

ELECTRONIC REGIOSELECTIVITY IN THE REACTIONS OF PYRIDINIUM YLIDES WITH TETRACYANOETHYLENE

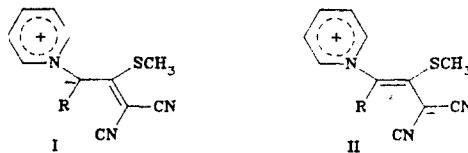
A. M. Shestopalov, Yu. A. Sharanin, I. A. Aitov,
V. N. Nesterov, Yu. T. Struchkov, and V. P. Litvinov

UDC 547.461:547.821.3

*Highly regioselective reactions of pyridinium ylides with tetracyanoethylene occur via an Ad_N-E mechanism to form *Z*-isomers of 3-aryl-3-(1-pyridinio)-1,1,2-tricyano-2-propenides-1, corresponding in structure to 1,4-ylides with maximum charge separation. If the unsaturated nitrile starting material contains a nucleofugal group 1,2-elimination predominates over 1,3-elimination.*

Nucleophilic substitution reactions occurring at an sp^2 -hybridized carbon atom by pyridinium, quinolinium, and isoquinolinium ylides have been reported in the literature. Among unsaturated compounds containing a nucleophilic group, *N*-bis(methylthio)methyleneamides [1], 1,1-bis(methylthio)-2-nitro- [2], 2,2-dicyanoethenes [2, 3], and other unsaturated nitriles [3] have been studied. Interest in these reactions derives from the search for convenient preparative-scale reactions for the synthesis of biologically active heterocycles in the indolizine, imidazo[1,2-*a*]pyridine, and isoquinoline series, and other compounds [1-6]. Although the regio(selective) direction or pathways of these reaction processes have been relatively well studied [1-3], their stereo(selective) pathways [2] have been less well studied, while their electronic regio- and stereoselectivity have been essentially ignored in the literature. By electronic regioselectivity we denote a reaction course leading to the formation of predominantly one compound, among several possible compounds, with charge separation, where all of the possible compounds differ only in the position of charge localization in the molecules, and in which an electron pair serves or functions in the role of a substituent. With respect to ylides, we refer to all compounds formed (either actually or hypothetically) via loss of a proton from either a central "onium ion" heteroatom directly bonded to it [7] (1,2-ylide), or from a more distant carbon atom (1,4-, 1,6-ylides, etc.).

It is not possible to establish unequivocally the structure of the reaction products from pyridinium ylides with 1,1-bis(methylthio)-2,2-dicyanoethane based solely on their UV, IR, and NMR spectral data. However, in a previous set of papers [1-3] the product of this reaction was assigned a 1,2-ylide structure I, rather than a 1,4-ylide structure II ($R = COOEt, CPh$). We feel that this data require more accurate information or verification.



Since nucleophilic substitution reactions at sp^2 -hybridized carbon atoms in substituted ethylenes occur via an addition—elimination mechanism (S_N2, Ad_N-E) [8, 9], we examined first of all the electronic regioselectivity in the reaction of pyridinium ylides with tetracyanoethylene. This made it possible to decide the question of charge distribution in the resulting pyridinium ylide products. If reaction occurs via an Ad_N-E mechanism, both geminal cyano groups would be capable of delocalizing the negative charge, as in compounds I and II, thus stabilizing the resulting intermediates in the form of their corresponding ylides. It should be possible to study the "electronic imprint" of this type of reaction in the same manner. Our assumptions have been confirmed in the present study.

Pyridinium ylides were generated without isolation directly in the reaction mixture, by treatment of pyridinium salts IIIa-c with triethylamine in methanol (see below).

Pyridinium ylides IIIa-c apparently react initially via addition to tetracyanoethylene V, giving adducts VIa-c. One of the cyano groups in these intermediates VI is located in a favorable position for *trans*-1,2-elimination of

