CYCLIZATION OF 1,1,2,2-TETRACYANOETHANE BY THE SEMICARBAZONES AND OXIMES OF CARBONYL COMPOUNDS

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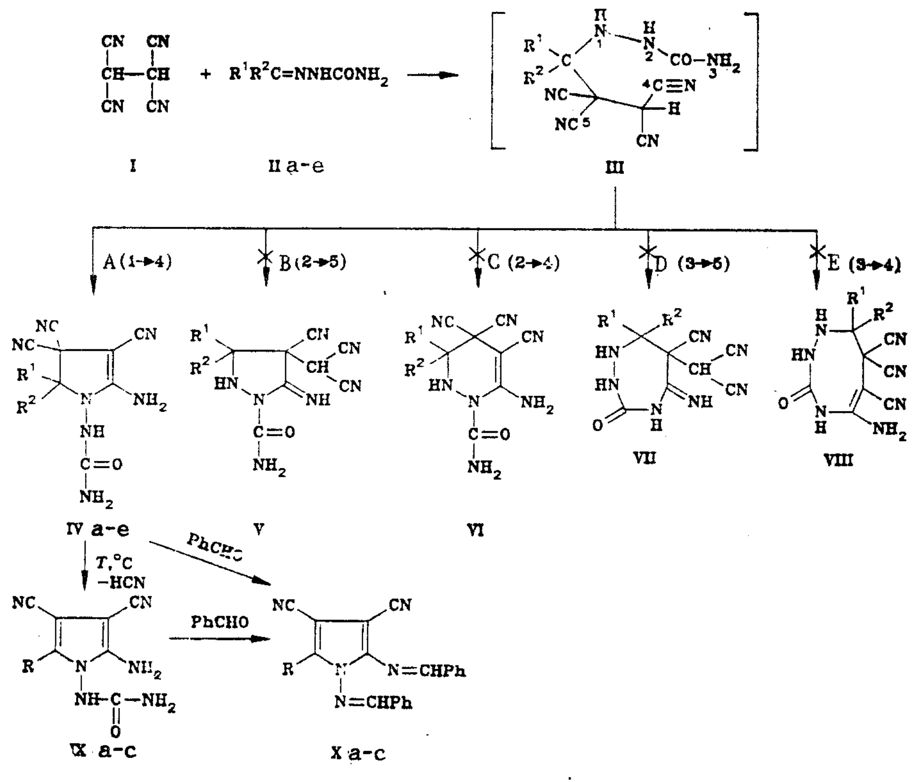
1,1,2,2-Tetracyanoethane undergoes cyclization with semicarbazones and oximes with the formation of 5-substituted 2-amino-3,4,4-tricyano-N-ureido(N-hydroxy)-2-pyrrolines. When heated, the latter readily eliminate HCN, forming the corresponding 3,4-dicyano-N-ureidopyrroles. The reaction of the N-ureidopyrroles with benzaldehyde leads to 1,2-di(benzylidenamino)-3,4-dicyanopyrroles.

The reaction of 1,1,2,2-tetracyanoethane (TCET) (I) with azomethine compounds is well known [1-3]. In these cases intramolecular cyclization takes place in the adduct by the only possible path through attack on the terminal nitrile group by the secondary amine center that forms.



IV a $R^1=CH_3$, $R^2=H$; b $R^1=C_3H_7$-n, $R^2=H$; c $R^1=C_5H_{11}$, $R^2=H$; d $R^1=C_6H_{13}$n, $R^2=H$; e $R^1=R^2=CH_3$; IX a $R=C_5H_{11}$-*n*, b $R=C_6H_{13}$n, c $R=C_3H_7$-*n*; X a $R=CH_3$, b $R=C_3H_7$-*n*, c $R=C_5H_{11}$-n

