Chemistry of Heterocyclic Compounds, Vol. 33, No. 3, 1997

TWO DIRECTIONS OF INTERACTION OF 2-ARYL-1,2,3,4-TETRAHYDROPYRIDINE-3,3,4,4-TETRACARBONITRILES WITH NUCLEOPHILES

Ya. S. Kayukov, O. E. Nasakin, Ya. G. Urman,
V. N. Khrustalev, V. N. Nesterov, M. Yu. Antipin,
A. N. Lyshchikov, and P. M. Lukin

Depending on the reaction conditions, 2-aryl-1,2,3,4-tetrahydropyridine-3,3,4,4-tetracarbonitriles react with alcohols, thiols and ketoximes to give 3-amino-4-aryl-1,1-di[R-oxy(thio)]-6,7-dialkyl-3a,4,5,7a-tetrahydro-1H-pyrrolo[3,4-c]pyridine-3a,7a-dicarbonitrles or 2-aryl-5,6-dialkylpyridine-3,4-dicarbonitriles.

We have observed earlier that 2,5-diarylpyrrolidine-3,3,4,4-tetracarbonitriles were able to undergo a variety of chemical reactions because of the presence of ring-chain isomers [1-4]. From this point of view, the 1,2,3,4-tetrahydropyridine-3,3,4,4-tetracarbonitriles (I), which we synthesized recently [5], are of considerable interest. The structure of I suggests the existence of ring-chain isomers. On comparing the reactivity of compounds I and 2,5-diarylpyrrolidine-3,3,4,4-tetracarbonitriles, we observed that, in contrast to the latter compound, I reacted with methanol in the presence of sodium methoxide to give the products of addition to the cyano group — 3-amino-4-aryl-1,1-dimethoxy-6,7-dialkyl-3a,4,5,7a-tetrahydro-1H-pyrrolo[3,4-*c*]pyridine-3a,7a-dicarbonitriles (XI). It can be concluded on the basis of single crystal x-ray crystallography of compound XIa (Fig. 1) that the initial attack of the methoxide anion during the formation of compounds XI is at the least hindered cyano group. Reaction of compounds I with ethylene glycol, ethanol, ethanethiol, butanethiol and the oximes of acetone methyl ethyl ketone and cyclopentanone in the presence of catalytic amounts of the corresponding sodium alkoxides, sodium thiolates and

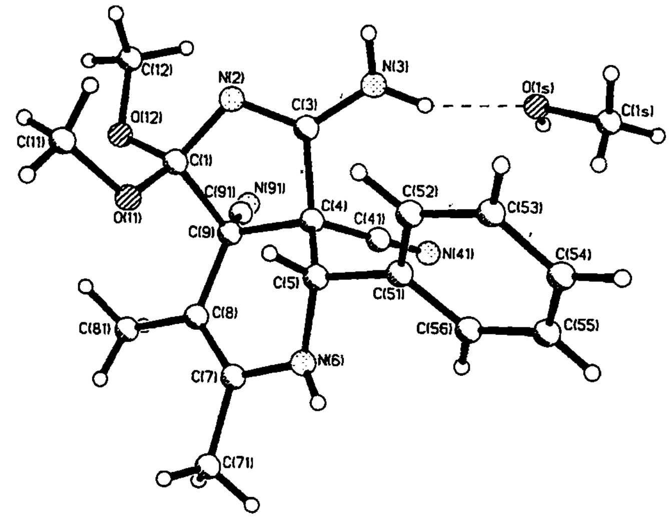


Fig. 1. Molecular structure of 3-amino-1,1-dimethoxy-6,7-tetramethylene-4-phenyl-3a,4,5,7a-tetrahydro-1H-pyrrolo[3,4-*c*]pyridine-3a,7a-dicarbonitrile (XIa).

Chuvash State University, Cheboksary 428015. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 367-375, March, 1997. Original article submitted August 27, 1996.