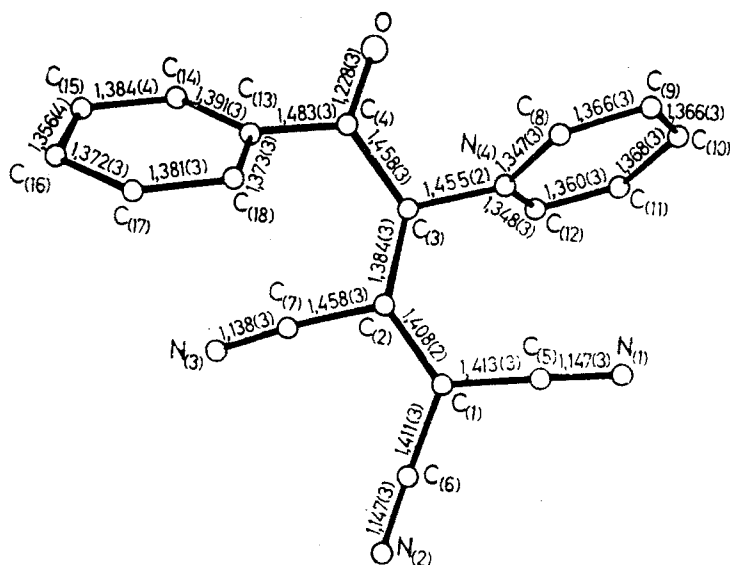
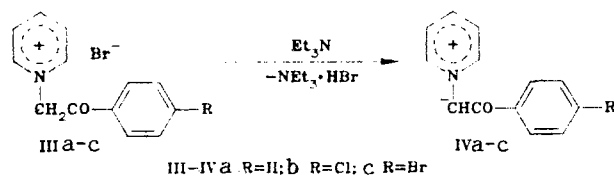
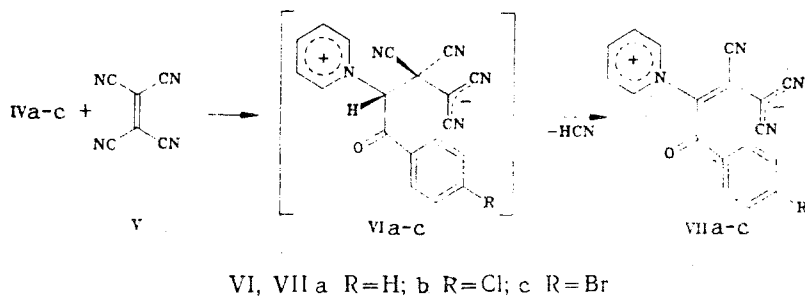


Fig. 1. Molecular structure of compound VIIa and its bond lengths in Å.

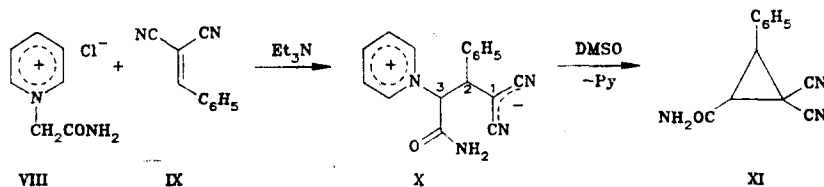


hydrogen cyanide, resulting in the formation of compounds VIIa-c.

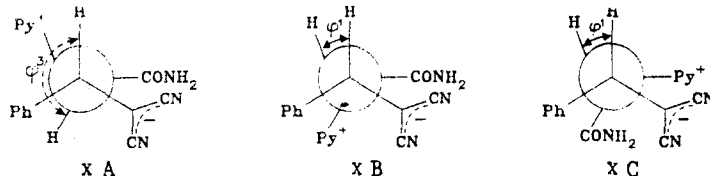


The substituent orientation in molecules VIIa-c may be the result of inversion in intermediate VI, if the latter is relatively stable, or may be due to highly regioselective attack of pyridinium ylides IV on tetracyanoethylene V. Regardless of the actual pathway leading to maximum spatial separation of the bulky Py^+ , COC_6H_5 , and $\text{C}(\text{CN})_2$ substituents (see Fig. 1), the molecular conformation in compounds VIIa-c appears to be favorable or advantageous. If the rate of 1,2-elimination of hydrogen cyanide is relatively slow, it is possible to postulate the formation of pyridinium 1,2-ylides via sigmatropic shift rearrangement in the intermediates VI. In addition, intermediates VI may also undergo intramolecular 1,3-pyridine elimination, resulting in the formation of the corresponding cyclopropanes, in analogy with or similar to cyclopropane formation from unsaturated compounds and phosphorus, sulfur, or selenium ylides [10].

Taking into account both the above discussion and literature data [1-3, 8, 10], we have modeled this reaction, using the pyridinium salt VIII and benzylidenemalononitrile IX. The presence of an amide group in ylide VIII reduces the solubility of the reaction products and thus facilitates their isolation, without interference due to temperature or other factors on the reaction mixture. Since benzylidenemalononitrile does not contain a nucleofugal group in this reaction, it is possible to exclude the possibility of a 1,2-elimination process in this case.



