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STEREOCHEMISTRY OF THE REACTION OF PYRIDINIUM YLIDES WITH
 α,β -UNSATURATED NITRILES

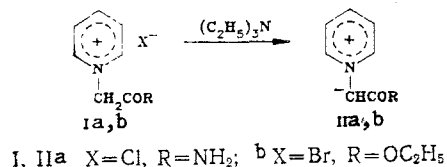
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 and V. P. Litvinov

UDC 547.821.3:543.422:541.634

Regioselective and stereoselective methods were developed for the synthesis of 4-aryl-2-oxo-3-(1-pyridinio)-5-cyano-3,4-trans-1,2,3,4-tetrahydropyridin-6-olates from pyridinium ylides and α,β -unsaturated nitriles. The compounds were also obtained by the condensation of aromatic aldehydes, cyanoacetamide, and pyridinium ylides. It was established that these reactions take place through the corresponding Michael adducts, which undergo heterocyclization in the form of the anti conformers to substituted 3,4-trans-1,2,3,4-tetrahydropyridin-6-olates.

The high reactivity of pyridinium ylides is due to the electron-withdrawing action of the pyridinium cation. Thus, pyridinium ylides enter readily into nucleophilic Michael addition to unsaturated compounds [1-3]. Here various heterocyclic nitrogen compounds are formed, depending on the conditions and on the structure of the initial compounds, i.e., pyridines, quinolines, indolizines, imidazopyridines, and others [1-5]. Pyridinium ylides have found wide use in the synthesis of pyridines, bipyridyls, and polypyridyls [2, 3, 6-8]. α,β -Unsaturated ketones and aldehydes of the aliphatic, carbocyclic, and heterocyclic series were investigated as unsaturated compounds.

Unsaturated nitriles containing an activated C=C double bond also enter readily into nucleophilic addition [9-11]. Until now, however, their reactions have hardly been investigated at all except for the reaction of acrylonitrile [12] with pyridinium ylides. In view of this we studied the reaction of the arylidene derivatives of cyanoacetic ester and cyanoacetamide with pyridinium ylides. Here the pyridinium ylides were not isolated in the individual state but were generated in the reaction mixture from the corresponding pyridinium salts by the action of bases

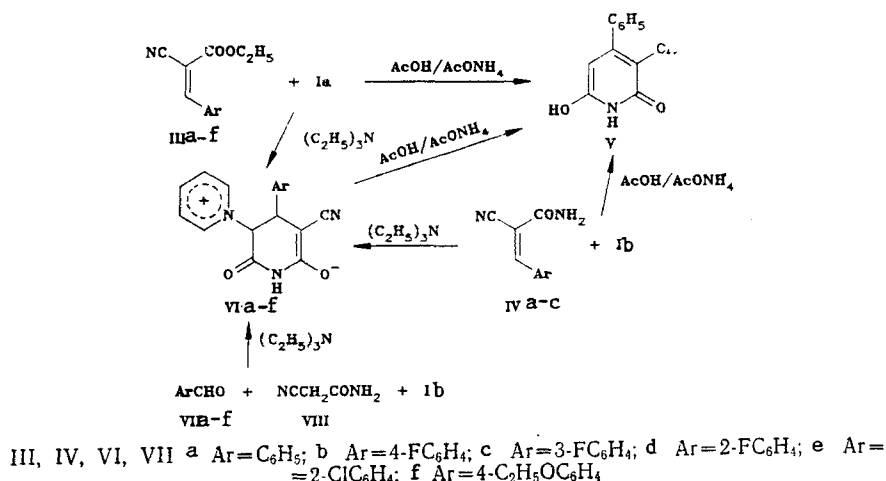


We found that when the pyridinium ylides are generated from the pyridinium salts (Ia, b) in boiling acetic acid in the presence of ammonium acetate by analogy with the method in

