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REACTIONS OF POLYHALOGENOPYRIDINES. 14.* REACTION OF ISOMERIC DICHLOROCYANOPYRIDINES AND PENTACHLOROPYRIDINE WITH POTASSIUM ETHYLXANTHATE

A. M. Sipyagin, V. V. Kolchanov, A. T. Lebedev, and N. K. Karakhanova

The reactions of isomeric tetrachlorocyanopyridines with potassium ethylxanthate were studied. It was found that tetrachloro-2-cyanopyridine was converted successively into 4-mono- and then 3,4-bisethylxanthate derivatives. In the presence of potassium ethylxanthate the last derivative undergoes intramolecular cyclization with the formation of derivatives of 1,3-dithiolo[4,5-c]pyridine. In the case of other initial polychloropyridines processes involving substitution of the chlorine atoms by the ethylxanthate fragment, sometimes accompanied by the loss of COS molecules, were observed instead of heterocyclization.

Earlier we described the synthesis of 1,3-dithiolo[4,5-*c*]pyridines and bis-1,3-dithiolo[4,5-*b*:4′,5′-*e*]pyridines from 2- and 4-monosubstituted and disubstituted tetrachloropyridines and alkali-metal N,N-dialkyldithiocarbamates [2]. We showed that the position of the accepting substituent (more accepting than the chlorine atom) in the molecule of the initial tetrachloropyridine determines the point of annellation of the 1,3-dithiole ring to the pyridine ring [3, 4], whereas the composition of the amide part of the dithiocarbamate does not have a significant effect on the heterocyclization process or on the structure of the final compound [2].

In connection with the development of methods for the annellation of sulfur-containing heterocycles to the pyridine ring by means of intramolecular nucleophilic reactions it seemed of interest to extend the range of derivatives of dithiocarbonic acids in reactions with polychloropyridines. With this aim in the present work we studied the reaction of a series of polychloropyridines [the isomeric tetrachlorocyanopyridines tetrachloro-2-cyanopyridine (Ia), tetrachloro-4-cyanopyridine (Ib), tetrachloro-3-cyanopyridine (Ic), and pentachloropyridine (Id)] with potassium ethylxanthate.

The conditions for the process were the same as in the reactions of polychloropyridines with N,N-dialkyldithiocarbamates and were described in detail in [2-4]. In most cases the results differed significantly from the earlier results. Thus, not even trace quantities of 4,7-dichloro-6-cyano-1,3-dithiolo[4,5-*c*]pyridin-2-one were formed in the reaction of tetrachloro-2-cyanopyridine (Ia) with potassium ethylxanthate. In addition, when equivalent amounts of these reagents were mixed, the formation of two new compounds (II, III) was detected in the reaction mixture, and they were isolated with yields of 36 and 17% respectively by column chromatography. In addition, about 20% of the unreacted initial (Ia) was obtained. Chromatographic control of the reaction by TLC showed that the formation of the 3,4-disubstituted derivative (III) began immediately after the appearance of the 4-monosubstituted compound (II) in the reaction mixture even in the presence of the cyanopyridine (Ia).

The obtained data show that the initial introduction of the ethylxanthate fragment facilitates substitution of the chlorine atom attached to position 3 of the pyridine ring by a second sulfur-containing substituent. However, the most interesting results were obtained during investigation of the reaction of compound (Ia) with an excess (e.g., 1.5 times) of potassium ethylxanthate.

*For Communication 13, see [1].

Chernogolovka Institute of Chemical Physics, Russian Academy of Sciences, Chernogolovka 142432. M. V. Lomonosov Moscow State University, Moscow 119899. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1510-1520, November, 1997. Original article submitted May 22, 1997.

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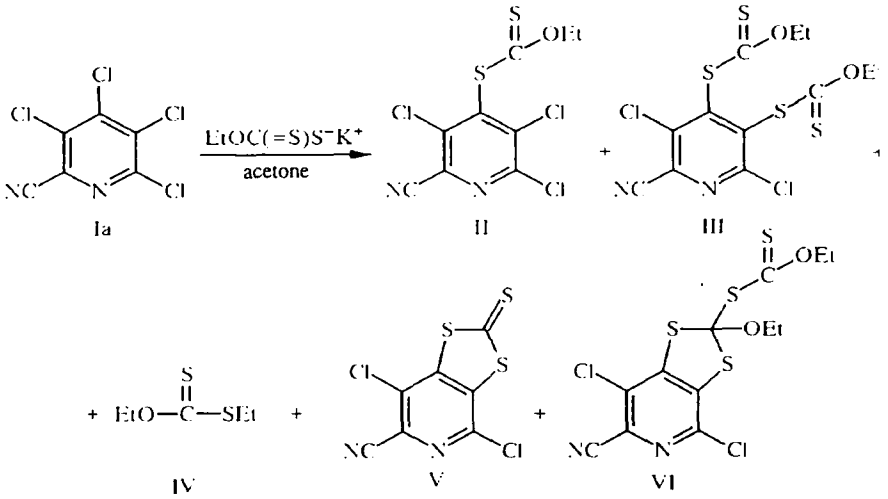
Thus, a few hours after mixing chromatographic analysis of the reaction mixture showed the presence of three new compounds, which were isolated and identified, in addition to compounds (II, III). It was found that the most chromatically mobile component of the mixture was a yellow liquid with an unpleasant odor, which turned out to be O,S-diethyl dithiocarbonate (IV). The ^{1}H NMR spectrum [(deuterochloroform) 1.33 (3H, t, Me); 1.41 (3H, t, Me); 3.11 (2H, q, J = 7.4 Hz, CH_2); 4.64 (2H, q, J = 7.1 Hz, CH_2)] agreed fully with the previously presented [5] ^{13}C NMR spectrum [13.4; 13.7 (Me); 30.0 (CH_2S); 69.6 (CH_2O); 207.7 (C=S)]. The next component was the yellow solid 4,7-dichloro-6-cyano-2-ethoxy-2-S-dithiocarbonyl-1,3-dithiolo[4,5-*c*]pyridine (VI). The whole range of compounds obtained as a result of the reaction of the polychloropyridine (Ia) with an excess of potassium ethylxanthate is presented in Scheme 1.