We were successful in isolating and characterizing the Michael adduct in the form of a pyridinium 1,4-ylide X. Compound X is sparingly soluble in methanol, ethanol, chloroform, and ether, but dissolves at 50–60°C in DMSO where it undergoes 1,3-pyridine elimination to form *s*-substituted trans-cyclopropane XI. Based on its IR and PMR spectral data compound X exists in the form of a pyridinium 1,4-ylide with maximum separation and delocalization of the positive and negative charges in the Py^+ and $\text{C}(\text{CN})_2^-$ fragments, respectively. This type of electron density distribution results in a sharp decrease in the frequency of the CN group stretching vibrations in its IR spectrum, to 2103 and 2266 cm^{-1} , relative to the frequency of an unconjugated nitrile [11]. In its PMR spectra, on the other hand, the proton signals for the pyridinium substituent are shifted downfield, which is characteristic of quaternized azines [12, 13]. Based on its PMR spectral data compound X consists of a mixture of isomers about the C(2)—C(3) bond. Thus, the C^2H and C^3H proton signals appear in the form of four doublets in the regions 3.63 and 3.81 ppm (SSCC $^3J_1 = 8.5$ Hz) and 3.83 and 5.56 ppm (SSCC $^3J_2 = 11.8$ Hz). Torsional angle calculations using the Karplus—Conroy equation [12] revealed that the value of the 3J_1 SSCC corresponds to two angles $\varphi^1 = 31^\circ$ and $\varphi^2 = 140^\circ$, while the value of the 3J_2 SSCC corresponds to an angle $\varphi^3 = 161^\circ$. Based on characteristic SSCC values for substituted ethanes [13], and steric strain, we can exclude the conformer with angle φ^2 . It would follow, therefore, that compound X consists of a mixture of isomers with antiperiplanar ($2R^*$, $3S^*$) (XA) and synclinal XB and XC [$(2R^*$, $3R^*)$, XB and/or ($2R^*$, $3S^*$), XC] orientations of hydrogen atoms, in a 4:3 (overall) ratio, respectively. We have isolated only the trans-cyclopropane XI however. Complete conversion of isomers XB and XC to isomer XA, via a retro-Michael reaction, would seem to be a necessary condition for formation of the trans cyclopropane. The very high, almost quantitative yield of cyclopropane XI provides evidence for the reversibility of the Michael reaction in this case.



These results and data support to a certain extent the assumption that reaction of compounds II and V occurs via an intermediate VI.

The structures of the newly synthesized compounds were established based on their spectral characteristics. The IR spectra of compounds IIIa-c contain two intense CN group absorption bands at 2185–2189 and 2206–2208 cm^{-1} (cf. Table 1). The less-pronounced decrease in the frequency of the CN absorption bands in the IR spectra of compounds IIIa-c, compared to the IR spectra of compound X, may be due to partial delocalization of the negative charge in the $\text{O}\cdots\text{C}\cdots\text{C}^3\cdots\text{C}^2\cdots\text{C}^1\cdots(\text{C}\cdots\text{N})_2$ fragment. This is supported by the observed sharp reduction in the frequency of the $\text{C}=\text{O}$ stretching vibration to 1627–1630 cm^{-1} . The PMR spectra of compounds VIIa-c exhibit characteristic signals for the Ar and Py^+ substituent protons (Table 1). As in compound X, the Py^+ substituent proton signals are shifted downfield, which is characteristic of quaternized pyridines [12, 13]. The ^{13}C -NMR spectrum of compound VIIb contains carbon atom signals for three CN groups, in the form of singlets at 114.6, 117.4, and 123.6 ppm. The position of the 114.6 and 117.4 ppm signals is similar to the chemical shift values observed for the carbon atom signals in sulfonium dicyanomethylides (δ 117.7 ppm) [14]. In addition to sp^2 -hybridized carbon atom signals, the ^{13}C -NMR spectrum of compound VIIb also exhibits a singlet for the ylide carbon atom at 51.2 ppm; its chemical shift value is significantly higher than that observed for the ylide carbon atom in dimethylsulfonium dicyanomethylide (δ 15.8 ppm) [14]. This would seem to indicate partial delocalization of electron density in the ylide carbon atom via the conjugated system of atoms shown above for ylide VIIb; charge delocalization results in partial conversion of the tetrahedral configuration about the carbon atom to a trigonal configuration.

It is thus possible to assess in this manner the regio(selective) pathway for the reaction of pyridinium ylides with tetracyanoethylene, based on the IR and NMR spectral data of the reaction products. The data are insufficient, however, to establish the electronic stereo(selective) pathway for this reaction and the corresponding (stereochemical) structure of the resulting pyridinium 1,4-ylides. In order to accomplish these goals we have carried out an x-ray structural investigation of compound VIIa (cf. Table 2).

TABLE 1. Properties of 3-Aroyl-3-(1-pyridinio)-1,1,2-tricyano-2-propenides-1 (VIIa-c)

Compound	Molecular formula	Mp, °C	IR spectrum, ν , cm^{-1}		PMR spectrum (in DMSO- D_6), δ , ppm				Yield, %
			C \equiv N	C=O	pyridinium protons			Ar, m	
					2-CH, 6-CH	4-CH	3-CH, 5-CH		
VIIa	C ₁₈ H ₁₀ N ₄ O	267 ... 269	2187, 2206	1627	9,22	8,69	8,25	7,49	59
VIIb	C ₁₈ H ₉ ClN ₄ O	275 ... 277	2188, 2205	1632	9,24	8,72	8,28	7,51 ... 7,66	55
VIIc	C ₁₈ H ₉ BrN ₄ O	280 ... 282	2185, 2208	1630	9,21	8,72	2,27	7,60	50

