

9. G. C. Levy and G. L. Nelson, Carbon-13 Nuclear Magnetic Resonance for Organic Chemists, Wiley, New York (1972).

sym-TETRACYANOETHANE IN THE SYNTHESIS OF HETEROCYCLES.

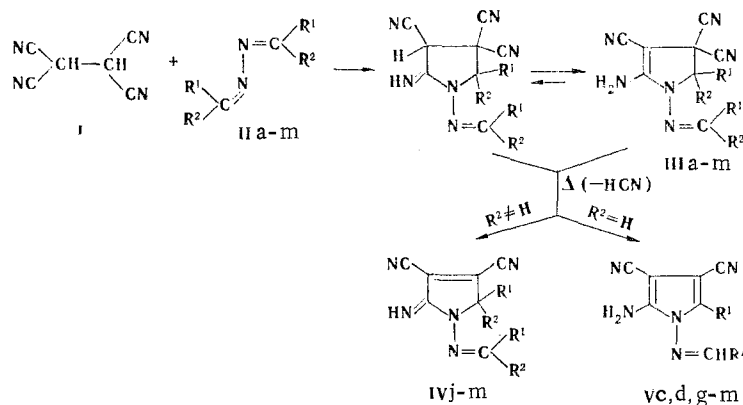
4.* SYNTHESIS OF 1-ALKYLIDENEIMINO-2-AMINO-3,4,4-TRICYANO-4,5-DIHYDROPYRROLES BY THE REACTION OF sym-TETRACYANOETHANE WITH AZINES

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sym-Tetracyanoethane reacts with aldazines and ketazines to give 1-alkylideneimino-2-amino-3,4,4-tricyano-4,5-dihydropyrroles, some of which are thermally converted to 1-alkylideneimino-2-amino-3,4-dicyanopyrroles or to 5,5-disubstituted 1-alkylideneimino-2-imino-3,4-dicyano-2,5-dihydropyrroles. The structures of the compounds were confirmed by the PMR, ^{13}C NMR, and mass spectra.

In a previous communication [1] we showed that azomethines, like carbonyl compounds [2, 3], react with sym-tetracyanoethane (I) via a scheme involving aldol addition, which ultimately leads to the formation of 4,5-dihydropyrrole derivatives. Inasmuch as azines contain two azomethine groupings that are capable of such reactions, the reaction of cyanide I with aldazines and ketazines II could lead to cyclization of the primary intermediate addition products to favor the formation of derivatives of piperidazine, pyrrolines, or dipyrrolines.



We have found that the reaction of cyanide I with aldazines, as well as with azomethines, takes place in aqueous alcohol or alcohol and also leads to 4,5-dihydropyrrole derivatives IIIa-m in high yields (see Table 1). The reaction with ketazines similarly leads to pyrrolines IIIj-m; however, the yields of final products do not exceed 45-48%, evidently as a consequence of steric hindrance. The results of elementary analysis, as well as the mass-spectrometric determination of the molecular masses, make it possible to exclude the possibility of the formation of dipyrrolines IX.

A broad singlet of two protons, which undergo a strong-field shift when the temperature is raised, is observed in the PMR spectra of III at weak field (7.6 ppm); this indicates the

*See [1] for communication 3.

TABLE 1. Properties of 1-Alkylideneimino-2-amino-3,4,4-tricyano-4,5-dihydropyrroles IIIa-i

