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SYNTHESIS OF 2-AMINO-4,5-DISUBSTITUTED 3,5-DICYANO-4,5-DIHYDROFURANS

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A new reaction was found for the preparation of difficult-to-obtain polyfunctional dihydrofurans, viz., the reaction of tetracyanoethylated ketones with hydrogen peroxide in the presence of a base.

Continuing our research on the synthesis and chemistry of tetracyanoethylated ketones [1, 2] we studied the reaction of tetracyanoethylated ketones Ia-e with hydrogen peroxide in an alkaline medium under the conditions of the Radzishevskii reaction [3, 4]. It is known that this reaction proceeds with the formation of acid amides from carboxylic acid nitriles; it is insensitive to the radicals or functional groups in the starting nitrile. Thus, for example, malonic acid dinitrile forms malonitrile monoamide with hydrogen peroxide [5].

We noted a vigorous reaction in alcohol solutions of tetracyanoethylated ketones I with hydrogen peroxide and the attendant liberation of gases, which were identified as hydrocyanic acid and carbon dioxide. When we carried out the same reaction in an aqueous solution of a base, viz., potassium bicarbonate (tetracyanoethylated ketones I decompose in

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TABLE 1. Characteristics of 4,5-Substituted 3,5-Dicyano-2-amino-4,5-dihydrofurans IXa-e

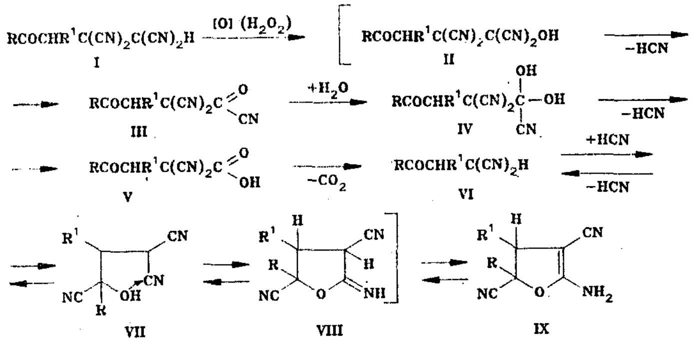
Compound	mp, deg C	Found, %			Empirical formula	Calculated, %			Yield, %
		C	H	N		C	H	N	
IXa	116—117	58,7	5,3	26,0	$C_8H_9N_3O$	58,9	5,5	25,8	57
IXb	130—131	59,1	5,3	25,5	$C_8H_9N_3O$	58,9	5,5	25,8	48
IXc	141—142	61,9	4,9	23,8	$C_9H_9N_3O$	61,7	5,1	24,0	79
IXd	142—143	63,7	5,6	22,0	$C_{10}H_{11}N_3O$	63,5	5,8	22,2	54
IXe	132—134	68,5	4,0	19,7	$C_{12}H_9N_3O$	68,2	4,3	19,9	93

TABLE 2. IR and Mass Spectra of 4,5-Substituted 3,5-Dicyano-2-amino-4,5-dihydrofurans IXa-e

Compound	IR spectrum, cm^{-1}	Mass spectrum* (relative intensity)
IXa	3415, 3350, 3310, 3245, 3200, 1665, 2200 **s** (C≡N), 1600 (C=C)	163 (45), 148 (100), 131 (29), 120 (5), 119 (7), 11 (10), 105 (6), 93 (27), 66 (7), 57 (7), 43 (29)
IXb	3400, 3340, 3292, 3230, 3180, 1660 (NH_2), 2270 **w**, 2200 **s** (C≡N), 1600 (C=C)	163 (53), 148 (8), 131 (7), 121 (7), 119 (9), 107 (18), 97 (51), 83 (10), 81 (10), 67 (25), 57 (100)
IXc	3420, 3380, 3325, 3306, 3240, 3190, 1660 (NH_2), 2260 **w**, 2200 **s** (C≡N) 1600 (C=C)	175 (100), 148 (34), 146 (19), 131 (439), 121 (71), 104 (24), 97 (26), 92 (35), 91 (23), 81 (21), 69 (45)
IXd	3410, 3328, 3289, 3240, 3180, 1660 (NH_2), 2270 **w**, 2200 **s** (C≡N), 1590 (C=C)	189 (10), 162 (11), 121 (17), 106 (18), 105 (7), 97 (8), 91 (40), 84 (8), 79 (6), 69 (11), 55 (100)
IXe	3400, 3360, 3310, 3255, 3210, 1680 (NH_2), 2271 **w** 2210 **s** (C≡N), 1620, 1600, 1585 (C=C)	211 (6), 194 (22), 184 (5), 147 (6), 118 (10), 105 (91) 83 (10), 81 (17), 77 (30), 69 (45), 43 (100)

Note. *The molecular-ion peak and the 10 most intense peaks are presented.