0009-3122/97/3303-0310$18.00

TABLE 1. Characteristics of the Compounds Synthesized

Compound	mp (decomp.), °C	Found, %			Molecular formula	Calculated, %			Recrystallization solvent	Yield, %
		C	H	N		C	H	N		
1	2	3	4	5	6	7	8	9	10	11
XIa	186...187	72,87	4,85	22,28	$C_{21}H_{23}N_5O_2$	66,83	6,14	18,56	1,4-Dioxane	81
XIb	>180	71,12	4,62	24,26	$C_{20}H_{21}N_5O_2$	66,10	5,83	19,27	DMF-water	85
XIc	169...170	70,42	4,10	25,48	$C_{19}H_{21}N_5O_2$	64,94	6,02	19,93	1,4-Dioxane	83
XId	176...178	72,25	4,40	23,35	$C_{18}H_{19}N_5O_2$	64,08	5,68	20,76	1,4-Dioxane	91
XIe	168...174	72,37	5,48	22,15	$C_{21}H_{25}N_5O_2$	66,47	6,64	18,46	1,4-Dioxane	67
XIg	138...139	72,42	5,51	22,07	$C_{22}H_{25}N_5O_3$	64,85	6,18	17,18	1,4-Dioxane	79
XIi	>110	67,25	4,31	23,17	$C_{20}H_{23}N_5O_3$	62,99	6,08	18,36	1,4-Dioxane	65
XIm	>150	69,92	4,99	20,31	$C_{19}H_{21}N_5O_2$	62,11	5,76	19,06	1,4-Dioxane	81
XIIa	205...207	68,15	4,81	17,11	$C_{23}H_{27}N_5O_2$	68,13	6,71	17,27	1,4-Dioxane	24
XIId	160...164	65,56	4,22	19,02	$C_{20}H_{23}N_5O_2$	65,74	6,34	19,16	1,4-Dioxane	24
XIIf	165...167	67,64	4,04	21,07	$C_{23}H_{29}N_5O_2$	67,79	7,17	17,18	1,4-Dioxane	42
XIIi	>135	64,46	6,52	16,97	$C_{22}H_{27}N_5O_3$	64,53	6,65	17,10	1,4-Dioxane	18
XIIIa	244...248	64,06	3,52	18,51	$C_{21}H_{21}N_5O_2$	67,18	5,64	18,65	DMF-water	76
XIIIc	>240	65,18	5,33	19,88	$C_{19}H_{19}N_5O_2$	65,32	5,48	20,05	DMF-water	71
XIIId	>240	64,32	4,97	20,66	$C_{18}H_{17}N_5O_2$	64,47	5,11	20,88	DMF-water	81
XIIIa	162...163	64,19	5,21	19,20	$C_{25}H_{29}N_7O_2$	64,34	6,36	21,34	1,4-Dioxane	22

TABLE 1 (continued)

Compound	mp (decomp.), °C	Found, %			Molecular formula	Calculated, %			Recrystallization solvent	Yield, %
		C	H	N		C	H	N		
1	2	3	4	5	6	7	8	9	10	11
XIVd	>110	62,85	5,87	23,17	$C_{22}H_{25}N_7O_2$	62,99	6,01	23,37	1,4-Dioxane	26
XVa	154...155	66,37	5,78	19,96	$C_{27}H_{33}N_7O_2$	66,51	6,82	20,11	1,4-Dioxane	28
XVc	147...150	64,92	6,61	21,07	$C_{25}H_{31}N_7O_2$	65,06	6,77	21,24	1,4-Dioxane	24
XVd	136...140	64,24	6,31	21,15	$C_{24}H_{29}N_7O_2$	64,41	6,53	21,29	1,4-Dioxane	35
XVIa	110...112	67,94	4,37	20,03	$C_{29}H_{33}N_7O_2$	68,08	6,50	19,16	2-Propanol	19
XVIIa	168...170	65,48	7,07	14,04	$C_{27}H_{35}N_5S_2$	65,68	7,14	14,18	2-Propanol	81
XVIIc	148...150	64,08	7,04	14,84	$C_{25}H_{33}N_5S_2$	64,20	7,11	14,98	2-Propanol	74
XVIId	143...148	63,41	4,72	15,29	$C_{24}H_{31}N_5S_2$	63,54	6,89	15,44	2-Propanol	80
XVIIIa	209...211	63,95	6,01	15,86	$C_{29}H_{27}N_5S_2$	63,12	6,22	16,00	2-Propanol	84
XVIIIc	193...194	61,11	5,99	16,87	$C_{21}H_{25}N_5S_2$	61,28	6,12	17,02	2-Propanol	72
XVIIId	177...179	60,31	5,65	16,56	$C_{20}H_{23}N_5S_2$	60,42	5,83	17,62	2-Propanol	87
XVIIIi	188...190	59,71	5,65	16,56	$C_{22}H_{27}N_5OS_2$	59,84	6,16	15,86	2-Propanol	80
XIXc	68...70	62,21	3,87	22,55	$C_{17}H_{12}N_5Na$	66,01	3,91	22,64	—	51
XIXg	>40	62,46	4,32	18,98	$C_{20}H_{16}N_5NaO$	65,75	4,41	19,17	—	80
XXa	149...150*	78,67	4,87	16,04	$C_{17}H_{13}N_3$	78,74	5,05	16,20	2-Propanol-water (1:1)	18
XXc	121...122*	77,17	4,67	17,84	$C_{15}H_{11}N_3$	77,28	4,75	18,01	2-Propanol-water (1:1)	8
XXg	168...170*	74,55	5,15	14,56	$C_{18}H_{15}N_3O$	74,72	5,23	14,52	2-Propanol	38
XXi	133...135*	72,83	4,84	15,86	$C_{17}H_{12}N_3$	72,99	4,97	15,96	2-Propanol	19
XX*l*	175...176*	60,26	3,42	12,35	$C_{17}H_{12}N_3Br$	60,37	3,58	12,42	2-Propanol	12
XXm	160...161*	72,14	4,37	16,74	$C_{15}H_{11}N_3O$	72,27	4,45	16,86	2-Propanol	11
XXn	187...189*	74,57	5,17	14,34	$C_{18}H_{15}N_3O$	74,72	5,23	14,52	2-Propanol	20