Com- pound	R ¹	R ²	mp, °C	Found				Empirical formula	Calc.				Synthetic method	Yield, %
				C, %	H, %	N, %	M ⁺		C, %	H, %	N, %	M ⁺		
IIIA	CH ₃	H	151—152	56.1	4.7	39.1	214	C ₁₀ H ₁₀ N ₆	56.1	4.7	39.2	214	A	82
IIIB	C ₂ H ₅	H	148—149	59.6	5.7	34.4	242	C ₁₂ H ₁₄ N ₆	59.5	5.8	34.7	242	B	84
IIIB	<i>n</i> -C ₃ H ₇	H	139—140	62.3	6.6	30.9	270	C ₁₄ H ₁₈ N ₆	62.2	6.7	31.1	270	B	84
IIIB	<i>i</i> -C ₃ H ₇	H	136—137	62.1	6.7	31.1	270	C ₁₄ H ₁₈ N ₆	62.2	6.7	31.1	270	B	81
IIIB	<i>i</i> -C ₄ H ₉	H	115—116	64.5	7.7	28.3	298	C ₁₆ H ₂₂ N ₆	64.4	7.5	28.1	298	B	82
IIIB	<i>n</i> -C ₆ H ₁₃	H	102—103	67.9	8.6	23.9	354	C ₂₀ H ₃₀ N ₆	67.7	8.6	23.7	354	B	80
IIIB	C ₆ H ₅	H	>177*	71.1	4.2	24.6	—	C ₂₀ H ₁₄ N ₆	71.0	4.2	24.8	—	B	85
IIIC	2-Furyl	H	>175*	60.7	3.1	26.6	318	C ₁₆ H ₁₀ N ₆ O ₂	60.4	3.2	26.4	318	C	86
IIIC	3-Pyridyl	H	>140*	63.8	3.6	32.8	—	C ₁₈ H ₁₂ N ₈	63.5	3.6	32.9	—	C	78
IIIB	CH ₃	CH ₃	>140*	59.6	5.7	34.8	242	C ₁₂ H ₁₄ N ₆	59.5	5.8	34.7	242	B	48
IIIB	CH ₃	C ₂ H ₅	>143*	61.9	6.5	31.2	270	C ₁₄ H ₁₈ N ₆	62.2	6.7	31.1	270	B	45
IIIB	C ₂ H ₅	C ₂ H ₅	>141*	64.5	7.6	28.0	298	C ₁₆ H ₂₂ N ₆	64.4	7.5	28.1	298	B	42
IIIB	—(CH ₂) ₅ —		>140*	67.1	7.0	26.1	322	C ₁₈ H ₂₂ N ₆	67.0	6.9	26.1	322	B	40

*With decomposition.

TABLE 2. ¹³C NMR Spectra of III, IV, and V (ppm)

Com- pound	C ₍₂₎	C ₍₃₎	C ₍₄₎	C ₍₅₎	CN
III b	160.66	49.95	41.45	67.26	116.57; 117.13; 113.95
III c	159.81	49.13	40.95	65.54	116.95; 115.79; 113.36
III d	159.89	49.42	39.52	69.43	116.84; 116.06; 113.62
III e	160.23	49.57	42.42	64.89	117.13; 116.08; 113.82
III f	160.56	50.16	41.64	66.54	116.94; 116.46; 113.95
III g	160.93	—*	—*	69.96	116.81; 116.27; 113.35
III h	160.34	50.38	42.80	63.84	116.76; 115.73; 112.85
III k	160.72	50.79	49.52	69.53	117.70; 115.25; 115.03
III l	162.72	50.79	48.84	72.04	117.67; 115.22; 115.02
IV j	165.52	123.18	141.65	68.37	112.36; 111.25
IV m	165.84	123.55	141.16	71.65	112.89; 111.25
V g	147.34	71.88	92.69	134.45	115.41; 115.06
V h	147.72	70.67	87.98	133.12	115.16; 114.98

*The signals were "drowned" in the noise.

TABLE 3. Properties of IV and V

Com- pound	mp, °C	Found				Empirical formula	Calc.				Yield, %
		C, %	H, %	N, %	M ⁺		C, %	H, %	N, %	M ⁺	
IV j	190—191	61.5	6.1	32.4	215	C ₁₁ H ₁₃ N ₅	61.3	6.1	32.6	215	72
IV k	165	64.0	7.1	28.5	243	C ₁₃ H ₁₇ N ₅	64.2	7.0	28.8	243	70
IV l	181	66.2	8.0	25.7	—	C ₁₅ H ₂₁ N ₅	66.4	7.8	25.8	—	74
IV m	186—188	69.0	7.2	23.7	295	C ₁₇ H ₂₁ N ₅	69.1	7.2	23.7	295	68
V a	195—196	57.5	5.0	37.2	187	C ₉ H ₉ N ₅	57.8	4.8	37.4	187	72
V c	139—140	63.9	7.2	28.4	243	C ₁₃ H ₁₇ N ₅	64.1	7.1	28.8	243	77
V d	148—150	64.0	7.3	28.6	243	C ₁₃ H ₁₇ N ₅	64.1	7.1	28.8	243	71
V g	215—216*	73.3	4.3	22.7	311	C ₁₉ H ₁₃ N ₅	73.3	4.2	22.5	311	92
V h	208—210 †	62.0	3.2	24.1	291	C ₁₅ H ₉ N ₅ O ₂	61.9	3.1	24.0	291	91
Vi	206—207	64.9	3.8	31.1	313	C ₁₇ H ₁₁ N ₇	65.1	3.6	31.3	313	84

*From aqueous DMF.