Scheme 1



During chromatographic investigation (TLC) of the transformations of the ethylxanthates of the polychloropyridines (II, III) by the action of potassium ethylxanthate in acetone solution it was shown that the key compound was (III), since only this compound is converted directly into the derivatives of 1,3-dithiolo[4,5-*c*]pyridine (V, VI), whereas compound (II) only undergoes such transformations through the intermediate formation of the 3,4-disubstituted compound (III). It must also be emphasized that the highest yields of 1,3-dithiolo[4,5-*c*]pyridines (V, VI) of 54 and 32% respectively were observed in the reaction of potassium ethylxanthate with compound (III).

On the basis of the obtained results and also of the data on the reactivity of the aromatic derivatives of alkylxanthates [5] the probable mechanism of the formation of compounds (V, VI) can be represented in the following way (Scheme 2).

Scheme 2

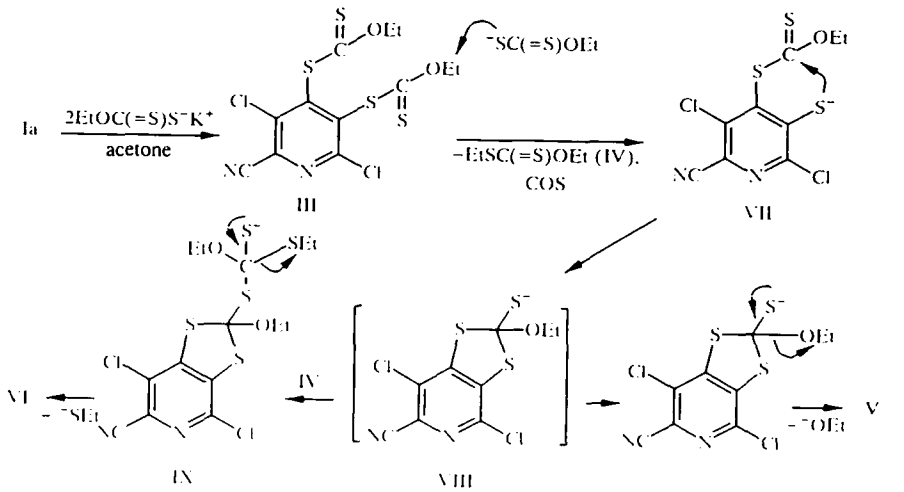


TABLE 1. Spectral Characteristics of Compounds (II, III, V, VI, X-XV)

Compound	^{13}C NMR spectrum, δ, ppm						^{1}H NMR spectra, δ, ppm
	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	other C atoms	
II	149.4	140.8	143.1	139.6	130.1	13.4 (Me); 71.6 (CH_2); 113.1 (CN); 202.1 (C=S)	1.39 (3H, t, Me); 4.66 (2H, q, CH_2)
III	155.1	139.3	149.7	138.3	133.0	13.4 (Me), 71.5, 71.6 (CH_2); 113.5 (CN); 203.3; 204.7 (C=S)	1.36 (3H, m, Me), 4.60 (2H, m, CH_2)
V	151.8	129.3	141.2	139.9	126.0	112.8 (CN); 203.6 (C=S)	
VI	148.8	127.7	140.0	138.0	126.3	13.7, 14.2 (Me); 64.9, 70.7 (CH_2); 110.3 quat. C atom 113.4 (CN); 204.6 (C=S)	1.31 (3H, t, Me); 1.46 (3H, t, Me); 3.80 (2H, q, CH_2); 4.72 (2H, q, CH_2)
X	163.1	128.5	129.5	122.5	153.6	13.4, 13.5 (Me); 25.9, 71.5 (CH_2); 112.0 (CN); 205.8 (C=S)	1.41 (6H, m, 2Me); 3.22 (2H, q, $\underline{CH_2}$—S); 4.65 (2H, q, $\underline{CH_2}$—O)
XI	160.3	128.6	129.2	127.3	153.8	13.6, 14.7 (Me); 25.6, 30.1 (CH_2); 112.8 (CN)	1.30 (3H, t, Me); 1.40 (3H, t, Me); 3.04 (2H, q, CH_2); 3.20 (2H, q, CH_2)
XII	149.7	116.0	146.6	134.5	152.7	13.4 (Me); 71.9 (CH_2); 112.1 (CN); 201.3 (C=S)	1.38 (3H, t, Me); 4.66 (2H, q, CH_2)
XIII	150.2	117.1	145.9	138.8	156.5	13.5 (Me); 71.3, 72.0 (CH_2); 201.9, 204.0 (C=S)	1.40 (3H, m, Me); 4.67 (2H, m, CH_2)
XIV	150.1	138.0	143.5	138.0	150.1	13.5 (Me); 70.9 (CH_2); 206.5 (C=S)	1.34 (3H, t, Me); 4.62 (2H, q, CH_2)
XV	146.0	133.9	148.6	133.9	146.0	14.8 (Me); 29.7 (CH_2)	1.23 (3H, t, Me); 3.09 (2H, q, CH_2)

