663.6(6) Å^3, M = 367.32, d = 1.447 g/cm^3, Z = 4, space group $P2_1/n$. The unit cell parameters and the experimental set of reflections were obtained on a KUMA Diffraction four-

TABLE 2. Bond Lengths d (Å) and Bond Angles ω (deg) in the Molecule of Compound (IX)

Bond	d	Angle	d
Cl(1)—C(12)	1,723(4)	Cl(2)—C(9)	1,742(4)
S(3)—C(11)	1,730(4)	S(3)—C(15)	1,862(4)
S(4)—C(10)	1,739(4)	S(4)—C(15)	1,869(4)
S(5)—C(15)	1,812(4)	S(5)—C(18)	1,827(4)
O(6)—C(15)	1,372(4)	O(6)—C(16)	1,442(5)
N(7)—C(9)	1,306(5)	N(7)—C(13)	1,341(5)
N(8)—C(14)	1,125(6)	C(9)—C(10)	1,394(5)
C(10)—C(11)	1,394(5)	C(11)—C(12)	1,395(5)
C(12)—C(13)	1,381(6)	C(13)—C(14)	1,459(7)
C(16)—C(17)	1,457(7)	C(18)—C(19)	1,495(7)
C(18)—C(20)	1,520(7)		
Bond	ω	**Angle**	ω
C(11)—S(3)—C(15)	96,4(2)	C(10)—S(4)—C(15)	95,9(2)
C(15)—S(5)—C(18)	102,8(2)	C(15)—O(6)—C(16)	118,4(3)
C(9)—N(7)—C(13)	116,6(3)	N(7)—C(9)—C(10)	125,3(4)
N(7)—C(9)—Cl(2)	116,5(3)	C(10)—C(9)—Cl(2)	118,2(3)
C(11)—C(10)—C(9)	117,6(4)	C(11)—C(10)—S(4)	117,1(3)
C(9)—C(10)—S(4)	125,3(3)	C(10)—C(11)—C(12)	117,9(3)
C(10)—C(11)—S(3)	117,6(3)	C(12)—C(11)—S(3)	124,5(3)
C(13)—C(12)—C(11)	118,9(4)	C(13)—C(12)—Cl(1)	122,1(4)
C(11)—C(12)—Cl(1)	119,0(3)	N(7)—C(13)—C(12)	123,6(4)
N(7)—C(13)—C(14)	115,1(4)	C(12)—C(13)—C(14)	121,2(4)
N(8)—C(14)—C(13)	178,7(6)	O(6)—C(15)—S(5)	107,6(2)
O(6)—C(15)—S(3)	113,9(3)	S(5)—C(15)—S(3)	103,9(2)
O(6)—C(15)—S(4)	112,9(3)	S(5)—C(15)—S(4)	111,7(2)
S(3)—C(15)—S(4)	106,4(2)	O(6)—C(16)—C(17)	108,1(5)
C(19)—C(18)—C(20)	112,6(6)	C(19)—C(18)—S(5)	112,4(4)
C(20)—C(18)—S(5)	104,9(4)		

circle diffractometer with monochromatic CuKα radiation.The structure was determined by the direct statistical method. The hydrogen atoms were determined by geometry. Least-squares refinement was carried out in full-matrix anisotropic approximation (isotropic for the hydrogen atoms) to R = 0.0326 in 1180 reflections with $I > 2\sigma(I)$. All the calculations were made with the SHELX 86 [7] and SHELXL 93 [8] software. The atomic coordinates are given in Table 3.

Reaction of Tetrachloro-2-cyanopyridine (Ia) with Potassium Isopropyltrithiocarbonate (II). A. A mixture of 1.21 g (5 mmole) of tetrachloro-2-cyanopyridine (Ia) and 1.056 g (6 mmole) of potassium isopropyltrithiocarbonate (II) in 100 ml of ethanol was stirred at room temperature for 5-6 h. The precipitate was separated by filtration, the solvent was evaporated under vacuum, and the residue was washed with water and extracted with chloroform. The organic layer was dried over sodium sulfate, the solvent was removed, and the residue was chromatographed on a column of silica gel with a 2:1 mixture of hexane and benzene as eluant. We obtained 1.2 g of compound (V).

B. A mixture of 1.21 g (5 mmole) of compound (Ia) and 1.056 g (6 mmole) of the reagent (II) in 100 ml of acetone was stirred for 5-6 h at room temperature. The reaction mixture was then treated by analogy with method A. We isolated 0.3 g of the initial compound (Ia) and 0.35 g of compound (III) as in the previous experiment.