---

*Melts without decomposition.

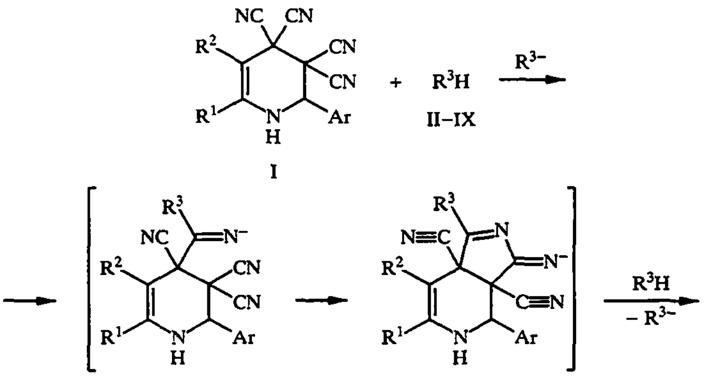
TABLE 2. Coordinates of Nonhydrogen Atoms ($\times 10^4$) and Isotropic Thermal Coefficients (Å $\times$ 10^3) for Compound XIc

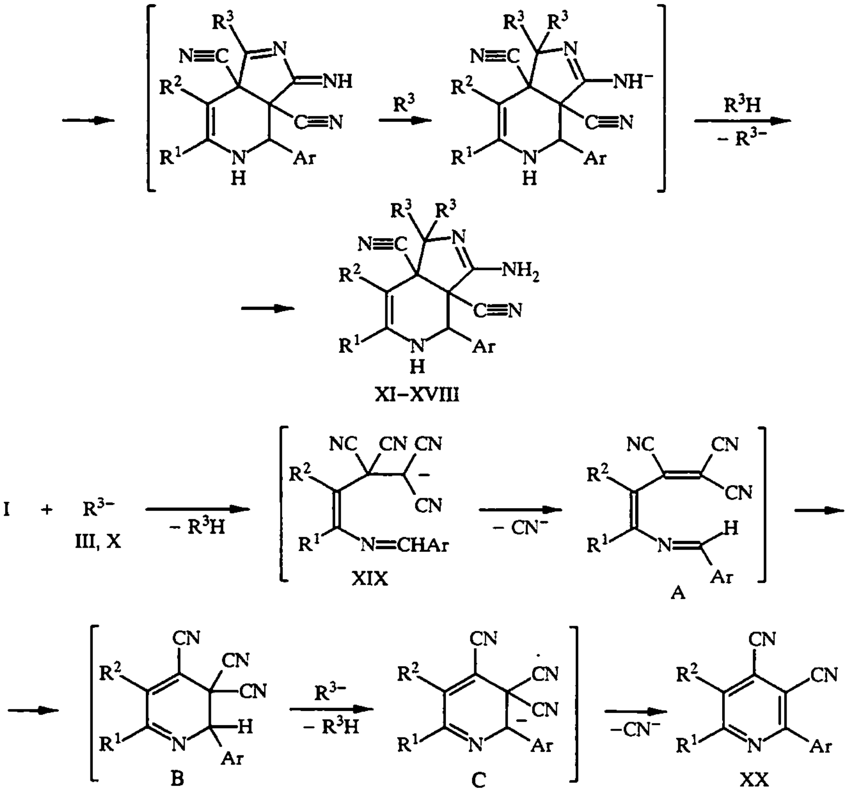
Atom	x	y	z	$U_{(eq)}$
$O_{(11)}$	-363(2)	9474(1)	13612(1)	25(1)
$O_{(12)}$	-3186(2)	9221(1)	13641(1)	28(1)
$N_{(2)}$	-795(2)	9298(1)	11731(1)	20(1)
$N_{(3)}$	814(2)	8502(2)	9983(2)	22(1)
$N_{(6)}$	2198(2)	6671(2)	13316(2)	20(1)
$N_{(41)}$	116(2)	5424(1)	11399(2)	25(1)
$N_{(91)}$	-4035(2)	6494(2)	13431(2)	29(1)
$C_{(1)}$	-1401(3)	8962(2)	13055(2)	19(1)
$C_{(3)}$	94(2)	8469(2)	11193(2)	16(1)
$C_{(4)}$	382(2)	7425(2)	12084(2)	15(1)
$C_{(41)}$	236(2)	6296(2)	11701(2)	16(1)
$C_{(5)}$	2221(2)	7545(2)	12277(2)	16(1)
$C_{(51)}$	3864(2)	7420(2)	11165(2)	19(1)
$C_{(52)}$	4690(3)	8407(2)	10334(2)	30(1)
$C_{(53)}$	6277(3)	8321(2)	9382(2)	38(1)
$C_{(54)}$	7075(3)	7253(2)	9252(2)	30(1)
$C_{(55)}$	6241(3)	6272(2)	10055(2)	27(1)
$C_{(56)}$	4640(3)	6349(2)	11004(2)	22(1)
$C_{(7)}$	814(3)	6681(2)	14436(2)	18(1)
$C_{(71)}$	1257(3)	6116(2)	15544(2)	29(1)
$C_{(8)}$	-767(2)	7125(2)	14486(2)	18(1)
$C_{(81)}$	-2313(3)	7125(2)	15663(2)	27(1)
$C_{(9)}$	-1130(2)	7593(2)	13310(2)	16(1)
$C_{(91)}$	-2781(2)	7000(2)	13351(2)	19(1)
$C_{(11)}$	-546(4)	10709(2)	13574(2)	37(1)
$C_{(12)}$	-4246(4)	9640(3)	12913(3)	51(1)
$O_{(1S)}$	1746(2)	6734(2)	8494(2)	40(1)
$C_{(1S)}$	3512(3)	6566(2)	7762(2)	35(1)