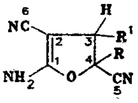
the presence of strong alkalis), we isolated crystalline substances, which were identified as 4,5-substituted 3,5-dicyano-2-amino-4,5-dihydrofurans IXa-e from data from the IR, ^{13}C NMR, and mass spectra. The results of the reaction suggest that it proceeds in a complex manner, probably via the scheme



IX a R=R¹=CH₃; b R=C₂H₅, R¹=H; c R=R¹=(CH₂)₃; d R=R¹=(CH₂)₄; e R=C₆H₅, R¹=H

In the first step ketones Ia-e are probably oxidized to keto alcohols IIa-e (the facile oxidizability of the tetracyanoethyl fragment was previously noted in [6]). Dehydrocyanation of IIa-e leads to ketones IIIa-e. The liberation of hydrocyanic acid was detected from a reaction with silver nitrate. The cyanohydrin fragment of IVa-e is formed again as a result of hydration of ketones IIIa-e, after which dehydrocyanation is repeated, and keto carbocylic acids Va-e, the decarboxylation of which leads to β,β-dicyano ketones VIa-e (the liberation of carbon dioxide was detected by the formation of barium carbonate), are probably formed. The subsequent course of the reaction is possibly characterized by the reversible addition

TABLE 3. Chemical Shifts of the ^{13}C Atoms (ppm) of the Dihydrofuran Ring and the Nitrile Groups of 4,5-Substituted 3,5-Dicyano-2-amino-4,5-dihydrofurans IXa-e



Compound	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5,6)}$
IXa	165,25	55,16	45,13	83,86	117,68; 118,11
IXb	165,89	47,70	39,31	82,04	118,88; 117,66
IXc	165.92	53,77	53,68	85,76	117,07; 118,53
IXd	166,09	54,54	44,54	79,57	120,08; 117,92
IXe	165,64	47,12	42,90	81,19	118,87; 117,98

in the presence of the base of the liberated hydrogen cyanide to ketones VIa-e to give hydroxy nitriles VIIa-e. The $VI \rightleftarrows VII \rightleftarrows VIII \rightleftarrows IX$ equilibrium is shifted to the right as a result of intramolecular cyclization to dihydrofurans IXa-e.

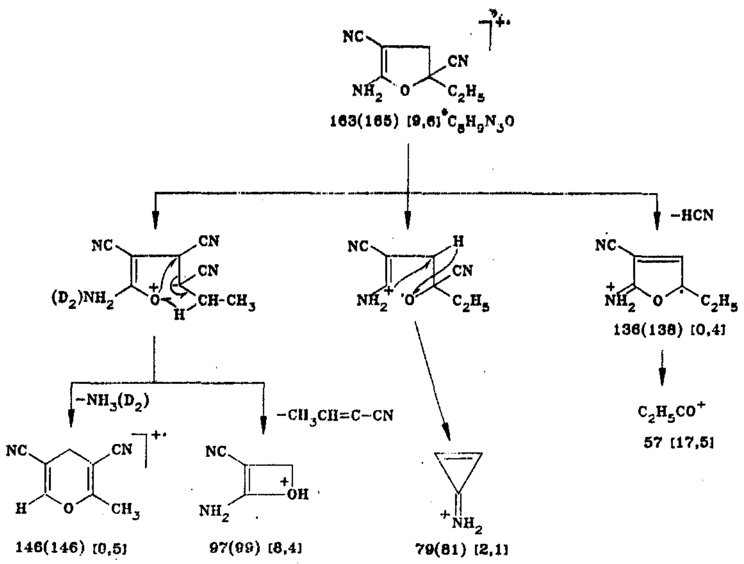
It is interesting to note that the introduction of alkyl groups or a chlorine atom into the aromatic ring of ketone I (R) hinders the formation of dihydrofurans IX; in our opinion, this is associated with a decrease in the electrophilicity of the carbonyl carbon atom.

The IR spectra of the compounds obtained contain characteristic absorption bands of an amino group and conjugated and unconjugated nitrile groups (Table 2).

The assignment of the signals of the ^{13}C NMR spectra was made on the basis of the spectra of structural analogs [7] and on the basis of the data in [8] (Table 3).

Intense peaks of molecular ions (except for the less thermally stable IXe), M — HCN ions, which have relatively low intensities (except for IXe), and M — NH_3 (determined by means of high-resolution mass spectroscopy) are characteristic for the mass spectra of dihydrofurans IXa-e. This unusual fragmentation is apparently explained by shifting of the preferred site of localization of the positive charge in the molecular ions of IXa-e from the oxygen atom to the nitrogen atom of the amino group. This is associated with the fact that the electronegative cyano group in the α position relative to the heterocyclic oxygen atom increases its ionization energy. In this connection, the mass spectra of dihydrofurans IXa-e do not contain the M — R^1 peaks that are characteristic for compounds with a similar structure [8], but one does observe preferred cleavage of the C—O bonds of the heteroring, which was demonstrated (see the scheme presented below) in the case of the fragmentation of dihydrofuran IXb. The compositions of the ions presented in the scheme were confirmed by the high-resolution mass spectra and an analysis of the mass spectra of the labeled (ND_2) compound. Similar fragmentation is also observed in the case of isomeric compound IXa; the ions with m/z 79 and 97 undergo a 14-amu shift in mass (m/z 93 and 111). The fragmentation of the molecular ions of IXc, d proceeds in a more complex manner, but M — NH_3 ions and relatively weak M — HCN ion peaks are also characteristic for them. A very intense ion peak at 184 (M — HCN) is observed only in the mass spectra of IXe; this is apparently associated with thermal processes involving the dehydrocyanation of this compound in the mass spectrometer (Table 2).