The intramolecular cyclization in the intermediate containing several nucleophilic centers must take place in a more complicated way. We studied this possibility in the reactions of TCET (I) with the semicarbazones (IIa-e) and oximes. If it is assumed that the first stage of the reaction with semicarbazones is addition of the tetracyanoethyl anion to the polar C=N bond, the intermediate (III) will contain three nucleophilic nitrogen centers. It is known that

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TABLE 1. PMR and IR Spectra of Compounds (IV, IX-XI)

Compound	Molecular formula	R¹	R²	T_{mp} °C	PMR spectrum, ppm (in DMFA-d_7)	IR spectrum, cm⁻¹			Yield, %
						NH	C≡N	C=O	
IVa	$C_9H_9N_7O$	CH_3	H	237...238 with decomp.	7,90 (2H, s, NH_2); 6,43 (2H, s, NH_2); 8,63 (1H, s, NH); 4,41 (1H, q, CH)	3580...3200, 1675	2275, 2225	1710	39
IVb	$C_{11}H_{13}H_7O$	n-C_3H_7	H	217...218 with decomp.	7,77 (2H, s, NH_2); 6,33 (2H, s, NH_2); 8,55 (1H, s, NH); 4,37 (1H, q, CH)	3510...3225, 1665	2260, 2220	1715	68
IVc	$C_{13}H_{17}N_7O$	n-C_5H_{11}	H	161...162 with decomp.	—	3505...3215, 1660	2265, 2215	1705	27
IVd	$C_{14}H_{19}N_7O$	n-C_6H_{13}	H	118...120 with decomp.	—	3500...3215, 1655	2255, 2210	1700	46
IVe	$C_{10}H_{11}N_7O$	CH_3	CH_3	176...178 with decomp.	—	3415...3170, 1660	2260, 2210	1700	50
IXa	$C_{12}H_{16}N_6O$	n-C_5H_{11}	—	215...216	—	3440...3210, 1650	2240, 2225	1685	55
IXb	$C_{13}H_{18}H_6O$	n-C_6H_{13}	—	184...185	—	3445...3210, 1650	2240	1675	66
IXc	$C_{10}H_{12}N_6O$	n-C_3H_7	—	247...248	—	3410...3210, 1670	2230, 2225	1690	68
Xa	$C_{21}H_{15}N_5$	CH_3	—	180...181	9,18 (1H, s, CH=N); 9,00 (1H, s, CH=N)	1610*	2240, 2225	—	24
Xb	$C_{23}H_{19}N_5$	n-C_3H_7	—	137...138	9,03 (1H, s, CH=N); 9,19 (1H, s, CH=N)	1615*	2240, 2227	—	43
Xc	$C_{25}H_{23}N_5$	n-C_5H_{11}	—	129...130	—	1610*	2240, 2230	—	13
XIa	$C_{10}H_{11}N_5O$	n-C_3H_7	H	107...108	—	3400...3200, 1670	2225	3540**	29
XIb	$C_{10}H_{11}N_5O$	i-C_3H_7	H	157...158	—	3410...3180, 1680	2220	3535**	50

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*The stretching vibrations of the C≡H bond.

**The stretching vibrations of the OH group.

TABLE 2. ^{13}C NMR Spectra of Compounds (IV) and (IX)

Compound	Chemical shifts, δ, ppm (in DMFA-d_7)					
	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	C=O	C≡N
IVa	164,19	46,75	40,81	64,22	157,60	113,53; 114,50; 117,36
IVb	164,42	47,04	—	68,10	157,84	113,50; 114,69; 117,33
IVc	164,20	46,92	35,09	68,14	157,47	113,48; 114,67; 117,18
IXa	148,84	65,69	86,29	138,99	156,42	114,99; 115,56

TABLE 3. Mass Spectra of Compounds (IV,* X)