sodium oximates occurred analogously by addition at the cyano group to give compounds XII-XVIII. It was noted that when ethanol was used the yield of XII was not large. Some of the compounds I formed 2-aryl-5,6-dialkyl-pyridine-3,4-dicarbonitriles (XX) along with compound XII. In some cases compounds XX became the sole product when the temperature was raised and the amount of sodium ethoxide was increased. The range of compounds XX can be increased by using sodium isopropoxide in isopropanol and sodium ethoxide in dimethylsulfoxide. We succeeded in isolating the intermediates, sodium 3,4-dialkyl-6-aryl-1,1,2,2-tetracyano-5-aza-3,5-hexadienides (XIXc and f) which were converted to compounds XXc and f in high yield on heating in 1,4-dioxane. The structures of compounds XIXc and f can be determined from their IR spectra (Table 4) and by their conversion into the starting materials in water. The most informative feature of the IR spectra of salts XIXc and f is the characteristic absorption bands of the dicyanomethane anion in the 2140-2195 cm^{-1} region [6].

Formation of the pyridines XX is facilitated by the presence of electron donor groups in the aryl substituent. Consequently it is suggested that formation of the pyridine occurs more rapidly via an electrocyclic reaction in intermediate A rather than by an intramolecular nucleophilic addition in the anion XIX. Elimination of two molecules of hydrogen cyanide probably occurs via an E_{1CB} mechanism since the postulated anion C is stabilized by resonance.