Scheme



EXPERIMENTAL

The purity of the compounds obtained was verified by means of chromatography on Silufol UV-254 (with ethyl acetate as the solvent). The starting tetracyanoethylated ketones were synthesized by the method in [1]. The ND_2 derivatives of IXa-e were obtained by repeated dissolving of the samples in CH_3COD.

The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer. The mass spectra were obtained with MKh 1303 and Varian MAT-212 spectrometers with direct introduction of the substances into the ion source at an ionization energy of 70 eV and at temperatures 20-25° below the melting points of the samples. The high-resolution mass spectra were recorded with an MAT-311 spectrometer.† The ^{13}C NMR spectra of solutions of the compounds in d_6-acetone with hexamethyldisiloxane as the standard were recorded with a Bruker WH-90 spectrometer by the method of Fourier transformation with the aid of broad-band decoupling of the spin-spin coupling with the protons.

Synthesis of 3,5-Dicyano-2-amino-4,5-dihydrofurans. General Method. A 6-g (0.06 mole) sample of potassium bicarbonate was added with stirring to 30-50 ml of water (300 ml of water was used for Ie), after which 0.05 mole of ketone I was added slowly, during which the liberation of carbon dioxide was observed. After all of the tetracyanoethylated ketone I had dissolved, 8 g of a 30% solution of hydrogen peroxide (an excess amount) was added dropwise at such a rate that the reaction temperature did not exceed 40-45°C (cooling with water). After the addition of the peroxide was complete, the reaction mass was stirred for 1.5 h. It was then cooled to 0°C, and the crystals were removed by filtration and recrystallized from isopropyl alcohol.

*The m/z values are presented; the intensities of the peaks in $\%\Sigma_{39}$ are given in parentheses.
†The authors thank N. A. Klyuev for recording the high-resolution mass spectra.

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PHOTO- AND THERMOCHROMIC SPIRANS.

16.* 2-OXO-3-PHENYL-5,5-DIMETHYLSPIRO(1,3-OXAZOLIDINE-4,2'-[2H]CHROMENES)

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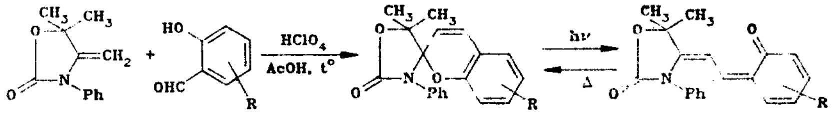
New spirans of the 5,5-dimethyl-3-phenyl-2-oxazolidone series that display photochromic properties in alcohol solutions at ~−80°C were synthesized. The photoinduced forms are characterized by the presence of two long-wave absorption bands at 350-420 nm and 500-650 nm. The ^1H and ^{13}C NMR spectra were studied. Anisochronicity of the diastereotopic methyl groups of the oxazolidone ring shows up only in the ^{13}C NMR spectra.

Calculation of the energy of anionic localization of the conjugate acid of 4-methylene-5,5-dimethyl-3-phenyl-2-oxazolidone (I) gives $L^- = 3.51$ eV. This is considerably lower than the critical value of 6.2 eV, below which it is expected [2] that the equilibrium of the spiran (II) and merocyanine (III) forms of spiro[2H]benzopyrans should be shifted to favor II in solutions and in the solid phase. On the basis of this prediction we undertook the synthesis of a new series of spiropyrans II via the scheme



I IIa-p IIIa-p

Spiropyrans of the 5,5-dimethyl-3-phenyl-2-oxazolidone series of the II general type were obtained in 60-70% yields by condensation of methylene base I with the corresponding o-hydroxy aromatic aldehydes in the presence of catalytic amounts of perchloric acid (Table 1). The IR spectra of the spirans obtained contain an intense absorption band at 1730-1750 cm^{-1} (Table 2), which is typical for the carbonyl group of the oxazolidone ring (1750 cm^{-1} for methylene base I), and an absorption band of medium intensity at 1630-1665 cm^{-1} ($\nu_{C=C}$ of the pyran ring).

In the case of irradiation with UV light with λ_{max} 313 nm under steady-state conditions in ethanol solutions at −100°C the spiropyrans undergo II $\rightleftarrows$ III valence isomerization and display photochromic properties. The long-wave absorption bands of the III form lie at 350-420 nm and 500-650 nm (Table 2). The typical pattern of the spectral photochromic transformations is presented in Fig. 1. Calculations of the electronic spectra of the open forms of the spirans by the SCF PPP MO (self-consistent field Pariser–Parr–Pople molecular orbital) method correctly predict the presence of two long-wave absorption bands in the visible region; however, the bands of the calculated electron transitions are shifted hypsochromically 0.3-0.4 eV as compared with the experimental values when the usual parametrization [2] is used.

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*See [1] for communication 15.

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