TABLE 2. Bond Angles in Compound VIIa

Angle	ω°	Angle	ω°	Angle	ω°
C ₍₅₎ C ₍₁₎ C ₍₆₎	115,1 (2)	OC ₍₄₎ C ₍₁₃₎	121,7 (2)	C ₍₁₀₎ C ₍₁₁₎ C ₍₁₂₎	119,9 (2)
C ₍₅₎ C ₍₁₎ C ₍₂₎	123,1 (2)	C ₍₁₎ C ₍₅₎ N ₍₁₎	178,0 (2)	C ₍₁₁₎ C ₍₁₂₎ N ₍₄₎	120,2 (2)
C ₍₆₎ C ₍₁₎ C ₍₂₎	121,7 (2)	C ₍₁₎ C ₍₆₎ N ₍₂₎	177,2 (3)	C ₍₄₎ C ₍₁₃₎ C ₍₁₄₎	119,8 (2)
C ₍₁₎ C ₍₂₎ C ₍₃₎	128,5 (2)	C ₍₂₎ C ₍₇₎ N ₍₃₎	174,3 (2)	C ₍₄₎ C ₍₁₃₎ C ₍₁₈₎	121,4 (2)
C ₍₁₎ C ₍₂₎ C ₍₇₎	113,3 (2)	C ₍₃₎ N ₍₄₎ C ₍₈₎	119,3 (2)	C ₍₄₎ C ₍₁₃₎ C ₍₁₈₎	118,8 (2)
C ₍₃₎ C ₍₂₎ C ₍₇₎	118,1 (2)	C ₍₃₎ N ₍₄₎ C ₍₁₂₎	119,9 (2)	C ₍₁₃₎ C ₍₁₄₎ C ₍₁₅₎	119,8 (2)
C ₍₂₎ C ₍₃₎ C ₍₄₎	128,5 (2)	C ₍₈₎ N ₍₄₎ C ₍₁₂₎	120,7 (2)	C ₍₁₄₎ C ₍₁₅₎ C ₍₁₆₎	120,7 (2)
C ₍₂₎ C ₍₃₎ N ₍₄₎	117,8 (2)	N ₍₄₎ C ₍₈₎ C ₍₉₎	119,8 (2)	C ₍₁₅₎ C ₍₁₆₎ C ₍₁₇₎	119,8 (2)
N ₍₄₎ C ₍₃₎ C ₍₄₎	113,5 (2)	C ₍₈₎ C ₍₉₎ C ₍₁₀₎	120,0 (2)	C ₍₁₆₎ C ₍₁₇₎ C ₍₁₈₎	120,2 (2)
C ₍₃₎ C ₍₄₎ O	120,4 (2)	C ₍₉₎ C ₍₁₀₎ C ₍₁₁₎	119,4 (2)	C ₍₁₇₎ C ₍₁₈₎ C ₍₁₃₎	120,6 (2)
C ₍₃₎ C ₍₄₎ C ₍₁₃₎	117,9 (2)				

TABLE 3. Short Nonbonded Intramolecular Contact Distances in the Molecular Structure of Compound VIIa*

Bond	$l, \text{Å}$	Bond	$l, \text{Å}$	Bond	$l, \text{Å}$
O...N ₍₄₎	2,696 (2)	C ₍₂₎ ...C ₍₁₃₎	3,061 (2)	C ₍₄₎ ...C ₍₁₂₎	3,402 (3)
O...C ₍₈₎	3,081 (3)	C ₍₂₎ ...C ₍₁₈₎	3,205 (3)	C ₍₅₎ ...C ₍₈₎	3,361 (3)
O...C ₍₁₄₎	2,966 (3)	C ₍₃₎ ...C ₍₅₎	3,047 (3)	C ₍₅₎ ...C ₍₁₂₎	3,029 (3)
N ₍₄₎ ...C ₍₁₎	2,961 (2)	C ₍₃₎ ...C ₍₁₈₎	3,035 (3)	C ₍₆₎ ...C ₍₇₎	2,730 (3)
N ₍₄₎ ...C ₍₅₎	2,820 (3)	C ₍₄₎ ...C ₍₇₎	2,995 (3)	C ₍₇₎ ...C ₍₁₃₎	2,863 (3)
C ₍₁₎ ...C ₍₁₂₎	3,288 (3)	C ₍₄₎ ...C ₍₈₎	3,042 (3)	C ₍₇₎ ...C ₍₁₈₎	2,948 (3)
C ₍₂₎ ...C ₍₁₂₎	3,057 (3)				

*The sum of the van der Waals radii for O and N atoms is 3.07; O and C 3.22; N and C 3.25 Å. The doubled van der Waals radius for a C atom is 3.40 Å [19].

