REACTION OF 3,3,4,4-TETRACYANOPYRROLIDINES WITH PRIMARY ALCOHOLS AND AMINES

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2,5-Substituted 3,3,4,4-tetracyanopyrrolidines react with primary alcohols in the presence of an excess of a base or with the base itself. 2-(N-Arylideneamino)-5-alkoxy-3,4-dicyanopyrroles are formed as a result of the reactions with alcohols, and 2,5-diamino-1-R-3,4-dicyanopyrroles are formed as the result of the reaction with primary aliphatic amines.

Ring—chain tautomerism was discovered during the study of 2,5-substituted 3,3,4,4-tetracyanopyrrolidines (I) [1]. Its presence probably explains the unusual reactivity of compounds (I) and the variety of the processes.

3,3,4,4-Tetracyanopyrrolidines (I) change into the acyclic form (II) in the presence of an equimolar amount of a base [1]. With an excess of the base it is possible to bring the pyrrolidines (I) into reaction with nucleophiles. Thus, when solutions of compounds (I) in primary alcohols were heated in the presence of a twofold excess of potassium hydroxide, 2-(N-arylideneamino)-5-alkoxy-3,4-dicyanopyrroles (Va-g) were isolated from the reaction mass.

Compounds (Va-g) (Table 1) are produced from the tetracyanopyrrolidines (I) according to the following scheme:



The presence of twice the amount of alkali is required both for ring opening with the formation of the dicyanomethane anion and for the production of the alkoxide ion, which may add at the more electrophilic carbon atom of the nitrile with subsequent cyclization at the vicinal nitrile group with the formation of the pyrrole ring. The intermediate product (III) may be stabilized by a rearrangement of the Claisen type with the formation of a new C-N bond in a fragment similar to the adduct from the addition of tetracyanoethane to hydrobenzamide [1]. In the structure of compound (IV), by analogy with [1], the elimination of an aldimine molecule, leading to the formation of the pyrroles (V), is possible.

In the PMR spectrum of compound (Vc), apart from the signals of the ethoxyl [δ 1.44 (3H, t, CH₃), 4.54 ppm (2H, q, CH₂)] and phenyl [7.93-7.60 ppm (5H, m, C₆H₅)] substituents, there is a signal at δ 8.88 ppm characteristic of the hydrogen of the aldimine fragment. The ¹³C NMR spectrum of this compound supports the proposed structure. ¹³C NMR spectrum of the pyrrole (Vc), δ , ppm: C₍₁₎ 151.84; C₍₂₎ 73.40; C₍₃₎ 85.33; C₍₄₎ 135.11; C₍₅₎ 160.47; C₍₆₎ 69.93; C₍₇₎ 14.66; C(CN) 113.97; 114.02; C(C₆H₅) 132.47...129.18.

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Fig. 1. Molecule of the ethoxypyrrole (Vc) without the hydrogen atoms.

The data from IR and mass spectroscopy (Table 1) also do not contradict the structure. In order to determine the structure of compounds (Va-g) unambiguously we undertook an x-ray crystallographic investigation of 2-(N-benzylideneamino)-3,4-dicyano-5-ethoxypyrrole (Vc) (Fig. 1).

As seen from the presented scheme, the addition of the alcohols requires at least a twofold quantity of the base. The reactions take place both in the presence of alkalis and in the presence of organic bases.

When primary aliphatic amines were used as base and reagent, 1-alkyl-2,5-diamino-3,4-dicyanopyrroles (VIIa, b) were obtained with yields of up to 40%, and with hydrazine 1,2,5-triamino-3,4-dicyanopyrrole (VIIc) was obtained.



The reaction probably takes place according to a scheme close to that for the addition of alcohols. After the opening of the pyrrolidine ring addition also takes place at one of the terminal nitrile groups. Further cyclization of the obtained diamine takes place through the more basic secondary nitrogen atom [2,3]. A rearrangement of the Claisen type then probably occurs with the formation of the N-benzylideneamine derivative (VI), which is transaminated under the reaction conditions with the excess of the initial aliphatic amine.