Scheme 1





XI—XVIII	R^1	R^2	Ar	XI—XVIII	R^1	R^2	Ar
a	$(CH_2)_4$		C_6H_5	g	$(CH_2)_4$		p-$CH_3OC_6H_4$
b	$(CH_2)_3$		C_6H_5	i	CH_3	CH_3	p-$CH_3OC_6H_4$
c	CH_3	CH_3	C_6H_5	k	CH_3	H	p-$CH_3OC_6H_4$
d	CH_3	H	C_6H_5	l	$(CH_2)_4$		o-$CH_3OC_6H_4$
e	CH_3	C_3H_7	C_6H_5	m	$(CH_2)_4$		2-Fu
f	CH_3	i-C_3H_7	C_6H_5	n	$(CH_2)_4$		p-BrC_6H_4

II, XI $R^3 = CH_3O$; III, XII $R^3 = C_2H_5O$; IV, XIII $R^3 + R^3 = OCH_2CH_2O$; V, XIV $R^3 = (CH_3)_2C = NO$; VI, XV $R^3 = C_2H_5(CH_3)C = NO$; VII, XVI $R^3 = (CH_2)_4C = NO$; VIII, XVII $R^3 = C_4H_9S$; IX, XVIII $R^3 = C_2H_5S$; X $R^3 = i\text{-}C_3H_7O$

EXPERIMENTAL

IR spectra of Nujol mulls were recorded with a UR-20 spectrometer; ^{13}C NMR spectra were recorded with a Varian Gemini-300 with a frequency of 75 MHz with hexamethyldisiloxane as standard. The purity of the compounds synthesized and the extent of completion of reactions was monitored by TLC (Silufol UV-254).

3-Amino-4-aryl-1,1-dialkoxy-6,7-dialkyl-3a,4,5,7a-tetrahydro-1H-pyrrolo-[3,4-*c*]-pyridine-3a,7a-dicarbonitrile (XXIa-e,g,i,m, Xa,d,f,n). General Method. A solution prepared from 0.01 g (0.5 mmol) of metallic sodium and 1 cm^3 of the corresponding alcohol, II or III, was added to a suspension of nitrile I (5 mmol) in the absolute alcohol, II or III (10 cm^3). The reaction mixture became somewhat warm. The precipitate formed during the reaction (5-15 min, TLC) was filtered off, washed with cold isopropanol, recrystallized and dried in vacuum.

X-Ray Structural Analysis of Compound XIc. Crystals of compound XIc obtained from methanol were triclinic: at 293 K $a = 7.975(2)$, $b = 11.630(2)$, $c = 11.661(2)$ Å, $\alpha = 80.91(1)$, $\beta = 70.21(1)$, $\gamma = 88.62(1)°$, $V = 1004.4(4)$ Å^3, $d_{calc} = 1.268$ g/cm^3, space group P1, Z = 2, F(000) = 408. Unit cell parameters and the intensities of 3971 reflexions were measured with a Siemens P3/PC automatic four-circle diffractometer ($\lambda_{Mo}K\alpha$, graphite monochromator, $\theta/2\theta$ scanning, $\theta_{max} = 26.05°$). The structure was determined by direct methods and refined by the full matrix least squares method in the aniso-