X-ray structure analysis confirmed that compound VIIa indeed represents 3-benzoyl-3-(1-pyridinio)-1,1,2-tricyano-2-propenide-1, i.e., a 1,4-ylide, in which the negative charge is delocalized among three C atoms in the ylide fragment and the terminal CN groups. A relatively planar C(3), C(2), C(1), C(5)N(1)C(6)N(2) fragment can be delineated in the molecular structure [plane A, with atomic deviations from planarity less than 0.058(2) Å]. The "ylide" carbon atom C(1) exhibits trigonal planar sp^2 hybridization (the sum of its bond angles is 360°), and its unshared electron pair is involved in conjugation with both the C(2)=C(3) double bond and the two adjacent nitrile groups. The formal C(2)=C(3) double bond is elongated to 1.384(3) Å, while the formal C(1)-C(2) single bond is significantly contracted, to 1.408(2) Å. Analogous bond-length patterns have been observed previously for tetracyanopropenide salts of substituted hexahydrobenzothiazolo[3,2-*a*]pyridinium (XII) [1.364(5) and 1.398(5) Å] [15] and triphenylpyrylium ions (XIII) [1.379(5) and 1.388(5) Å] [16].

The fact that the unshared electron pair on the C(1) atom is involved in conjugation with the CN groups results, on the one hand, in contraction of the C(1)-C(5) and C(1)-C(6) bond lengths to 1.413(3) and 1.411(3) Å [compared to C(2)-C(7) 1.458(3) Å, and a standard C(sp^2)-C(sp) bond length in TCNQ, for example, of 1.427 Å [17]], and, on the other hand, in a slight elongation of the C \equiv N bond length to 1.147(3) Å (versus C(7) \equiv N(3)

equal to 1.138(3) Å, and 1.144 Å [17] in TCNQ). The C(sp²)—C(sp) and C≡N bond length values in the tetracyanopropenide anions in salts XII and XIII are comparable to those found for compound VIIa.

The coordination plane about the C(4) atom [plane B, which is formed with an accuracy of 0.009(2) Å] is noncoplanar with the conjugated fragment plane A mentioned above (the A/B dihedral angle is equal to 142.5°); this inhibits further delocalization of electron density between the C(2)=C(3) and C(4)=O bonds. Nevertheless, the C(3)—C(4) bond [1.458(3) Å] is somewhat shortened, while the C(4)=O bond length [1.228(3) Å] is also slightly elongated, leading us to conclude the existence of a weak conjugative interaction between fragments A and B in the molecular structure of VIIa.

The molecular conformation of VIIa appears to reflect a compromise between the tendency mentioned above, namely formation of a completely delocalized electron system involving fragments A and B, and a large number of short nonbonded distances involving the benzene ring and the CN group attached to C(2), the carbonyl group oxygen atom and the pyridine substituent, as well as between these groups and the C(5)≡N(1) CN group attached to C(1) (Table 3). These short contact distances are responsible for rotation of the Py⁺ and Ph substituents by 107.5° and 60.9°, respectively, relative to plane A, and by 75.5° and 133.4° relative to plane B. The large rotations exhibited by these substituents precludes their participation in electron conjugation with the other fragments A and B. In fact, the value of the C(3)—N(4) bond length [1.455(2) Å] substantially exceeds the standard or normal bond length value for a conjugated N(sp²)—C(sp²) bond (1.355 Å) [17], and is characteristic instead of a single N⁺(sp²)—C(sp²) bond length (for example, 1.447(8) and 1.448(7) Å for the E- and Z-isomers copresent in the crystal structure of 1-(2-amino-1-cyano-2-thioethylene)pyridinium ylide [18]).

The short nonbonded intramolecular contact distances also result in substantial enlargement of the C(1)C(2)C(3) and C(2)C(3)C(4) bond angles to 128.5 and 128.5(2)°. The C(1)C(2)C(7) [113.2(2)°] and N(4)C(3)C(4) [113.5(2)°] bond angles are commensurately reduced. Steric interaction involving Py⁺⋯O is weaker than Py⁺⋯C(5)≡N(1) (Table 4).

The intermolecular distances O⋯C(12') 3.119(2) and O⋯H(12') 2.37(2) Å [where the C(12') and H(12') coordinates were obtained by transformation $x, 1/2 - y, -1/2 + z$] in the crystal structure of ylide VIIa are somewhat shorter than the sums of the van der Waals radii for the corresponding O and C, and O and H atoms (3.22 and 2.72 Å [19]).

The C(4)=O carbonyl group in the crystal structure of VIIa has adopted an orientation which is unfavorable for cyclization of CIIa to a substituted pyran or pyridine. The ¹³C-NMR spectrum of compound VIIb upon heating the latter in DMSO-D₆ to 120° remains practically unchanged, indicating that compound VIIb itself remains unchanged and stable under these conditions.