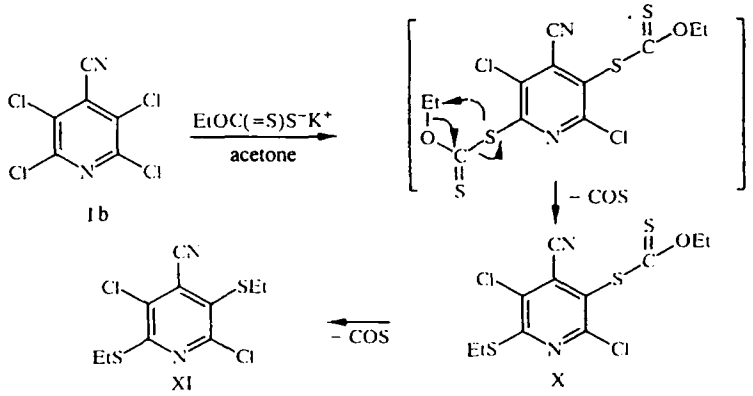
According to the proposed mechanism, the reaction of the xanthate anion with one of the ethoxydithiocarbonyl substituents at position 3 or 4 of the pyridine ring in compound (III), which takes place with removal of the ethyl group and loss of a COS molecule, results in transformation into the derivative (VII), which undergoes subsequent intramolecular cyclization with the formation of the intermediate (VIII). The latter can then react with the diethyl dithiocarbonate (IV) present in the reaction mixture, giving the final compound (VI) through the derivative (IX) (with the removal of the ethylthiolate [6]). Alternatively, it can be transformed into the corresponding 1,3-dithiolo[4,5-*c*]pyridine-2-thione (V) with loss of the alcoholate anion.

The structure of the synthesized compounds (II-VI) was proved by physicochemical methods, including ^{1}H and ^{13}C NMR (Table 1) and mass spectrometry. The ^{13}C NMR chemical shifts were assigned on the basis of published data [7-9]. Thus, the S-ethylxanthate substituent is characterized by the presence of the resonance absorption of the ethyl group at 13.4 (Me) and 71.5-71.7 ppm (CH_2) and also the thiocarbonyl group in the region of 202.1-204.7 ppm. The introduction of this substituent at position 4 of the pyridine ring, like the N,N-dialkyldithiocarbamate [3], leads to a significant downfield shift (by more than 5 ppm) of the $C_{(3)}$ and $C_{(5)}$ signals [compared with the initial polychloropyridine (Ia)], whereas the positions of the other peaks of the pyridine carbons change in a range of 1 ppm (Table 1). For the pyridine carbon atoms of compound (II) the calculated effects of substitution of the chlorine atom in the polychloropyridine (Ia) by the ethylxanthate group amount to the following: $C_{(2)}$ −0.6; $C_{(3)}$ +5.3; $C_{(4)}$ −0.9; $C_{(5)}$ +5.8; $C_{(6)}$ −0.8 ppm. The ^{13}C NMR spectrum for compound (III) was calculated from them: $C_{(2)}$ 115.2; $C_{(3)}$ 139.3; $C_{(4)}$ 148.4; $C_{(5)}$ 139.0; $C_{(6)}$ 130.1 ppm. Good agreement was obtained between these values and the experimental values for the $C_{(2)}$-$C_{(5)}$ atoms. Final evidence for the 3,4 arrangement of the ethylxanthate substituents in the molecule of compound (III) was obtained by tandem mass spectrometry with collision activation. The spectra of ions with *m/z* 234, which are the $[M-CSOEt)_2]^+$ and $[M-CS]^{+\cdot}$ fragments of compounds (III) and (V) respectively, were obtained. As seen from Figs. 1 and 2, the spectra of these ions are completely identical, which demonstrates the identity of their structures. Here, the formation of the fragment with *m/z* 234 during the dissociation of M^+ is only possible with the *ortho* arrangement of the sulfur-containing substituents.

In the ^{13}C NMR spectrum of compound (V) a substantial downfield shift (by 5 ppm) is observed in the signals of the pyridine carbon atoms adjacent to the position where the 1,3-dithiolethione ring is located in comparison with the analogous signals in the 1,3-dithiolone derivative [2]. The peak of the thiocarbonyl carbon atom appears in the downfield region at 203.6 ppm. The spectrum of compound (VI) is characterized by signals for the two different ethoxy groups, only one of which belongs to the ethylxanthate fragment [13.7 (Me) and 70.7 ppm (CH_2)], further evidence for the presence of which is provided by the peak of the thiocarbonyl carbon atom at 204.6 ppm. The presence of the 1,3-dithiole ring annellated with the pyridine ring is demonstrated both by the peak of the quaternary carbon atom at 110.3 ppm and by the similar values for the chemical shifts of the pyridine carbon atoms of compounds (V) and (VI).