Compound	m/z (I_{rel} %)**
IVa	–, 204 (23), 161 (16), 145 (100), 77 (24), 76 (14), 61 (15), 44 (33), 43 (37), 42 (73), 41 (15)
IVb	259 (0,2), 232 (24), 203 (49), 189 (12), 186 (22), 173 (19), 160 (100), 145 (27), 144 (23), 131 (12), 77 (20)
IVc	–, 260 (4), 203 (11), 186 (11), 171 (2), 160 (100), 145 (22), 144 (11), 133 (3), 77 (6), 60 (16)
IVd	–, 274 (5), 231 (11), 203 (16), 186 (27), 171 (12), 160 (100), 145 (51), 144 (16), 103 (7), 55 (12)
IVe	245 (2), 218 (21), 201 (21), 187 (17), 175 (27), 160 (100), 145 (10), 144 (6), 119 (26), 92 (13), 73 (24)
Xa	337 (100), 234 (99), 233 (99), 218 (99), 206 (75), 165 (56), 104 (65), 103 (53), 89 (51), 77 (96), 51 (31)
Xb	365 (100), 336 (95), 267 (80), 261 (99), 234 (80), 233 (99), 210 (81), 195 (99), 194 (99), 105 (99), 77 (88)
Xc	393 (47), 365 (16), 336 (29), 289 (16), 261 (16), 233 (76), 104 (85), 103 (100), 91 (18), 77 (88), 51 (58)

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*The mass spectra of compounds (IXa-c) were identical with the mass spectra of the corresponding pyrrolines (IV), beginning with the M — 27 ion.

**The molecular ion peak and the ten strongest peaks of the fragment ions are given.

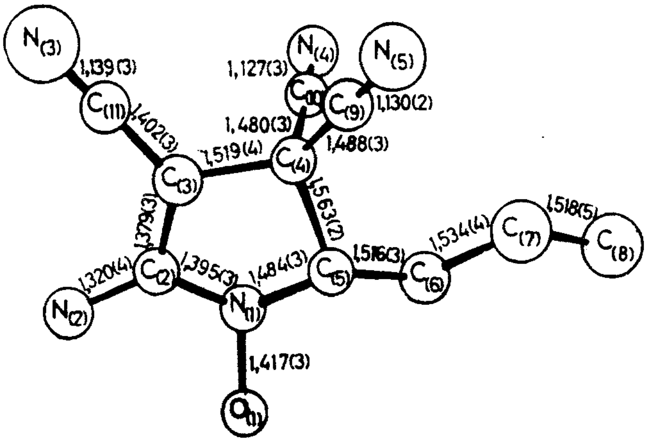


Fig. 1. Molecular geometry of the pyrroline (XIa).

in addition to the secondary amine center the amide nitrogen readily undergoes an intramolecular reaction with the nitrile group [4]. Thus, cyclization by a number of paths with the inclusion of three nucleophilic centers (nitrogen atoms 1-3) and two electrophilic centers (the carbon atoms of the nitrile groups 4 and 5) with the formation of the heterocycles (IV-VIII) can be expected in the intermediate (III). According to TLC, the selective formation of only one structure was detected (see the scheme).

It follows from elemental analysis that the target compounds are 1:1 adducts. A preliminary choice between the structures was made from the IR spectra. The presence of the amino nitrile fragment (3580-3170 and 2225-2210 cm^{-1}) (Table 1) makes it possible to rule out structures (V) and (VII).

TABLE 4. Atomic Coordinates in the Molecule of (XIa)

Atom	x	y	z	Atom	x	y	z
$O_{(1)}$	0,3687(2)	0,4940(2)	0,8409(2)	$C_{(4)}$	0,5963(3)	0,1017(2)	0,7316(2)
$N_{(1)}$	0,4909(2)	0,3757(2)	0,7679(2)	$C_{(5)}$	0,4195(3)	0,2433(2)	0,7633(2)
$N_{(2)}$	0,7067(2)	0,3570(2)	0,8999(2)	$C_{(6)}$	0,2882(3)	0,3246(3)	0,6472(2)
$N_{(3)}$	0,9945(3)	−0,1302(3)	0,9082(2)	$C_{(7)}$	0,2306(3)	0,1807(3)	0,6345(3)
$N_{(4)}$	0,5782(3)	−0,2215(2)	0,8162(2)	$C_{(8)}$	0,0844(3)	0,2592(3)	0,5332(3)
$N_{(5)}$	0,6974(3)	0,2115(2)	0,4401(2)	$C_{(9)}$	0,6537(3)	0,1599(2)	0,5658(2)
$C_{(2)}$	0,6434(3)	0,2799(2)	0,8398(2)	$C_{(10)}$	0,5808(3)	−0,0802(2)	0,7795(2)
$C_{(3)}$	0,7107(3)	0,1124(2)	0,8256(2)	$C_{(11)}$	0,8694(3)	−0,0189(3)	0,8688(2)