The spectral data for compounds (VIIa-c) and the results of x-ray structure analysis of compound (VIIa) confirm our earlier hypothesis that compounds VIIa-c exist in the form of 1,4-ylides. We conclude, therefore, that

TABLE 4. Atomic Coordinates ($\times 10^4$ for O, N, C; $\times 10^3$ for H) and Their Equivalent Isotropic Thermal Parameters (isotropic for H) in the Molecular Structure of Compound VIIa

Atom	x	y	z	B _{equiv} / iso, Å ²	Atom	x	y	z	B _{equiv} / iso, Å ²
O	1042(2)	3241(1)	826(1)	4.6(1)	C ₍₁₃₎	-1152(2)	3993(1)	519(2)	3.0(1)
N ₍₁₎	2924(2)	4261(2)	6537(2)	6.7(1)	C ₍₁₄₎	-2124(2)	3547(1)	-592(2)	4.3(1)
N ₍₂₎	-1475(2)	3911(2)	6245(2)	7.0(1)	C ₍₁₅₎	-3474(3)	3905(2)	-1320(2)	5.1(1)
N ₍₃₎	-2921(2)	3460(1)	2493(2)	4.2(1)	C ₍₁₆₎	-3850(2)	4695(2)	-980(2)	4.8(1)
N ₍₄₎	2265(2)	3467(1)	3545(1)	2.7(1)	C ₍₁₇₎	-2872(3)	5158(1)	75(2)	4.6(1)
C ₍₁₎	310(2)	3874(1)	5011(2)	2.9(1)	C ₍₁₈₎	-1528(2)	4805(1)	825(2)	3.6(1)
C ₍₂₎	-137(2)	3723(1)	3601(2)	2.5(1)	H ₍₈₎	280(2)	456(1)	293(2)	3.8(4)
C ₍₃₎	716(2)	3624(1)	2829(2)	2.7(1)	H ₍₉₎	531(2)	429(1)	403(2)	5.6(5)
C ₍₄₎	259(2)	3585(1)	1351(2)	3.0(1)	H ₍₁₀₎	610(3)	304(1)	523(2)	5.6(5)
C ₍₅₎	1760(2)	4075(1)	5847(2)	3.9(1)	H ₍₁₁₎	449(2)	205(2)	540(2)	6.1(6)
C ₍₆₎	-691(2)	3879(2)	5675(2)	4.1(1)	H ₍₁₂₎	199(2)	239(1)	428(2)	3.5(4)
C ₍₇₎	-1704(2)	3600(1)	2930(2)	2.9(1)	H ₍₁₄₎	-183(2)	304(1)	-78(2)	4.2(4)
C ₍₈₎	3232(2)	4057(1)	3449(2)	3.7(1)	H ₍₁₅₎	-415(3)	359(2)	-205(3)	7.8(7)
C ₍₉₎	4689(2)	3900(2)	4074(2)	4.5(1)	H ₍₁₆₎	-481(3)	469(1)	-145(2)	5.6(5)
C ₍₁₀₎	5163(2)	3156(2)	4816(2)	4.6(1)	H ₍₁₇₎	-316(3)	547(2)	33(2)	6.5(6)
C ₍₁₁₎	4165(2)	2568(1)	4912(2)	4.4(1)	H ₍₁₈₎	-87(2)	512(1)	154(2)	4.9(5)
C ₍₁₂₎	2718(2)	2726(1)	4261(2)	3.6(1)					

reaction of pyridinium ylides with tetracyanoethylene occurs via an $\text{Ad}_N\text{-E}$ mechanism resulting in the formation of Z-isomers of 3-aryl-3-(1-pyridinio)-1,1,2-tricyano-2-propenides-1, i.e., 1,4-pyridinium ylides — compounds with maximum charge separation. If the nitrile starting material in these reactions contains a nucleofugal group 1,2-elimination predominates over 1,3-elimination processes. In some cases it is possible to obtain an "electronic imprint" of the reaction and thus evaluate both in electronic regio- and stereo(selective) pathways.

EXPERIMENTAL

IR spectra were recorded on a Perkin—Elmer 577 spectrophotometer using KBr pellets. PMR spectra were obtained on a Bruker WM-250 (250 MHz) spectrometer in DMSO-D_6 relative to TMS; $^{13}\text{C-NMR}$ spectra were obtained on a Bruker AM-300 spectrometer (300 MHz) in DMSO-D_6 solution.

X-Ray Structural Analysis of 3-Benzoyl-3-(1-pyridinio)-1,1,2-tricyano-2-propenide-1. Ruby-colored crystals of VIIa are monoclinic, at 20°C : $a = 9.8958(8)$, $b = 15.3406(19)$, $c = 10.5753(11)$ Å, $\beta = 111.803(7)^\circ$, $V = 1490.6(3)$ Å³, $d = 1.329$ g/cm³, $Z = 4$, $\text{C}_{18}\text{H}_{10}\text{N}_4\text{O}$, space group $\text{P2}_1/\text{c}$. The unit cell parameters and the intensities of 2738 reflections were measured on a four-circle automatic diffractometer (Hilger—Watts) (λ MoK α , graphite monochromator, $\theta/2\theta$ scanning to $\theta_{\text{max}} = 30^\circ$). The structure was solved by direct methods using the MULTAN program and was refined by full-matrix least squares using anisotropic thermal parameters for the nonhydrogen atoms, based on 1997 independent reflections with $I \geq 2\sigma$. The hydrogen atoms were visualized in a difference synthesis and were refined isotropically. The final discrepancy factors were $R = 0.041$ and $R_w = 0.052$. All calculations were carried out on an Eclipse S/200 computer using the INEXTL system of programs [20].