On the basis of the fact that one and the same reaction product is obtained from the various pyrrolidines (I) and one amine and that the mass-spectral dissociation of compounds (I) is characterized by the ejection of tetracyanoethylene and 1,1,2,2-tetracyanoethane (TCET) it could be supposed that they react through total cleavage of the tetracyanopyrrolidines (I) with regeneration of the TCET.



It is known that 1,2,5-triamino-3,4-dicyanopyrrole is formed during the cyclization of TCET by hydrazine [3]. At the same time the transformation of TCET into a "black resinous mass" during storage in the presence of traces of moisture and bases has been described [4]. However, the experiments showed that TCET undergoes cyclization by amines to the 2,5-diamino-3,4-dicyanopyrroles (VIIa-e) (Table 2).

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Characteristics
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punod	tormula		č		IR spectru	աղ Ն, cm ⁻¹		Mass spectrum, m/z (I _{rel} ,%)*	Yield
		×	×		HN	C≡N	C=N		%
۲a ا	C ₁₄ H ₁₀ N ₄ O	C ₆ H ₅	CH ₃	209 210	3240, 3170	2240, 2235	1615	268 (67), 254 (19), 253 (100), 150 (23), 122 (30), 103 (7), 95 (28), 83 (23), 69 (38), 55 (41), 45 (89)	80
Λp	C ₁₄ H ₉ FN ₄ O	4-FC ₆ H ₄	CH ₃	239241 (decomp.)	3220, 3165	2250, 2235	1600	250 (61), 236 (21), 235 (100), 180 (7), 132 (12), 130 (18), 104 (24), 103 (14), 81 (20), 77 (33), 45 (78)	92
Nc	C ₁₅ H ₁₂ N4O	C ₆ H ₅	C ₂ H ₅	232 233	3245, 3180	2230	1610	264 (88), 263 (8), 236 (99), 235 (100), 208 (21), 180 (20), 132 (21), 131 (22), 130 (21), 104 (57), 77 (51)	72
νq	C ₁₅ H ₁₂ N4O2	2-H ₃ COC ₆ H ₄	CH ₃	233234 (decomp.)	3175	2245, 2230	1605	280 (65), 266 (19), 265 (100), 159 (24), 147 (9), 134 (4), 119 (27), 107 (62), 103 (17), 91 (33), 77 (22)	62
Ve	C ₁₂ H ₈ N ₄ O ₂	2-Fu	CH ₃	155 156	3130	2230	1605	240 (49), 225 (100), 130 (8), 122 (12), 120 (4), 103 (8), 94 (9), 78 (12), 77 (11), 51 (12), 44 (22)	92
Vť	C ₁₄ H ₉ CIN4O	3-CIC ₆ H ₄	CH ₃	261262 (decomp.)	3240, 3180	2230	1600	284 (43), 270 (19), 269 (100), 164 (10), 138 (16), 130 (16), 103 (15), 91 (10), 77 (15), 69 (33), 45 (96)	68
٧g	C ₁₅ H ₁₂ N ₄ O ₂	4-H ₃ COC ₆ H ₄	CH ₃	217218	3220, 3155	2225	1600		88

*The molecular ion peak and the 10 strongest peaks of the fragment ions are given.