In contrast to the reactions of tetrachloro-4-cyanopyridine (Ib) with sodium N,N-dimethyldithiocarbamate, which lead successively to annellation of at first one and then a second 1,3-dithiole ring to the pyridine ring, heterocyclization was not detected in the analogous processes with potassium ethylxanthate. Instead, processes involving the loss of one or two COS molecules by the S-ethylxanthate substituents occur. Thus, it was established that compound (Ib) in reaction with a twofold excess of potassium ethylxanthate in acetone at room temperature was converted into the disubstituted derivative (X) with the extrusion of one molecule of COS from position 2 of the pyridine ring. At a higher temperature (boiling in acetone) two molecules of COS were removed at once with the formation of compound (XI). (The mechanism is presented in Scheme 3 by analogy with data in [4].)

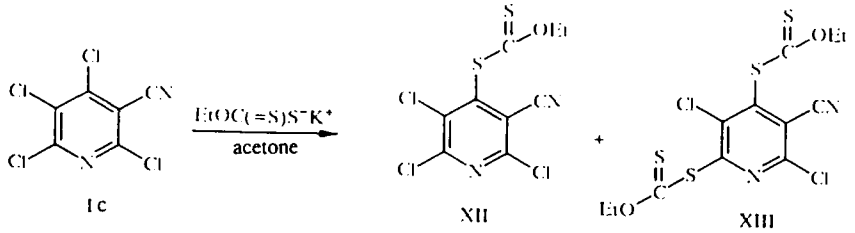
Scheme 3



In the ^1H and ^{13}C NMR spectra of compound (X) there are signals for the two different ethyl groups, and according to the values of the chemical shift one belongs to the ethylxanthate (with due regard to the singlet of the thiocarbonyl carbon atom at 205.8 ppm) and the other [with peaks at 1.41 and 3.22 ppm (^1H) and 13.5 and 25.9 ppm (^{13}C)] to the ethylthio substituent. The assignment of the signals for the pyridine carbon atoms was made with due regard to the chemical shifts in 2-isopropylthio-3,5,6-trichloro-4-cyanopyridine. [In the proton-coupled spectrum of the latter a long-range spin—spin coupling constant was found for the methine proton of the isopropyl group and $C_{(2)}$ (1.85 Hz), which made it possible to assign the resonances of the pyridine ring as follows: $C_{(2)}$ 158.7; $C_{(3)}$ 122.8; $C_{(5)}$ 129.4; $C_{(6)}$ 147.2.] The previously obtained values of the substitution effects for compound (II) were also taken into account. The calculated chemical shifts of the pyridine carbon atoms in compound (X) [$C_{(2)}$ 160.0; $C_{(3)}$ 122.2; $C_{(4)}$ 131.1; $C_{(5)}$ 128.5; $C_{(6)}$ 153.0] agree well with the experimental data (see Table 1). In the ^1H and ^{13}C NMR spectra of compound (XI) there are two pairs of signals each for the unsymmetrical ethylthio groups, which are clearly localized at positions 2 and 5 of the pyridine ring. The resonance signals of the carbon atoms were assigned by analogy with 2,5-diisopropylthio-3,6-dichloro-4-cyanopyridine, synthesized in a separate experiment. In the proton-coupled ^{13}C NMR spectra of the latter the following chemical shifts were found after consideration of the long-range spin—spin coupling constants between the protons of the CH groups of the isopropyl substituents and the pyridine carbon atoms: $C_{(2)}$ 160.5; $C_{(3)}$ and $C_{(4)}$ 129.0; $C_{(5)}$ 127.2; $C_{(6)}$ 154.2 ppm.

It was then found that potassium ethylenexanthate reacted with tetrachloro-3-cyanopyridine (Ic) like the N,N-dialkyldithiocarbamates with the formation of the 4-monosubstitution [compound (XII)] and 4,6-disubstitution [compound (XIII)] products (Scheme 4). The yields of the final products were determined by the ratios of the initial reagents.