3-(Benzoyl-3-(1-pyridinio)-1,1,2-tricyano-2-propenide-1 (VIIa). To a cooled mixture of 1.11 g (4 mmoles) pyridinium salt IIIa and 0.42 ml (3 mmoles) triethylamine in 3 ml methanol at 0°C was added with stirring 0.26 g (2 mmoles) tetracyanoethylene. The mixture was stirred for 1 h. The resulting precipitate was removed by filtration, washed with water and methanol, and recrystallized from acetonitrile. $^{13}\text{C-NMR}$ spectrum (DMSO-D_6): 51.23 (s, C^1); 113.68 (s, C^2); 114.62, 117.44, and 123.59 [s, ($\text{C}\equiv\text{N}$)₃]; 126.72 (s, C^3); 128.52 and 130.14 (m, C^3 -, C^5 -, C^4 -, C^6 -phenyl); 128.61 (d, C^3 - and C^5 -pyridinio, $J = 170$ Hz); 136.35 (t, C^4 -phenyl, $J = 11$ Hz); 137.32 (t, C^1 -phenyl, $J = 7$ Hz); 147.66 (d, C^4 -pyridinio, $J = 172$ Hz); 149.45 (d, C^2 - and C^6 -pyridinio, $J = 194$ Hz); 182.62 ppm (s, $\text{C}=\text{O}$).

3-(1-Pyridinio)-3-(4-chlorobenzoyl)-1,1,2-tricyano-2-propenide-1 (VIIb) and 3-(4-Bromobenzoyl)-3-(1-pyridinio)-1,1,2-tricyano-2-propenide-1 (VIIc). These were prepared in an analogous manner to compound VIIa.

1,1-Dicyano-3-carbamoyl-3-(1-pyridinio)-2-phenyl-1-propenide (X, $\text{C}_{17}\text{H}_{14}\text{N}_4\text{O}$). To a mixture of 1.73 g (10 mmoles) pyridinium salt VIII, 1.54 g (10 mmoles) compound IX in 30 ml ethanol was added in one portion 1.38 ml (10 mmoles) triethylamine, and the mixture was then stirred for 6 h at 25°C ; the resulting precipitate was removed by filtration. Compound X was obtained in the form of a yellow powder, mp $174\text{--}176^\circ\text{C}$ (decomp.) IR spectrum: 1633, 1705 (CONH_2); 2103, 2166 ($\text{C}\equiv\text{N}$); 3186, 3277, 3328 cm^{-1} (NH_2). PMR spectrum: 3.63 [16H, d, $\text{C}(2)\text{H}$, $^3J = 8.5$ Hz]; 3.83 [1H, total, d, $\text{C}(2)\text{H}$, $^3J = 11.8$ Hz]; 3.81 [1H, d, $\text{C}(3)\text{H}$, $^3J = 8.5$ Hz]; 5.58 [1H, total, d, $\text{C}(3)\text{H}$, $^3J = 11.8$ Hz]; 7.2–7.5 (5H, m, C_6H_5); 7.52 (1H, br.s, NH); 7.78 and 7.93 [2H, m, $\text{C}(3)\text{H}$ and $\text{C}(5)\text{H}$, piperidinio]; 8.12 (1H, br.s, NH); 8.25 [1H, t, $\text{C}(4)\text{H}$ piperidinio]; 8.73 and 9.12 ppm [2H, d, $\text{C}(2)\text{H}$ and $\text{C}(6)\text{H}$ piperidinio].

1,1-Dicyano-2-carbamoyl-3-phenyl-trans-cyclopropane (XI, $\text{C}_{12}\text{H}_9\text{N}_3\text{O}$). Compound X (2.9 g, 10 mmoles) was heated in 20 ml DMSO for 10 min. The mixture was diluted at 25°C with 60 ml water, and the resulting precipitate was removed and washed with ethanol and hexane. Compound XI was obtained, mp 158°C . IR spectrum: 1660, 1732 (CONH_2), 2260 ($\text{C}\equiv\text{N}$), 3288 cm^{-1} (NH_2). PMR spectrum: 3.49 [1H, d, $\text{C}(2)\text{H}$, $^3J = 5.1$ Hz]; 4.08 [1H, d, $\text{C}(3)\text{H}$]; 7.40 (5H, m, C_6H_5); 9.03 (1H, br.s, NH); 9.18 ppm (1H, br.s, NH).