†From ethanol.

presence of a primary amino group. In the case of both aldazines and ketazines a signal of a C₍₂₎ atom at 159–162 ppm is observed at weak field in the ¹³C NMR spectra of the adducts (Table 2); this is characteristic for 2-amino-4,5-dihydropyrroles [1]. In addition, the spectra of the compounds obtained (when R₂ = H) contain three signals of CN groups, two signals (39–50 ppm) of unprotonated C₍₃₎ and C₍₄₎ atoms, and one signal (69–63 ppm) of the C₍₅₎ atom. The data obtained also make it possible to exclude the alternative piperidine structure, in the spectrum of which (when R₂ = H) there should be two signals of the CN group and

one signal of unprotonated carbon atoms. The presence of the imino tautomer, in the spectrum of which (when $R_2 = H$) there should be two signals of CH groups, is also excluded. Thus, within the limits of the sensitivity of the method ($\sim 10\%$), the equilibrium is shifted in solution to favor the tautomeric amino form III.

Most of these compounds readily lose a molecule of hydrocyanic acid, even in the case of slight heating, and are converted to pyrrole derivatives V or 3-pyrroline derivatives IV in high yields (see Table 3). (Compounds III undergo a similar facile disproportionation also under the influence of electron impact.) Pyrroles V are rather high-melting stable compounds, in the PMR spectra of which a broad singlet of two protons of the NH_2 group at 7.5-7.7 ppm, which depends on the temperature, is retained. Signals of four unprotonated carbon atoms of the pyrrole ring [1] are observed in the ^{13}C NMR spectrum (Table 2); the chemical shift of the $C_{(2)}$ atom, as compared with the signal of the same atom in VI, undergoes a 12-13 ppm strong-field shift, whereas the signals of the $C_{(3)}$, $C_{(4)}$, and $C_{(5)}$ atoms display an appreciable [particularly the $C_{(5)}$ atom] shift to weak field. In the ^{13}C NMR spectrum of 3-pyrrolines IV the chemical shift of the $C_{(2)}$ atom increases by 2.5-3 ppm and is observed at 165 ppm, which is characteristic for the quaternary carbon atom of an imino group [4, 5]. In the PMR spectrum of IVj the ratio of the integral intensities of the broad singlet at 7.6 ppm (NH) and the singlet of the methyl groups attached to $C_{(5)}$ (1.58 ppm) is six, which, together with the results of elementary analysis and the mass-spectrometric determination of the molecular mass, also confirms pyrroline structure IV. It is interesting to note that 2-pyrroline III, 3-pyrrolines IV, and pyrroles V do not react with cyanide I; this is apparently associated with the existence of steric hindrance to approach of the sym-tetracyanoethane anion to the azomethine multiple bond in the 1 position of the heteroring.

Thus the reaction of sym-tetracyanoethane with azines can also serve as a convenient and simple method for the synthesis of 1-alkylideneimino-2-pyrrolines and 1-alkylideneimino-3-pyrrolines, as well as pyrroles that contain two reactive groups such as amino and cyano groups in the ortho positions of the heteroring.

EXPERIMENTAL

The PMR (90 MHz) and ^{13}C NMR (22.63 MHz) spectra were recorded with a Bruker H-90 spectrometer by Fourier transformation with the aid (in the recording of the carbon spectra) of both broad-band decoupling of the spin-spin coupling with the protons and incomplete decoupling of the protons. The internal standard was hexamethyldisiloxane (2.4 ppm). The mass spectra were obtained with a Varian MAT-212 spectrometer at an ionization energy of 70 eV with introduction of the substances into the ionization region at vaporization temperatures 15-20°C below the melting (decomposition) points of the samples.

Compounds III. A) A 0.01-mole sample of azine II was added at 10-18°C in a nitrogen atmosphere to a solution of 0.01 mole of cyanide I in tetrahydrofuran (THF), and the mixture was allowed to stand for 5-10 min. The solvent was removed by distillation *in vacuo*, and the precipitate was reprecipitated from solution in ethyl acetate by the addition of hexane.

B) A 0.01-mole sample of azine II was added to a solution of 0.01 mole of the cyanide in 20% aqueous ethanol in a nitrogen atmosphere at 25-30°C in the course of 1-2 h, after which the mixture was diluted with water, and the precipitate was removed by filtration, dried, and recrystallized from benzene or ethyl acetate-hexane.