TABLE 3. Bond Lengths and Bond Angles in the Molecule of Compound XIc

Bond	λ, Å	Angle	ω, deg	Angle	ω, deg
$O_{(11}$—$C_{(1)}$	1,404(2)	$C_{(1)}$—$O_{(11)}$—$C_{(11)}$	114,4(2)	$C_{(1)}$—$O_{(12)}$—$C_{(12)}$	119,3(2)
$O_{(11)}$—$C_{(11)}$	1,435(3)	$C_{(3)}$—$N_{(2)}$—$C_{(1)}$	110,4(2)	$C_{(7)}$—$N_{(6)}$—$C_{(5)}$	118,0(2)
$O_{(12)}$—$C_{(1)}$	1,403(2)	$O_{(12)}$—$C_{(1)}$—$O_{(11)}$	107,6(2)	$O_{(12)}$—$C_{(1)}$—$N_{(2)}$	113,6(2)
$O_{(12)}$—$C_{(12)}$	1,417(3)	$O_{(11)}$—$C_{(1)}$—$N_{(2)}$	112,8(2)	$O_{(12)}$—$C_{(1)}$—$C_{(9)}$	110,3(2)
$N_{(2)}$—$C_{(3)}$	1,297(2)	$O_{(11)}$—$C_{(1)}$—$C_{(9)}$	105,8(2)	$N_{(2)}$—$C_{(1)}$—$C_{(9)}$	106,4(1)
$N_{(2)}$—$C_{(1)}$	1,444(2)	$N_{(2)}$—$C_{(3)}$—$N_{(3)}$	125,3(2)	$N_{(2)}$—$C_{(3)}$—$C_{(4)}$	114,3(2)
$N_{(3)}$—$C_{(3)}$	1,326(2)	$N_{(3)}$—$C_{(3)}$—$C_{(4)}$	120,3(2)	$C_{(41)}$—$C_{(4)}$—$C_{(3)}$	113,3(2)
$N_{(6)}$—$C_{(7)}$	1,397(3)	$C_{(41)}$—$C_{(4)}$—$C_{(9)}$	113,1(2)	$C_{(3)}$—$C_{(4)}$—$C_{(9)}$	100,8(1)
$N_{(6)}$—$C_{(5)}$	1,448(2)	$C_{(41)}$—$C_{(4)}$—$C_{(5)}$	110,0(2)	$C_{(3)}$—$C_{(4)}$—$C_{(5)}$	111,2(1)
$N_{(41)}$—$C_{(41)}$	1,141(2)	$C_{(9)}$—$C_{(4)}$—$C_{(5)}$	108,0(1)	$N_{(41)}$—$C_{(41)}$—$C_{(4)}$	179,5(2)
$N_{(91)}$—$C_{(91)}$	1,141(3)	$N_{(6)}$—$C_{(5)}$—$C_{(51)}$	110,0(2)	$N_{(6)}$—$C_{(5)}$—$C_{(4)}$	106,8(1)
$N_{(1)}$—$C_{(9)}$	1,595(3)	$C_{(51)}$—$C_{(5)}$—$C_{(4)}$	115,5(2)	$C_{(56)}$—$C_{(51)}$—$C_{(52)}$	118,8(2)
$C_{(3)}$—$C_{(4)}$	1,535(2)	$C_{(56)}$—$C_{(51)}$—$C_{(5)}$	121,3(2)	$C_{(52)}$—$C_{(51)}$—$C_{(5)}$	119,8(2)
$C_{(4)}$—$C_{(41)}$	1,472(3)	$C_{(53)}$—$C_{(52)}$—$C_{(51)}$	120,4(2)	$C_{(52)}$—$C_{(53)}$—$C_{(54)}$	120,4(2)
$C_{(4)}$—$C_{(9)}$	1,564(2)	$C_{(55)}$—$C_{(54)}$—$C_{(53)}$	119,2(2)	$C_{(54)}$—$C_{(55)}$—$C_{(56)}$	120,6(2)
$C_{(4)}$—$C_{(5)}$	1,571(3)	$C_{(55)}$—$C_{(56)}$—$C_{(51)}$	120,4(2)	$C_{(8)}$—$C_{(7)}$—$N_{(6)}$	121,9(2)
$C_{(5)}$—$C_{(51)}$	1,523(3)	$C_{(8)}$—$C_{(7)}$—$C_{(71)}$	124,2(2)	$N_{(6)}$—$C_{(7)}$—$C_{(71)}$	113,9(2)
$C_{(51)}$—$C_{(56)}$	1,388(3)	$C_{(7)}$—$C_{(8)}$—$C_{(81)}$	123,9(2)	$C_{(7)}$—$C_{(8)}$—$C_{(9)}$	120,3(2)
$C_{(51)}$—$C_{(52)}$	1,394(3)	$C_{(81)}$—$C_{(8)}$—$C_{(9)}$	115,7(2)	$C_{(91)}$—$C_{(9)}$—$C_{(8)}$	107,9(2)
$C_{(52)}$—$C_{(53)}$	1,387(3)	$C_{(91)}$—$C_{(9)}$—$C_{(4)}$	108,1(2)	$C_{(8)}$—$C_{(9)}$—$C_{(4)}$	115,6(2)
$C_{(53)}$—$C_{(54)}$	1,389(3)	$C_{(91)}$—$C_{(9)}$—$C_{(1)}$	107,2(2)	$C_{(8)}$—$C_{(9)}$—$C_{(1)}$	116,7(2)
$C_{(54)}$—$C_{(55)}$	1,378(3)	$C_{(4)}$—$C_{(9)}$—$C_{(1)}$	100,8(1)	$N_{(91)}$—$C_{(91)}$—$C_{(9)}$	176,1(2)
$C_{(55)}$—$C_{(56)}$	1,390(3)				
$C_{(7)}$—$C_{(8)}$	1,337(3)				
$C_{(7)}$—$C_{(71)}$	1,502(3)				
$C_{(8)}$—$C_{(81)}$	1,502(3)				
$C_{(8)}$—$C_{(9)}$	1,512(3)				
$C_{(9)}$—$C_{(91)}$	1,484(3)				
$O_{(1S)}$—$C_{(1S)}$	1,405(3)				
$C_{(8)}$—$C_{(81)}$	1,502(3)				

tropic approximation for all nonhydrogen atoms using 3623 reflexions with $I > 2\sigma(I)$. All hydrogen atoms were revealed by Fourier difference series and were refined isotropically. The final residual factors were $R = 0.0676$ and $R_w = 0.1451$ for all 3672 independent reflexions. All calculations were carried out with the SHELXTL PLUS program. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Centre for Crystallographic Data.