LITERATURE CITED

1. Y. Tominaga, S. Motokawa, Y. Shiroshita, and A. Hosomi, *J. Heterocycl. Chem.*, **24**, 1365 (1987).
2. Y. Tominaga and Y. Matsuda, *J. Heterocycl. Chem.*, **22**, 937 (1985).
3. Y. Tominaga, Y. Shiroshita, and A. Hosomi, *Heterocycles*, **27**, 2251 (1988).
4. R. K. Dieter, *Tetrahedron*, **42**, 3029 (1986).
5. Y. Tominaga, A. Ushiroguchi, and Y. Matsuda, *J. Heterocycl. Chem.*, **24**, 1325 (1987).
6. R. K. Dieter, L. A. Silks, J. R. Fishpugh, and M. F. Kastner, *J. Am. Chem. Soc.*, **107**, 4679 (1985).
7. N. P. Beletskii and O. M. Nefedev (eds.), *IUPAC Chemistry Nomenclature Rules* [in Russian], Vol. 5, VINITI, Moscow (1985), p. 55.
8. Z. Rappoport, *Rec. Trav. Chim. Pays-Bas.*, **104**, 309 (1985).
9. A. J. Fatiadi, *Synthesis*, No. 9, 749 (1987).

10. L. A. Yanovskaya, V. A. Dombrovskii, and A. Kh. Khusid, *Cyclopropanes with Functional Groups* [in Russian], Nauka, Moscow (1980).
11. E. N. Zil'berman, *Reactions of Nitriles* [in Russian], Nauka, Moscow (1972), p. 13.
12. W. Sliwa and G. Matusiak, *Heterocycles*, **23**, 1513 (1985).
13. H. Günther, *Introduction to NMR Spectroscopy* [in Russian], Mir, Moscow (1984).
14. V. S. Bogdanov, V. V. Semenov, O. P. Shitov, S. A. Shevelev, and K. Ya. Burshtein, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 7, 1528 (1983).
15. A. M. Shestopalov, V. N. Nesterov, Yu. A. Sharanin, V. P. Litvinov, V. E. Shklover, Yu. T. Struchkov, and V. K. Promonenkov, *Khim. Geterotsikl. Soedin.*, No. 12, 1682 (1988).
16. T. Tamamura, T. Yamane, N. Yasuoka, and N. Vasai, *Bull. Chem. Soc. Jpn.*, **47**, 832 (1974).
17. F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, No. 1, 1 (1987).
18. E. Fischer, M. Knippel, K.-M. Wollin, A. Kalman, and G. J. Argay, *J. Prakt. Chem.*, **325**, 261 (1983).
19. A. Bondi, *J. Phys. Chem.*, **70**, 3006 (1966).
20. R. G. Gerr, A. I. Yanovskii, and Yu. T. Struchkov, *Kristallografiya*, **20**, 1029 (1983).

CYCLIZATION OF 2,4-DICHLORO-1,5-PENTANEDIONES WITH NUCLEOPHILIC REAGENTS

O. V. Litvinov, S. N. Chalaya, and V. G. Kharchenko

UDC 547.422.5'829'749.04

The mechanism of reaction of 2,4-dichloro-1,5-pentanediones with ammonia has been studied. Intramolecular cyclization of the intermediate resulting from nucleophilic attack at the carbonyl group can occur in two ways, depending on the reaction conditions, either at the α -chloromethylene fragment or at the second carbonyl group, leading to the formation of 2-arylpyrroles or 3-chloropyridines, respectively. In reactions with thio- and phenylthiourea both chlorophenacyl fragments are involved, resulting in the formation of di(2-amino-4-arylthiazotyl-5)methanes.

We have previously demonstrated that in reactions of 2,4-dichloro-1,5-pentanediones with ammonia 2-arylpyrroles [1] are formed, in addition to the expected chloropyridine products; the formation of 2-arylpyrroles represents a novel heterocyclization pathway for 1,5-dicarbonyl compounds, and can be attributed to the presence of a chloromethylene fragment in the structure.

In the present paper we have attempted to elucidate the mechanism of aroylpyrrole formation, and have also examined the cyclization characteristics of 2,4-dichloro-1,5-pentanediones I with other nucleophiles, such as thio- and phenylthiourea.

The presence of several reactive sites in the molecular structure of compounds I opens up the possibility of the existence of different cyclization pathways. Based on literature reports [2] concerning the synthesis of pyrroles from β , γ -dichloroalkylketones, we postulated that aroylpyrrole formation from dichloropentanediones I could occur via dehydrochlorination resulting in the formation of 4-chloro-2-pentene-1,5-dione (II) as an intermediate. It was found, however, that reaction of 1,3,5-triphenyl-2,4-dichloro-1,5-pentanedione (Ie) with triethylamine, acting as a dehydrochlorinating agent, concluded unexpectedly with the formation of 2-benzoyl-4-chloro-3,5-diphenyl-2,3-dihydrofuran (IIIe).

N. G. Chernyshevskii Saratov State University, Saratov. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 8, pp. 1095-1099, August, 1991. Original article submitted July 14, 1989; revision submitted June 27, 1990.