C. A mixture of 1.21 g (5 mmole) of (Ia) and 1.9 g (10 mmole) of (II) in 120 ml of acetonitrile was stirred at room temperature for 5 h. The solvent was evaporated, and the residue was washed with dilute hydrochloric acid. The reaction mixture was then treated as in expt. A. We isolated 0.2 g of compound (III), 0.4 g of compound (VIII), 0.12 g of (VII), and 0.1 g of compound (IX).

TABLE 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Parameters ($Å^2 \times 10^3$) in the Molecule of Compound (IX)

Atom	x	y	z	U(eq)
Cl(1)	3639(1)	1756(1)	8797(2)	65(1)
Cl(2)	6488(1)	-880(1)	6062(1)	65(1)
S(3)	2293(1)	304(1)	9889(1)	47(1)
S(4)	3736(1)	-977(1)	8673(1)	48(1)
S(5)	1384(1)	-959(1)	11473(1)	49(1)
O(6)	1066(2)	-743(1)	8616(3)	44(1)
N(7)	6204(3)	438(2)	6293(4)	49(1)
N(8)	6736(5)	2127(3)	5782(7)	102(2)
C(9)	5649(4)	-140(2)	6824(5)	41(1)
C(10)	4448(4)	-208(2)	7927(4)	36(1)
C(11)	3792(4)	388(2)	8534(4)	39(1)
C(12)	4388(4)	1010(2)	8010(5)	43(1)
C(13)	5571(4)	1008(2)	6893(5)	47(1)
C(14)	6220(5)	1644(3)	6278(6)	65(1)
C(15)	2026(4)	-619(2)	9529(4)	39(1)
C(16)	1328(5)	-507(3)	7009(5)	53(1)
C(17)	322(8)	-817(5)	6201(8)	83(2)
C(18)	548(5)	-1748(2)	11049(5)	52(1)
C(19)	1531(7)	-2256(3)	10192(9)	82(2)
C(20)	-168(9)	-2007(4)	12646(8)	85(2)
H(16A)	2195(46)	-623(22)	6556(47)	53(13)
H(16B)	1227(48)	-43(26)	7032(57)	72(17)
H(17A)	456(49)	-681(26)	5200(68)	82(17)
H(17B)	-518(70)	-837(31)	6791(77)	114(25)
H(17C)	535(68)	-1285(35)	6157(74)	116(28)
H(18)	-94(37)	-1665(17)	10425(41)	36(10)
H(19A)	1826(61)	-2090(31)	9063(76)	125(24)
H(19B)	1093(53)	-2630(30)	10053(61)	91(19)
H(19C)	2245(47)	-2369(23)	10812(56)	73(16)
H(20A)	-899(44)	-1705(22)	13197(50)	48(14)
H(20B)	525(63)	-2058(31)	13483(80)	135(24)
H(20C)	-524(51)	-2333(27)	12426(55)	66(17)

4-Isopropylthio-2,3,5-trichloro-6-cyanopyridine (V) ($C_9H_7Cl_3N_2S$). The product formed yellow crystals; mp 119.5-121°C (from hexane). The yield was 85%. Found %: C 38.6; H 2.7; N 9.7. Calculated %: C 38.4; H 2.5; N 10.0. Mass spectrum *m/z* (*I*, %): 280 (M^+, 2); 265 ($[M-CH_3]^+$, 0.3); 238 ($[M-C_3H_6]^+$, 6); 202 ($[M-C_3H_6-HCl]^+$, 2).

(2,5-Dichloro-6-cyanopyridine) 3,4-Bis[isopropyltrithiocarbonate] (III) ($C_{14}H_{14}Cl_2S_6$). The product formed yellow crystals; mp 52-54°C. The yield was 25%. Found %: C 35.7; H 2.9; N 5.7. Calculated %: C 35.5; H 3.0; N 5.9. Mass spectrum, *m/z* (*I*, %): 353 ($[M-CS_2C_3H_7]^+$, 0.3); 278 ($[353-C_3H_7]^+$, 4); 234 ($[278-CS]^+$, 4); 199 ($[234-Cl]^+$, 0.3).