TABL	,Е 2. T	haracteristics or	f the 2,5-Diam	ino-3,4	4-dicya	nopyrrc	oles (VIIa-e				
Com-		Molecular	mp, °C		1 ³ C N	MR spec	trum, ppm	A	R spectrum, ô, ppm	Yiel	d. %
punod	ĸ	formula	(decomp.)		C(2) (C(5))	C(3) (C(4)	C (C=N)	$ m NH_2$	H (R)	from I	from TCET
VIIa	CH ₃	C ₇ H ₇ N ₅	260		144,34	64,50	117,04	$6,00 (4H, s, 2NH_2)$	3,14 (3H, s, N-CH ₃)	40	39
VII b VII c	C ₂ H ₅ NH ₂	C ₈ H ₉ N ₅ C ₆ H ₆ N ₆	$283 \dots 285 \dots 286$ $285 \dots 286$		145,01	60,05	117,42			44	62
VIId	i-C ₃ H ₇	C ₉ H ₁₁ N ₅	272 274	4.4 - 2			, [6,01 (4H, s, 2NH ₂)	1,21 (6H, m, 2CH ₃); 4,13 (1H, m, CH)	1	34 58
VII,e	C ₆ H ₅	C ₁₂ H ₉ N ₅	$238 \dots 240$		143,7(67,36	117,01				00
Com-			IR spectrum	, cm ⁻¹				Mass	spectrum,* m/z (I _{rel} , %)		
pumod	×	NA	H	v c≡N	vc=c	б _{NH}					
VII.a	CH ₃	3400, 3335, 325	0, 3205	2215	1585	1630	$\begin{array}{ccc} 161 & (99), \\ 103 & (9), \\ 77 \end{array}$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	(100), 132 (26), 129 (11), 110 (15	5), 105	(25),
d IIV	C ₂ H ₅	3390, 3330, 325	0,3210	2210	1590	1635	169 (17)	190 196 1900 196		10) 77	(35)
VII c	NH ₂	3385, 3315, 325	5, 3200	G122	OACT	001	76 (12), 69	101 (2), 140 (100), 123 (12) (12)			* (nn)
٧II٠d	<i>i</i> -C ₃ H ₇	3410, 3370, 333	5, 3280	2210	1580	1625					ć
VII e	C ₆ H ₅	3440, 3410, 332	0, 3250, 3210	2210	1590	1630	223 (49), 2 77 (29), 51	222 (15), 221 (100), 194 1 (16)	(43), 167 (9), 146 (12), 118 (25), 103 ((10), 9	1 (12),
				-							

*The molecular ion peak and the 10 strongest peaks of the fragment ions are given.

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Fig. 2. Molecule of the dicyanopyrrole (VIIe) without the hydrogen atoms.

Following the proposed scheme, the diaminopyrrole (VIId) should also be obtained from the pyrrolidines (1) and isopropylamine. However, their reaction leads to the formation of 2,5-diphenyl-3,4-dicyanopyrrole (VIII). This result contradicts the suggestion about the regeneration of TCET under the process conditions. The formation of 2,5-diphenyl-3,4-dicyanopyrrole (VIII) is probably explained by steric hindrance by the bulky substituent in the amine for attack at the nitrile group of a more complex molecule than TCET. In this reaction isopropylamine acts as a dehydrocyanating agent.

For the unambiguous determination of the structures (VII) we undertook an x-ray crystallographic investigation of 2,5-diamino-1-phenyl-3,4-dicyanopyrrole (VIIe) (Fig. 2). The data from the IR spectra, mass spectra (Table 3), and PMR spectra (Table 2) agree fully with the structure (VII).

The reaction of the pyrrolidines (I) with primary aromatic amines will be considered in the next communication.

EXPERIMENTAL

The reactions and the purity of the synthesized compounds were monitored by TLC on Silufol UV-254 plates with development by iodine vapor and UV light.

The IR spectra were obtained in thin layers on a UR-20 instrument. The ¹³C NMR spectra were recorded in DMFA-d₆ on a Bruker WH-90 spectrometer at 22.63 MHz with HMDS as internal standard. The PMR spectra were recorded on a Bruker WP 200 SY spectrometer at 200 MHz with TMS as internal standard. The mass spectra were obtained on a Kratos MS 25PFA instrument with direct injection at 50 eV. The x-ray crystallographic investigations were conducted on an automatic CAD-4 four-circle diffractometer with MoK_{α} radiation and a ω scan.