The signals from the two amino groups in the PMR spectra of compounds (IVa) and (IVb), observed in the regions of 7.90 and 7.77 ppm and 6.43 and 6.33 ppm respectively, like the data from IR spectroscopy (Table 1) fully exclude the formation of structures (V, VII, VIII). Here the protons of the NH group appear in the regions of 8.63 and 8.55 ppm for compounds (IVa, b) respectively. At room temperature the signal for the proton of the CH unit [4.42 and 4.37 ppm for compounds (IVa, b)] is greatly broadened, and this does not make it possible to assign it unambiguously. However, by recording the spectrum at 80°C it is possible to reveal the fine structure (a quadruplet at 4.41 ppm, $J = 6.22$ Hz), and this gives reason to propose structure (IV). In addition, the signal from the NH group for structure (VI) must be observed in the upfield region.

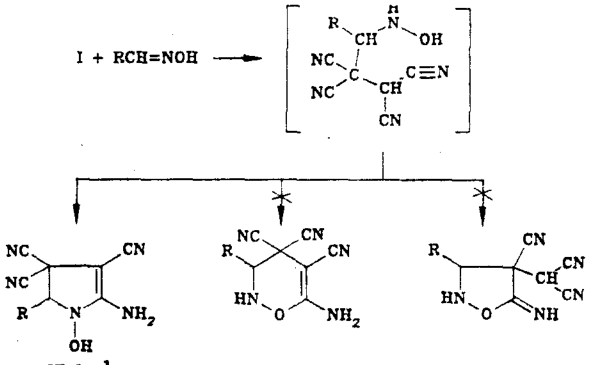
The data from the ^{13}C NMR spectra (Table 2), in which there is a set of signals for the carbon atoms of the heterocycle, do not make it possible to make an unambiguous choice between structures (IV) and (VI).

The mass spectra proved most informative. They are characterized by low-intensity molecular ion peaks, which lose the urea residue after elimination of a molecule of hydrogen cyanide [$(M^+ - 27) - 59$] (Table 3). Such dissociation is only possible for compounds with the structure (IV).

The ease of elimination of the hydrogen cyanide molecule during mass-spectral dissociation was confirmed experimentally. The pyrroles (IXa-c) are formed when the pyrrolines (IV) are heated in high-boiling solvents.

The pyrrolines (IV) and pyrroles (IX) undergo an unexpected transformation in reaction with benzaldehyde; in addition to the formation of a Schiff base at the amino group, the urea fragment is split with the formation of the derivatives (Xa-c) (Tables 1 and 2).

The cyclization of TCET by oximes takes place similarly. Of the three possibilities for intramolecular cyclization the one with the formation of N-hydroxpyrrolines (XIa, b) is realized.



XI a, b

XI a $R=C_3H_7$-n, b $R=C_3H_7$-i

The structure of the N-hydroxypyrrolines (XI) was confirmed unambiguously by the data from x-ray crystallographic analysis. The five-membered ring of the molecule has the envelope conformation (Fig. 1), where the $C_{(2)}—C_{(3)}—C_{(4)}—C_{(5)}$ torsion angle is 25°. The $N_{(1)}$, $C_{(2)}$, $C_{(3)}$, and $C_{(4)}$ atoms lie almost in one plane. The inductive action of the donor—acceptor pair — the amino and nitrile groups linked through a double bond — is clearly defined. The donating effect of the amino and accepting nitrile groups leads to a decrease in the lengths of the $N_{(2)}—C_{(2)}$ and $C_{(3)}—C_{(11)}$ bonds and an increase in the $C_{(2)}—C_{(3)}$ and $C_{(11)}—N_{(3)}$ bonds (Fig. 1, Table 4).