4,7-Dichloro-6-cyano-1,3-dithiolo[4,5-*c*]pyridine-2-thione (VII) ($C_7Cl_2N_2S_3$). The product formed yellow crystals; mp 158-160°C. Published data [1]: 158-160°C. Found %: C 30.3; N 9.9. Calculated %: C 30.2; N 10.1. Mass spectrum, *m/z* (*I*, %): 278 (M^+, 100); 234 ($[M-CS]^+$, 91); 202 ($[M-CS_2]^+$, 2).

4,7-Dichloro-2-isopropylthio-2-mercapto-1,3-dithiolo[4,5-*c*]pyridine (VIII) ($C_{10}H_8Cl_2N_2S_4$). The product formed white crystals; mp 53-54°C. The yield was 22%. Found %: C 34.0; H 2.4; N 7.7. Calculated %: C 33.8; H 2.3; N 7.9. Mass spectrum, *m/z* (*I*, %): 321 ($[M-SH]^+$, 3); 279 ($[M-SH-C_3H_7]^+$, 18); 234 ($[279-HCS]^+$, 2); 199 ($[234-Cl]^+$, 2).

4,7-Dichloro-2-isopropylthio-6-cyano-1,3-dithiolo[4,5-*c*]pyridine (IX) ($C_{12}H_{12}Cl_2N_2OS_3$). The product formed white crystals; mp 93-95°C (from acetonitrile). The yield was 5%. Found %: C 39.3; H 3.3; N 7.5. Calculated %: C 39.2; H 3.3; N 7.6. Mass spectrum, *m/z* (*I*, %): 291 ($[M-C_3H_7]^+$, 28); 263 ($[291-C_2H_4]^+$, 78); 234 ($[291-CO-C_2H_5]^+$, 3); 199 ($[234-Cl]^+$).

Reaction of Tetrachloro-4-cyanopyridine (Ib) with Potassium Isopropyltrithiocarbonate (II). A. A mixture of 0.95 g (3.93 mmole) of compound (Ib) and 1.49 g (7.85 mmole) of the reagent (II) in 100 ml of ethanol was stirred at room temperature for 4 h. The reaction mixture was treated as in the previous experiments. The product was chromatographed on a column of silica gel with a 3:1 mixture of hexane and benzene as eluant. We obtained 0.165 g of compound (XIV) and 0.505 g of compound (XV).

B. A mixture of 0.95 g (3.93 mmole) of compound (Ib) and 1.49 g (7.85 mmole) of the reagent (II) in 200 ml of acetone was stirred at room temperature for 2 h. The mixture was treated as in the previous experiments. The product was chromatographed on a column of silica gel with a 3:1 mixture of hexane and benzene as eluant. We obtained 0.7 g of the initial pyridine (Ib) and 0.33 g of compound (XIII).

3-Isopropylthio-2,5-dichloro-4-cyano-6-pyridyl Isopropyltrithiocarbonate (XIII) ($C_{13}H_{14}Cl_2N_2S_4$). The product formed light-yellow crystals; mp 103.5-105°C. The yield was 80%. Found %: C 39.5; H 3.4; N 6.9. Calculated %: C 39.3; H 3.6; N 7.1. Mass spectrum, *m/z* (*I*, %): 361 ($[M-Cl]^+$, 0.4); 319 ($[M-Cl-C_3H_6]^+$, 0.2); 277 ($[M-CS_2C_3H_7]^+$, 1); 240 (4), 238 (7), 236 ($[M-CS_2C_3H_6-C_3H_6]^+$, 5).

2-Isopropylthio-3,5,6-trichloro-4-cyanopyridine (XIV) ($C_9H_7Cl_3N_2S$). The product formed white crystals; mp 72-73°C (from methanol). The yield was 15%. Found %: C 38.7; H 2.7; N 9.7. Calculated %: C 38.4; H 2.5; N 10.0. Mass spectrum, *m/z* (*I*, %): 280 (M^+, 21); 247 ($[M-SH]^+$, 22); 238 ($[M-C_3H_6]^+$, 98); 203 ($[M-C_3H_6-Cl]^+$, 42).

2,5-Bisisopropylthio-3,6-dichloro-4-cyanopyridine (XV) ($C_{12}H_{14}Cl_2N_2S_2$). The product formed yellow crystals; mp 63-65°C (from methanol). The yield was 40%. Found %: C 44.8; H 4.6; N 9.0. Calculated %: C 44.9; H 4.4; N 8.8. Mass spectrum, *m/z* (*I*, %): 320 (M^+, 2); 278 ($[M-C_3H_6]^+$, 3); 245 ($[M-SC_3H_7]^+$, 5); 236 ($[M-2C_3H_6]^+$, 17); 200 ($[236-HCl]^+$, 3).