3-Amino-4-aryl-1,1-alkylidenaminoxy-6,7-dialkyl-3a,4,5,7a-tetrahydro-1H-pyrrolo[3,4-*c*]-pyridine-3a,7a-dicarbonitriles (XIVa,d, XVa,c-g, XVIa). General Method. Metallic sodium (0.01 g, 0.5 mmol) and 10 mmol of the ketone oxime V, VI, or VII were dissolved in absolute isopropanol (10 cm^3). Nitrile I (5 mmol) was added to the mixture with stirring and the completion of the reaction was monitored by TLC (5-15 min). The precipitate was filtered off, washed with cold isopropanol, recrystallized and dried in vacuum

3-Amino-4-phenyl-1,1-ethylenedioxy-6,7-dialkyl-3a,4,5,7a-tetrahydro-1H-pyrrolo[3,4-*c*]-pyridine-3a,7a-dicarbonitriles (XIIIa, c, d) were prepared analogously to compounds XIV-XVI using absolute ethylene glycol (2 cm^3) and the corresponding nitrile I (5 mmol).

3-Amino-4-aryl-1,1-dialkylthio-6,7-dialkyl-3a,4,5,7a-tetrahydro-1H-pyrrolo[3,4-*c*]-pyridine-3a,7a-dicarbonitriles (XVIIa, c, d, XVIIIa, c, d, i) were prepared analogously to compounds XIV-XVI using nitrile I (5 mmol) and the corresponding thiol VIII and I (1 and 2 cm^3).

Sodium 3,4-Dialkyl-6-aryl-1,1,2,2-tetracyano-5-aza-3,5-hexadienide (XIXc and g). Metallic sodium (0.12 g, 5 mmol) was dissolved in absolute ethanol (3 cm^3) and most of the ethanol was removed in vacuum. Absolute diethyl ether was added to the residue and then nitrile Ic or g (5 mmol) was added with stirring. Formation of a new precipitate began to form almost at the same time the reagent was added. The precipitate was filtered off, washed with diethyl ether, and dried in vacuum over phosphorus pentoxide.

TABLE 4. IR Spectra (cm^{-1}) of the Synthesized Compounds

Compound	ν (C=N), ν (C=C), δ (NH$_2$)	ν (C ≡ N)	ν (N—H)
XIa	1650	2240, 2260	3340, 3400, 3440
XIb	1630, 1665	2260	3340, 3410, 3430
XIc	1620, 1660	2240, 2255	3350, 3380, 3440
XId	1625, 1630, 1650	2255	3290, 3320, 3400
XIe	1665	2255	3330, 3410, 3430
XIg	1600, 1630, 1655	2255	3343, 3400, 3440
XIl	1630, 1660	2240, 2255	3335, 3410, 3430
XIm	1660	2255	3345, 3375, 3450
XIIa	1665	2255, 2270	3335, 3380
XIId	1630	2250	3355, 3400
XIIe	1670	2255	3360, 3400
XIIi	1660, 1670	2245	3385, 3465
XIIIa	1630, 1650	2250	3340, 3370, 3430
XIIIc	1625, 1650	2250	3350, 3375, 3410
XIVd	1630, 1650	2245	3340, 3430
XIVa	1665	2245	3300, 3480
XIIId	1645	2250	3260, 3470
XVa	1660	2250	3300, 3480
XVc	1640, 1660	2250	3260, 3470
XVd	1660	2248	3400, 3480
XVIa	1630, 1640	2250	3340, 3370
XVIIa	1660	2270	3370
XVIIc	1645	2240	3355
XVIId	1640	2240	3380
XVIIIa	1660, 1670	2250	3340, 3370
XVIIIc	1680	2260	3350
XVIIId	1600, 1680	2260	3350
XVIIIi	1650	2240, 2260	3390, 3470
XIXc	1710	2140, 2195, 2260	—
XIXg	1700	2138, 2195, 2230	—
XXa	1535	2235	—
XXc	1535	2238	—
XXg	1600	2235	—
XXi	1580	2240	—
XX*l*	1595	2240	—
XXm	1575	2235	—
XXn	1595	2240	—