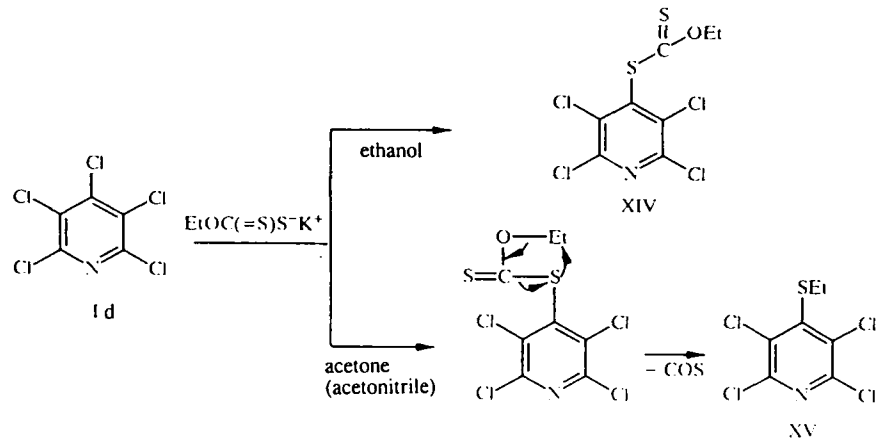
Scheme 4



The structure of compounds (XII, XIII) was proved by means of the ^{13}C NMR spectra. For compound (XII) signals for the ethylxanthate substituent were found at 13.4 and 71.9 ppm (EtO) and 201.3 (C=S). For the peaks of the carbon atoms of the pyridine ring there was a downfield shift of the signals of the $C_{(3)}$ and $C_{(5)}$ carbon atoms characteristic of 4-substitution with not such a significant change in the position of the others. The calculated increments for substitution of a chlorine atom by the ethylxanthate group in compound (XII) were as follows: $C_{(2)}$ +0.8; $C_{(3)}$ +4.3; $C_{(4)}$ −1.5; $C_{(5)}$ +5.3; $C_{(6)}$ +1.7 ppm, i.e., the tendency characteristic of the analogous derivatives of isomeric cyanopyridines is preserved. In the spectrum of compound (XIII) there are two signals for the two ethylxanthate groups, having different values for the chemical shifts of the methylene and thiocarbonyl groups, which can be assigned to the substituents at positions 4 and 6 of the pyridine ring. In the last case the chemical shifts of the $C_{(5)}$ and $C_{(6)}$ atoms undergo the largest changes. The effects of substitution of the second chlorine atom by the ethylxanthate group in compound (XIII) are as follows: $C_{(2)}$ +0.5; $C_{(3)}$ +1.1; $C_{(4)}$ −0.7; $C_{(5)}$ +4.3; $C_{(6)}$ +3.6. It should be noted that compounds (XII, XIII) do not undergo heterocyclization when heated in a solvent.

In the reaction of the pentachloropyridine (Id) with potassium ethylxanthate it was found that the composition of the reaction products depended on the solvent in which the reaction was carried out. Whereas in acetone and acetonitrile the ethylxanthate substituent of compound (XIV) lost the COS molecule with the preferential formation of 4-ethylthiotetrachloropyridine (XV), in ethanol the ethylxanthate derivative (XIV) was the main component of the reaction mixture (Scheme 5).

Scheme 5



The molecular structure of compounds (XIV, XV) was demonstrated by means of the ^{13}C NMR spectra. Thus, in the first case the ethylxanthate group was detected by means of the signals at 13.5, 70.9 (EtO), and 206.6 (C=S). In the second the ethylthio group was detected by means of the resonance at 14.8 and 29.7 ppm. In both cases the presence of the sulfur-containing substituent at position 4 is supported by the presence of only three signals for the pyridine atoms [7-9]. Whereas the ethylxanthate substituent in the pyridine ring leads to a substantial downfield shift of the $C_{(3)}$ and $C_{(5)}$ signals and a somewhat weaker shift of $C_{(2)}$ and $C_{(6)}$ (substitution effects: $C_{(2)}$, $C_{(6)}$ +3.9; $C_{(4)}$ −1.2; $C_{(3)}$, $C_{(5)}$ +8.3), the introduction of the ethylthio group leads to an approximately equivalent downfield shift of the resonance signals of $C_{(3)}$, $C_{(4)}$, and $C_{(5)}$ in relation to those in the polychloropyridine (Id) (increments of chemical shifts: $C_{(2)}$, $C_{(6)}$ −0.2; $C_{(3)}$, $C_{(5)}$ +4.2; $C_{(4)}$ +3.91 ppm). As in the previous case, the absence of thermal heterocyclization of compound (XIV) was observed, but analysis of the

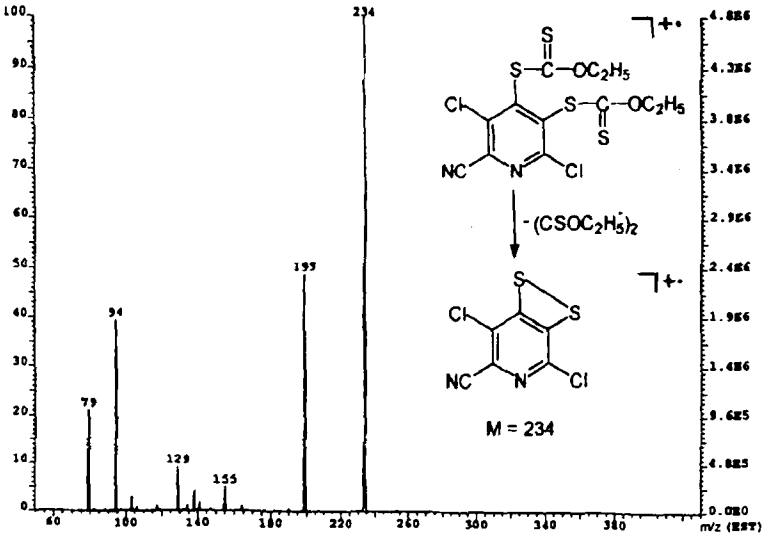


Fig. 1. Collision activation spectrum of the $[M-(CSOC_2H_5)_2]^+$ ion (*m/z* 234) of compound (III).