Reaction of Tetrachloro-3-cyanopyridine (Ic) with Potassium Isopropyltrithiocarbonate (II). A. A mixture of 0.95 g (3.93 mmole) of compound (Ic) and 1.49 g (7.85 mmole) of the reagent (II) in 150 ml of ethanol was stirred at room temperature for 4 h. The mixture was treated as in the previous experiments. The product was chromatographed on a column of silica gel with a 3:1 mixture of hexane and benzene as eluant. We isolated 1.12 g of compound (XVII).

B. A mixture of 0.95 g (3.93 mmole) of the pyridine (Ic) and 1.49 g (7.85 mmole) of the reagent (II) in 100 ml of acetonitrile was stirred at room temperature for 2 h. The reaction mixture was treated as in the previous experiments. The product was chromatographed on a column of silica gel with a 4:1 mixture of hexane and benzene as eluant. We obtained 0.6 g of compound (XVI) and 0.55 g of compound (XVII).

2,3,6-Trichloro-5-cyano-4-pyridyl Isopropyltrithiocarbonate (XVI) ($C_{10}H_7Cl_3N_2S_3$). The product formed light-yellow crystals; mp 75-76.5°C (from hexane). The yield was 43%. Found %: C 33.8; H 1.9; N 7.7. Calculated %: C 33.6; H 2.0; N 7.8. Mass spectrum, *m/z* (*I*, %): 321 ($[M-Cl]^+$, 2), 279($[M-Cl-C_3H_6]^+$, 1,3); ($[M-CS_2C_3H_6]^+$, 2); 202 ($[238-HCl]^+$, 2).

2,5-Dichloro-3-cyanopyridine 4,6-Bis[isopropyltrithiocarbonate] (XVII) ($C_{14}H_{14}Cl_2N_2S_6$). The product formed yellow crystals; mp 60.5-62°C (from hexane). The yield was 60% (A) and 30% (B). Found %: C 35.7; H 2.9; N 5.6. Calculated %: C 35.5; H 3.0; N 5.9. Mass spectrum, *m/z* (*I*, %): 437 ($[M-Cl]^+$, 0.2); 319 ($[M-Cl-CS_2C_3H_6]^+$, 0.1); 276 ($[319-C_3H_7]^+$, 0.6); 236 ($[M-CS_2C_3H_6]^+$, 3).

Reaction of Pentachloropyridine (Id) with Potassium Isopropyltrithiocarbonate (II). A. A mixture of 0.83 g (3.3 mmole) of compound (Id) and 1 g (5.3 mmole) of the reagent (II) in 50 ml of ethanol was stirred at room temperature for 6 h. The reaction mixture was treated as in the previous experiments. The product was chromatographed on a column of silica gel with a 10:1 mixture of hexane and benzene as eluant. We obtained 0.8 g of compound (XIX).

B. A mixture of 0.83 g (3.3 mmole) of compound (Id) and 1 g (5.3 mmole) of the reagent (II) in 80 ml of acetonitrile was stirred at room temperature for 6 h. The reaction mixture was treated as in method A. We obtained 0.53 g of compound (XVIII), and we also isolated 0.43 g of the initial pyridine (Id).

4-Isopropylthio-2,3,5,6-tetrachloropyridine (XVIII) ($C_8H_7Cl_4NS$). The product formed yellowish crystals; mp 34-35°C (from hexane). The yield was 83%. Found %: C 30.3; H 2.5; N 4.9. Calculated %: C 33.0; H 2.4; N 4.8. Mass spectrum, *m/z* (*I*, %): 289 (M^+, 1); 247 ($[M-C_3H_6]^+$, 4); 211 ($[247-HCl]^+$, 2).

2,3,5,6-Tetrachloro-4-pyridyl Isopropyltrithiocarbonate (XIX) ($C_9H_7Cl_4NS_3$). The product formed yellowish crystals; mp 59.5-61°C (from hexane). The yield was 87%. Found %: C 29.7; H 2.0; N 3.6. Calculated %: C 29.4; H 1.9; N 3.8. Mass spectrum, *m/z* (*I*, %): 330 ($[M-Cl]^+$, 1); 288 ($[M-Cl-C_3H_6]^+$, 3); 247 ($[M-CS_2C_3H_6]^+$, 1.4); 211 ($[247-HCl]^+$, 2).

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