C) A 0.01-mole sample of the azine was added to a solution of 0.01 mole of cyanide I in ethanol in a nitrogen atmosphere at 35-40°C. After 15-20 min, the mixture was poured into water, the aqueous mixture was filtered, and the precipitate was recrystallized from aqueous alcohol.

Compounds IV and V. A solution of pyrrolines III in benzene or chloroform was refluxed until the starting compound vanished completely (according to TLC); this took 0.5-1 h. The solvent was evaporated, and the residue was recrystallized.

LITERATURE CITED

1. O. E. Nasakin, V. V. Alekseev, P. B. Terent'ev, A. Kh. Bulai, and M. Yu. Zablotskaya, Khim. Geterotsikl. Soedin., No. 8, 1062 (1983).
2. O. E. Nasakin, V. V. Alekseev, P. B. Terent'ev, A. Kh. Bulai, and V. A. Shmorgunov, Khim. Geterotsikl. Soedin., No. 12, 1605 (1982).

3. O. E. Nasakin, V. V. Alekseev, A. Kh. Bulai, and S. Yu. Sil'vestrova, *Khim. Geterotsikl. Soedin.*, No. 8, 1137 (1980).
4. G. C. Levy and G. L. Nelson, *Carbon-13 Nuclear Magnetic Resonance for Organic Chemists*, Wiley, New York (1972).
5. F. de Roy Johnson and W. C. Jankowski, *Carbon-13 NMR Spectra*, Wiley-Interscience, New York (1972).
6. F. Wehri and T. Wirthlin, *Interpretation of ^{13}C NMR spectra*, London (1976).

MASS-SPECTROMETRIC BEHAVIOR OF 5-SUBSTITUTED
1-ALKYLIDENEIMINO-2-AMINOPYRROLES AND THEIR
2,5- AND 4,5-DIHYDRO DERIVATIVES*

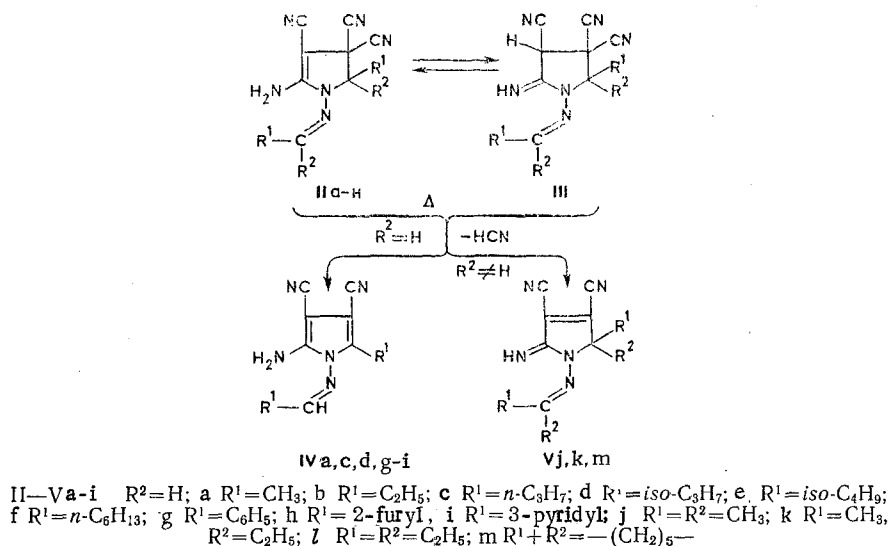
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A comparative analysis of the mass spectra of 5-substituted 1-alkylideneimino-2-amino-3,4-dicyanopyrroles and their 2,5-dihydro and 4,5-dihydro derivatives makes it possible to find the typical fragmentation pathways that characterize each group of compounds and to detect the presence of tautomeric amino-imino forms in the gas phase.

In our previous communications we demonstrated that the reaction of sym-tetracyanoethane (I) with azomethines leads to the formation of 1,5-disubstituted 2-amino-3,4,4-tricyano-4,5-dihydropyrroles [1, 2], while the reaction of the same cyanide I with azines makes it possible to obtain 5-substituted 1-alkylideneimino-2-amino-3,4,4-tricyano-4,5-dihydropyrroles (II) in high yields [3]; it was established by NMR spectroscopic methods that the presence of tautomeric imino form III (Scheme 1) cannot be detected in solutions by spectral methods. The Δ^2 -pyrrolines obtained undergo dehydrocyanation even in the case of slight heating; the 5-mono-

Scheme 1



*Communication 5 from the series "sym-Tetracyanoethane in the synthesis of heterocycles."
See [1] for communication 4.

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