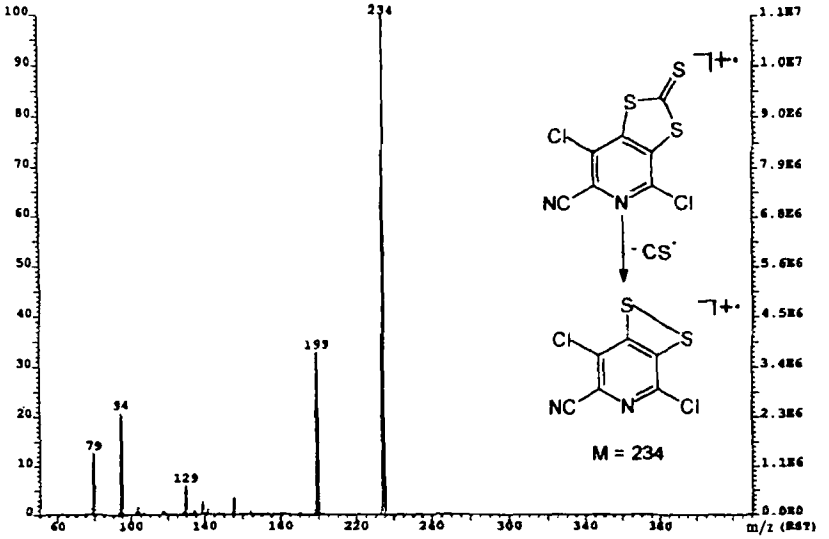


Fig. 2. Collision activation spectrum of the $[M-CS]^+$ ion (*m/z* 234) of compound(V).

mass spectra of the S-ethylxanthate derivatives (II, X, XII-XIV) indicates the possibility of cyclization under electron impact. As a result of attack by the sulfur atom of the thiocarbonyl group at the *ortho* position of the pyridine ring the M^+ ions readily lose chlorine atoms, and the molecular ions are not always recorded in the mass spectra. As the most convincing evidence it is possible to cite the collision activation spectrum of the $[M-Cl, -Et]^+$ ion (*m/z* 262), formed during the dissociation of M^+ in compound (II) (Fig. 3). As seen, the spectrum is fully identical to the spectrum of the M^+ ion of 4,7-dichloro-6-cyano-1,3-dithiolo[4,5-*c*]pyridin-2-one [3] (Fig. 4), indicating that these ions have identical structure. Analogous intramolecular cyclization processes under electron impact are also observed in compounds (X, XII-XIV).

Thus, in the course of the investigations another approach was found to annellation of the 1,3-dithiole fragment to the pyridine ring with the formation of the 1,3-dithiolo[4,5-*c*]pyridine system as a result of the intramolecular reactions of two adjacent ethylxanthate substituents. The substantial differences in the reactivity of the N,N-dialkyldithiocarbamate and S-ethylxanthate substituted polychloropyridines may also be due to the easy occurrence of intramolecular cyclization in the first case with the intermediate formation of stable iminium derivatives of the 1,3-dithiole rings [3, 10].

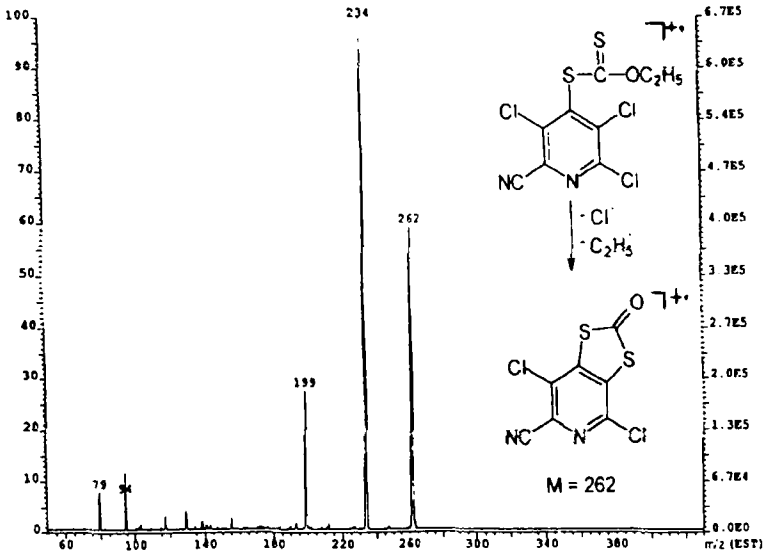


Fig. 3. Collision activation spectrum of the $[M-Cl, -C_2H_5]^+$ ion (*m/z* 262) of compound (II).

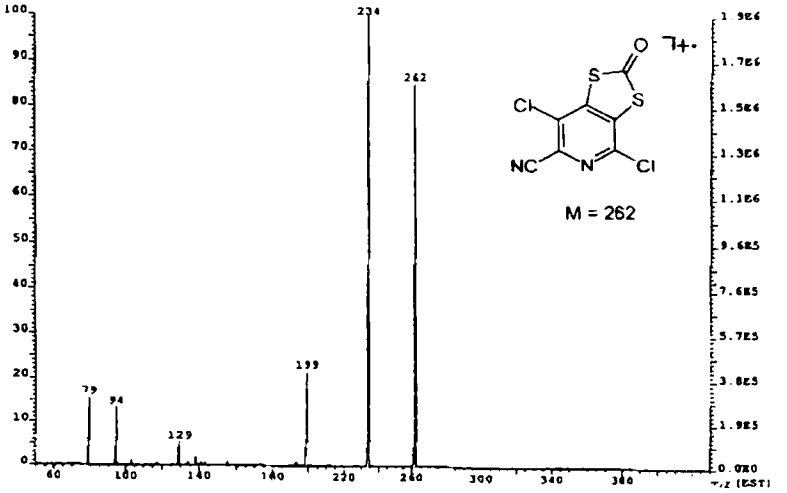


Fig. 4. Collision activation spectrum of the M^+ ion (*m/z* 262) of 4,7-dichloro-6-cyano-1,3-dithiolo[4,5-*c*]pyridin-2-one [3].