5-Alkoxy-2-(N-arylideneamino)-3,4-dicyanopyrroles (Va-g). In 20 ml of the respective primary alcohol we dissolved 1.12 g (20 mmole) of potassium hydroxide, and at 20°C we added 10 mmole of the initial pyrrolidine (I) to this solution in a single portion. The obtained mixture was stirred until completely dissolved and was then heated and boiled for 1 min. After cooling an excess of acetic acid was added (~40 mmole), and the mixture was again cooled to 20°C. The precipitate was filtered off, washed with isopropyl alcohol, and recrystallized from acetonitrile.

Principal Crystallographic Data of the Pyrrole (Vc). a = 10.613(2), b = 14.991(3), c = 9.330(3) Å; $\beta = 114.47(2)^{\circ}$; space group P 21/c, Z = 4, V = 1350 Å³. Of the obtained 1608 nonzero reflections 1127 with I > $3\sigma(I)$ were used for 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 software. The positions and thermal parameters of the nonhydrogen atoms were refined in full-matrix anisotropic approximation. The hydrogen atoms were localized from Fourier syntheses and were refined in isotropic approximation. The final R value was 0.052.

2,5-Diamino-1-R-3,4-dicyanopyrroles (VIIa, b). To 10 ml of a 30% aqueous solution of the respective amine we added 10 mmole of tetracyanopyrrolidine (I) in one portion. The mixture was stirred until completely

dissolved and was then heated to boiling. After cooling we added an equal volume of isopropyl alcohol and acidified the solution with acetic acid. The precipitate was filtered off, washed with isopropyl alcohol, and recrystallized.

2,5-Diphenyl-3,4-dicyanopyrrole (VIII). The compound was obtained under similar conditions with a yield of 19% from the reaction of the 2,5-diphenyl-substituted compound (I) with isopropylamine; mp 257-258°C. IR spectrum (thin layer), cm⁻¹: 3285 (NH); 2245, 2235 (C=N). ¹³C NMR spectrum (DMFA-d₇), δ , ppm: C₍₂₎ (C₅) 141.43; C₍₃₎ (C₍₄₎) 92.66; C(C=N) 114.78; C(C₆H₅) 127.29...130.09. M⁺ 269. C₁₈H₁₁N₃. **2,5-Diamino-1-R-3,4-dicyanopyrroles (VIIa-d).** To 15 ml of a 33% aqueous solution of the respective

2,5-Diamino-1-R-3,4-dicyanopyrroles (VIIa-d). To 15 ml of a 33% aqueous solution of the respective amine we added 1.3 g (10 mmole) of 1,1,2,2-tetracyanoethane. The mixture was stirred until the initial cyanide had completely dissolved and was then allowed to stand overnight. The next day the precipitate was filtered off, washed with isopropyl alcohol, and recrystallized.

2,5-Diamino-1-phenyl-3,4-dicyanopyrrole (VIIe). To a suspension of 13 g (100 mmole) of 1,1,2,2-tetracyanoethane in 40 ml of dioxane we added 10.2 g (110 mmole) of aniline. The mixture was heated to boiling with stirring and boiled for 2 min. After cooling with water the precipitate was filtered off, washed with dioxane, and recrystallized from aqueous methylcellosolve (1:1).

X-Ray Crystallographic Investigation of the Pyrrole (VIIe). a = 8.399 (2), b = 11.117 (3), c = 13.882 (3) Å; $\alpha 114.16$ (23), $\beta = 106.39$ (2), $\gamma 83.08$ (2)°; space group P1, Z = 4, V = 1134.6 Å³. In the region of $\theta < 24^{\circ}$ we found 2704 nonzero reflections, of which 1775 with I > 3σ were used for 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 software. The parameters of the nonhydrogen atoms were refined in anisotropic full-matrix approximation. The hydrogen atoms were localized from Fourier syntheses and refined in isotropic approximation. The final R value was 0.04.

1,2,5-Triamino-3,4-dicyanopyrrole (VIIc). To 3 g of hydrazine hydrate with vigorous stirring and cooling in water we added 10 mmole of tetracyanopyrrolidine (I) in small portions. When all the pyrrolidine had been added, the reaction mass was stirred and cooled for 15 min. The precipitate was filtered off, washed with water, and recrystallized from methylcellosolve.

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