EXPERIMENTAL

The reactions and the purity of the synthesized compounds were monitored by TLC on Silufol UV-254 plates with development by UV light and iodine vapor. The IR spectra were recorded in thin layers in Vaseline oil on a

UR-20 instrument. The ^{1}H NMR spectra were recorded on a Bruker WP-200SY spectrometer at 200 MHz with TMS as internal standard. The mass spectra were recorded on a KRATOS MS 25PFA instrument at 50 eV.

2-Amino-3,4,4-tricyano-N-ureido-2-pyrrolines (IVa-e). A mixture of 0.05 mole of compound (I) and 0.05 mole of the semicarbazone of the carbonyl compound was dissolved in 30 ml of DMFA. After dissolution 30 ml of water was added. Depending on the initial semicarbazone, the pyrrolines crystallized from the reaction mass after dilution after times ranging from 5 min to 10 h. The isolation time increased with increase in the chain length of the radical. The precipitate was filtered off, washed with water and with isopropyl alcohol, and recrystallized from isopropyl alcohol.

2-Amino-3,4,4-tricyano-N-hydroxy-2-pyrrolines (XIa, b). To a suspension of 0.02 mole of TCET in 30 ml of a 1:1 mixture of isopropyl alcohol and water, while stirring, we added dropwise 0.02 mole of the oxime. At the end of the reaction the obtained solution was diluted with water until cloudy and kept for 5 h to crystallize. The precipitate was filtered off, washed with a 1:1 mixture of isopropyl alcohol and water, and reprecipitated from ethyl acetate with hexane.

The single crystals of compound (XIa) were investigated on an Enraf Nonius CAD-4 automatic four-circle diffractometer. The principal crystallographic data were as follows: $a = 8.369$ (2), $b = 8.560$ (3), $c = 9.544$ (3) Å, $\alpha = 66.99$ (2)°, $\beta = 76.80$ (2)°, $\gamma = 67.97$ (2)°. Fedorov group P1, $Z = 2$, $V = 580.8$ Å^3. In the region of $\theta \leq 25$ there were 1986 nonzero reflections, of which 1752, greater than 3σ, were used in the refinement of the position and thermal parameters of the molecule, the motif of which was obtained by direct methods using the MULTAN program of the SDP package. The position and thermal parameters of the nonhydrogen atoms were refined in anisotropic full-matrix approximation. The hydrogen atoms were localized from Fourier syntheses and were refined in isotropic approximation. The final R value was 3.9%.

2-Amino-3,4-dicyano-N-ureidopyrroles (IXa-c). A 0.02-mole sample of the pyrroline (IV) was boiled in 20 ml of DMFA for 5 min until it had disappeared from the solution. The solution was then diluted with 20 ml of hot water (70°C) and cooled. The precipitated pyrrole (IX) was filtered off, washed with water and a small amount of isopropyl alcohol, and recrystallized from isopropyl alcohol.

1,2-Di(N-benzylideneamino)-3,4-dicyanopyrroles (Xa-c). To a suspension of 0.01 mole of the pyrroline (IV) or pyrrole (IX) in 10 ml of benzaldehyde we added two drops of acetic acid. The mixture was then boiled for 2 h under a reflux condenser until the initial compound had disappeared from the reaction mixture. At the end of the reaction the obtained solution was cooled and diluted with an equal volume of isopropyl alcohol. After rubbing the walls with a glass rod a yellow precipitate separated. It was filtered off, washed with a small amount of isopropyl alcohol, and recrystallized from isopropyl alcohol [compound (Xa) from methylcellosolve].

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