EXPERIMENTAL

The NMR spectra were recorded in deuterochloroform solutions on a Bruker AC-250 instrument at 200 (^{1}H) and 50 (^{13}C) MHz with TMS as internal standard. The electron-impact and collision-activation mass spectra were obtained on a VG70-250 SEQ instrument with direct injection of the sample into the ion source. The temperature of the source was 250°C, the ionization energy was 70 eV, and the accelerating potential was 7 kV. The temperature of the samples was kept at the lowest level in order to prevent thermolysis. Argon was used in the collision chamber, and its pressure was selected so as to reduce the signal of the investigated ion by 20%. The energy of the collisions was 100 eV. The reactions were monitored by chromatography on Silufol UV-254 plates with various mixtures of hexane and benzene as eluant.

Reaction of Tetrachloro-2-cyanopyridine (Ia) with Potassium Ethylxanthate. A mixture of 1.21 g (5 mmole) of tetrachloro-2-cyanopyridine (Ia) and 1 g (5.1 mmole) of potassium ethylxanthate in 20 ml of acetone was stirred at room temperature for 1.5 h. The reaction mixture was evaporated, the residue was washed with water, and the product was extracted

with chloroform. The organic layer was dried with sodium sulfate. The solvent was evaporated, and the residue was chromatographed on a column of silica gel with a 2:1 mixture of hexane and benzene as eluant. We isolated 0.23 g of the initial compound (Ia), 0.48 g (36%) of the derivative (II), and 0.28 g (17%) of compound (III).

Reaction of Compound (III) with Potassium Ethylxanthate. To a solution of 0.37 g (0.9 mmole) of compound (III) in 30 ml of acetone at room temperature with stirring we added 0.18 g (9.2 mmole) of potassium ethylxanthate in 40 ml of acetone. The mixture was stirred for 1 h and treated as in the previous experiment. By chromatography we isolated 0.2 g (54%) and 0.08 g (32%) of compounds (VI) and (V) respectively.

S-(2,3,5-Trichloro-6-cyano-4-pyridyl) Ethylxanthate (II) ($C_9H_5Cl_3N_2OS_2$). The product formed white crystals; mp 89.5-91°C (from hexane). Found %: C 33.2; H 1.6; N 6.7. Calculated %: C 33.1; H 1.6; N 6.8. Mass spectrum, *m/z* (*I*, %): 291 ($[M-Cl]^+$, 12); 263 ($[M-ClC_2H_4]^+$, 66); 238 ($[M-CSOC_2H_4]^+$, 24); 202 ($[238-HCl]^+$, 21).

S,S'-(2,5-Dichloro-6-cyanopyridyl 3,4-Bis[ethylxanthate] (III) ($C_{12}H_{10}Cl_2N_2O_2S_4$). The product formed yellow crystals; mp 59.5-61°C (from hexane). Found %: C 35.3; H 2.0; N 6.6. Calculated %: C 35.0; H 2.5; N 6.8. Mass spectrum, *m/z*, (*I*, %): 291 ($[M-CS_2OC_2H_5]^+$, 62); 263 ($[291-C_2H_4]^+$, 64); 234 ($[291-COC_2H_5]^+$, 33); 199 ($[234-Cl]^+$, 33).

4,7-Dichloro-6-cyano-dithiolo[4,5-*c*]pyridine-2-thione (V) ($C_7Cl_2N_2S_3$). The product formed yellow crystals; mp 158-160°C (from hexane). 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 ($[M-CS_2]^+$, 12).

4,7-Dichloro-6-cyano-2-ethoxy-2-S-ethoxydithiocarbonyl-1,3-dithiolo[4,5-*c*]pyridine (VI) ($C_{12}H_{10}Cl_2N_2O_2S_4$). The product formed light-yellow crystals; mp 80-82.5°C (from hexane). Found %: C 35.2; H 2.4; N 6.5. Calculated %: C 35.0; H 2.5; N 6.8. Mass spectrum, *m/z* (*I*, %): (M^+-CS_2OEt, 38), 263 ($[291-C_2H_4]^+$, 100); 262 ($[291-C_2H_5]^+$, 37); 234 ($[262-CO]^+$, 12).

Reaction of Tetrachloro-4-cyanopyridine (Ib) with Potassium Ethylxanthate. A. A mixture of 2.28 g (9.4 mmole) of compound (Ib) and 4.3 g (2.2 mmole) of potassium ethylxanthate in 200 ml of acetone was stirred at room temperature for 24 h. The reaction mixture was treated as in the previous experiment and chromatographed on a column of silica gel with a 3:2 mixture of hexane and benzene as eluant. We obtained 0.8 g (24%) of compound (X).

B. A mixture of 1.6 g (6.6 mmole) of compound (Ib) and 2.6 g (13.2 mmole) of potassium ethylxanthate in 15 ml of acetone was boiled for 4 h. The reaction mixture was treated as in method A. The product was chromatographed on a column of silica gel with a 1:1 mixture of hexane and benzene as eluant. We obtained 0.6 g (31%) of compound (XI).