Reaction of Sodium 3,4-Dialkyl-6-aryl-1,1,2,2-tetracyano-5-aza-3,5-hexadienide (XIXc and g) with Water. Water (3 cm^3) was added to a suspension of salt XIXc or g (1 mmol) in ethyl acetate (10 cm^3) and the mixture shaken until the salt dissolved. The organic layer was separated, washed with distilled water and dried over magnesium sulfate. The ethyl acetate was evaporated, isopropanol was added to the residue, the precipitate was filtered off, washed with isopropanol and dried in vacuum. The products had identical IR spectra to nitriles Ic and g and did not cause depression of the melting points. Yields of compounds Ic and g were 56 and 78% respectively.

2-(*p*-Methoxyphenyl)-6,7-tetramethylenepyridine-3,4-dicarbonitrile (XX g). A. Metallic sodium (0.12 g, 5 mmol) was dissolved in absolute ethanol (10 cm^3) and nitrile Ig (1.72 g, 5 mmol) was added to the solution in a single portion, heated rapidly to boiling and allowed to cool naturally to room temperature, kept at that temperature for 2h, water (1 cm^3) was added and the mixture filtered after 30 min. The product was purified firstly by recrystallization from isopropanol and then by sublimation in vacuum to give colorless crystals (0.56 g, 38%). ^{13}C NMR spectrum (acetone-D$_6$): $C_{(2)}$ 162.49, $C_{(3)}$ 105.62, $C_{(4)}$ 125.87, $C_{(5)}$ 134.43, $C_{(6)}$ 164.44, $C_{(CN)}$ 114.37, 116.56, $C_{(CH2)}$ 22.27, 22.61, 27.98, 33.99, $C_{C_6H_5}$ 123.75, 114.75, 131.41, 158.39 ppm.

B. Compound XXg was obtained analogously using isopropanol (10 cm^3) (0.48 g, 32%).

C. Metallic sodium (0.12 g, 5 mmol) was dissolved in absolute ethanol (3 cm^3), the excess ethanol was evaporated in a stream of dry nitrogen, absolute dimethylsulfoxide (10 cm^3) and nitrile Ig (1.72 g, 5 mmol) were added, the mixture was heated to 70°C, cooled, water (2 cm^3) was added, the mixture kept for 2 h, the precipitate which formed was filtered off, dried and purified by sublimation in vacuum to give XX g (0.76 g, 51.7%).

D. Salt XIXg (0.36 g, 1 mmol) was dissolved in absolute 1,4-dioxane (3 cm^3), heated to 70°C, cooled kept for 2 h, and water (0.5 cm^3) added. The precipitate was filtered off, washed with isopropanol and dried in vacuum to give XXg (0.21 g, 73%).

2-Aryl-5,6-dialkylpyridine-3,4-dicarbonitriles (XXi, *l*, n) were prepared analogously to pyridine XIXg, using the corresponding nitrile I (5 mmol).

5,6-Dialkyl-2-arylpyridine-3,4-dicarbonitriles (XXa, c, m) were obtained analogously to compound XIXg by method C using the corresponding nitrile I (5 mmol).

REFERENCES

1. O. E. Nasakin, A. N. Lyshchikov, P. M. Lukin, A. Kh. Bulai, V. A. Tafeenko, and P. A. Sharbatyan, Khim. Geterotsikl. Soedin., No. 11, 1325 (1991).
2. O. E. Nasakin, A. N. Lyshchikov, V. A. Tafeenko, A. Kh. Bulai, and S. V. Medvedev, Khim. Geterotsikl. Soedin., No. 10, 1325 (1992).
3. O. E. Nasakin, A. N. Lyshchikov, P. M. Lukin, and V. A. Tafeenko, Khim. Geterotsikl. Soedin., No. 11, 1472 (1992).
4. O. E. Nasakin, A. N. Lyshchikov, P. M. Lukin, and A. Kh. Bulai, Khim. Geterotsikl. Soedin., No. 1, 42 (1995).
5. Ya. S. Kayukov, O. E. Nasakin, Ya. G. Urman, V. N. Khrustalev, V. N. Nesterov, M. Yu. Antipin, A. N. Lyshchikov, and P. M. Lukin, Khim. Geterotsikl. Soedin., No. 10, 1395 (1996).
6. C. E. Looney and J. R. Downing, J. Amer. Chem. Soc., **80**, No. 11, 2840 (1958).