S-(2,5-Dichloro-4-cyano-6-ethyl-3-pyridyl) Ethylxanthate (X) ($C_{11}H_{10}Cl_2N_2OS_3$). The product formed light-yellow crystals; mp 82-83.5°C (from hexane). Found %: C 35.8; H 2.8; N 8.3. Calculated %: C 35.5; H 2.9; N 8.0. Mass spectrum, *m/z* (*I*, %): 264 ($[M-CSOC_2H_4]^+$, 3); 231 ($[M-CS_2OC_2H_5]^+$, 39).

2,5-Dichloro-3,6-bisethylthio-4-cyanopyridine (XI) ($C_{10}H_{10}Cl_2N_2S_2$). The product formed yellow crystals; mp 90.5-91.5°C (from hexane). Found %: C 41.4; H 3.6; N 9.4. Calculated %: C 41.1; H 3.5; N 7.8. Mass spectrum, *m/z* (*I*, %): 292 (M^+, 56); 259 ($[M-SH]^+$, 100); 257 ($[M-Cl]^+$, 13); 231 ($[M-SC_2H_5]^+$, 42).

Reaction of Tetrachloro-3-cyanopyridine (Ic) with Potassium Ethylxanthate. A mixture of 1.21 g (5 mmole) of compound (Ic) in 80 ml of acetone and 1.6 g (8.2 mmole) of potassium ethylxanthate in 20 ml of acetone was stirred at room temperature for 2 h. The precipitate was filtered off, and the mother solution was evaporated under vacuum. The remaining oil was chromatographed on a column of silica gel with a 2:1 mixture of hexane and benzene as eluant. We isolated 0.4 g (24%) and 0.9 g (44%) of compounds (XII) and (XIII) respectively.

S-(2,3,6-Trichloro-5-cyano-4-pyridyl) Ethylxanthate (XII) ($C_9H_5Cl_3N_2O_2$). The product formed light-yellow crystals; mp 56.5-58.5°C (from hexane). Found %: C 33.2; N 1.4; N 8.7. Calculated %: C 33.1; H 1.6; N 8.6. Mass spectrum, *m/z* (*I*, %): 326 (M^+, 1.4); 291 ($[M-Cl]^+$, 12); 263 ($[M-ClC_2H_4]^+$, 75); 238 ($[M-CSOC_2H_4]^+$, 54); 202 ($[238-HCl]^+$, 58).

S,S'-(2,5-Dichloro-5-cyanopyridyl) 4,6-Bis[ethylxanthate] (XIII) ($C_{12}H_{10}Cl_2N_2O_2S_4$). The product formed yellow crystals; mp 30-31.5°C (from hexane). Found %: C 35.2; H 2.4; N 7.0. Calculated %: C 35.0; H 2.5; N 6.8. Mass spectrum, *m/z* (*I*, %): 412 (M^+, 2); 377 ($[M-Cl]^+$, 24); 289 ($[M-ClCSOC_2H_4]^+$, 100); 261 ($[289-C_2H_4]^+$, 87).

Reaction of the Pentachloropyridine (Id) with Potassium Ethylxanthate. A. The reaction mixture, consisting of 2.5 g (9.9 mmole) of compound (Id) and 2.5 g (12.8 mmole) of potassium ethylxanthate in 80 ml of acetone, was stirred at room temperature for 12 h. The precipitated inorganic salts were filtered off, and the filtrate was evaporated under vacuum. The residue was washed with water, the product was extracted with chloroform, and the organic layer was dried over sodium sulfate. The solvent was evaporated, and the residue was chromatographed on a column of silica gel with a 3:1 mixture of hexane and benzene as eluant. We obtained 0.9 g (33%) of compound (XV).

B. The reaction mixture, consisting of 1.25 g (5 mmole) and 1.2 g (6.1 mmole) of potassium ethylxanthate in 50 ml of acetonitrile, was stirred at room temperature for 4 h. The reaction mixture was treated as in method A. We obtained 0.76 g (55%) of compound (XV).

C. The reaction mixture, consisting of 2.5 g (10 mmole) of compound (Id) and 2.42 g (12.3 mmole) of potassium ethylxanthate in 70 ml of ethanol, was stirred at room temperature for 4 h. The reaction mixture was treated as in method A. (The eluant for chromatography was a 1:1 mixture of hexane and benzene.) We obtained 1.58 g (47%) of compound (XIV).

4-Ethylthio-2,3,5,6-tetrachloropyridine (XV) ($C_7H_5Cl_4NS$). The product formed white crystals; mp 47.5-48.5°C. Found %: C 30.7; H 1.7; N 4.9. Calculated %: C 30.4; H 1.8; N 5.1. Mass spectrum, *m/z* (*I*, %): 275 (M^+, 73); 247 ($[M-C_2H_4]^+$, 80); 240 ($[M-Cl]^+$, 34); 211 ($[M-C_2H_4HCl]^+$, 47).

S-(2,3,5,6-Tetrachloro-4-pyridyl) Ethylxanthate (XIV) ($C_8H_5Cl_4NOS_2$). The product formed white crystals; mp 91.5-93°c (from hexane). Published data [7]: 95°C. Mass spectrum, *m/z* (*I*, %): 300 ($[M-Cl]^+$, 54); 272 ($[M-ClC_2H_4]^+$, 99); 247 ($[M-CSOC_2H_4]^+$, 32); 211 ($[247-NCl]^+$, 61).

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