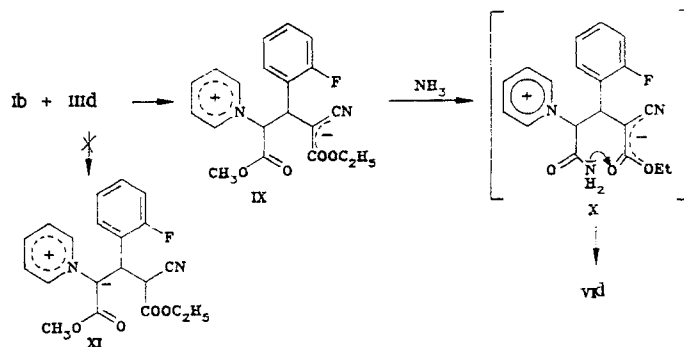
T. G. Shevchenko State Pedagogical Institute, Lugansk 348011. N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow 117913. Translated from Khimiya Geterotsiklicheskih Soedinenii, No. 3, pp. 363-369, March, 1990. Original article submitted July 25, 1988; revision submitted January 18, 1989.

[7, 8] the reaction with the unsaturated nitriles (III, IV) leads to the formation of 6-hydroxy-4-phenyl-3-cyanopyridin-2(1H)-one (V). When the reaction was conducted with heating in ethanol in the presence of triethylamine, the 4-aryl-2-oxo-3-(1-pyridinio)-5-cyano-3,4-trans-1,2,3,4-tetrahydropyridin-6-olates (VIa-f) were isolated with high yields.

The betaines (VIa-f), obtained from the pyridinium salts (Ia, b) and the unsaturated nitriles (IIIa-f, IVa-c) by the various methods, were identical in their physicochemical characteristics. Compounds (VI) are formed through identical intermediates.



We showed that the three-component condensation of the aromatic aldehydes (VII), cyanoacetamide (VIII), and the salt (Ib) in ethanol in the presence of triethylamine takes place regioselectively with the formation of the corresponding pyridin-6-olates (VI). The heating of (VIa) in acetic acid in the presence of ammonium acetate is accompanied by the elimination of pyridine and hydrogen and leads to the pyridone (V). Consequently, the pyridin-6-olates are intermediates in the synthesis of the pyridone (V). The pyridinium ylides enter into nucleophilic Michael addition and act as active carriers of the methylenecarbonyl functions to the unsaturated nitrile. Here variation of the unsaturated nitriles and pyridinium salts makes it possible to isolate the Michael adducts and study their structure. Thus, the reaction of the nitrile (IIIId) with the pyridinium salt (Ib) in ethanol at 40°C in the presence of triethylamine leads to the adduct (IX). Treatment of the adduct (IX) with ammonia leads to its heterocyclization to the pyridin-6-olate (VIId) evidently through the intermediate (X).

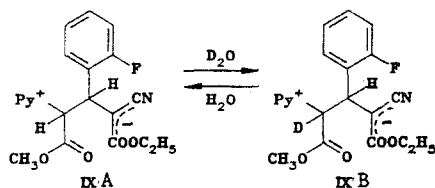


The isolation of the intermediate (IX) and the study of its structure by IR and PMR spectroscopy enabled us to approach for the first time a study of the stereochemistry of the reaction of pyridinium ylides with unsaturated nitriles. The Michael adducts are stabilized in the form of the pyridinium 1,4-ylides and do not undergo intramolecular cyclization to the indolizines, which is a distinguishing feature of the above-mentioned reactions and the reactions of pyridinium ylides with acrylonitrile [12].

Since the CHPy⁺ proton is extremely "acidic" and evidently differs little in acidity from the methylene protons of the pyridinium ylides (Ia, b) while the anionic part of the cyanoacetate residue is fairly basic, the products from the reaction of compounds (Ib)

and (IIIId) could be assigned the structure of the pyridinium 1,2-ylides (XI). However, on the basis of the chemical shifts of the products from the addition of pyridinium ylides (like other ylides) to α,β -unsaturated nitriles, i.e., the formation of cyclopropanes by a mechanism of the intramolecular 1,3-elimination type [9, 10, 13, 14], the product from the reaction of (Ib) and (IIIId) must be regarded as the pyridinium 1,4-ylide (IX). (We will publish data on the detailed chemical characteristics, spectroscopic investigations, and x-ray crystallographic investigations of related pyridinium 1,4-ylides separately.) In addition, the data from physicochemical analysis of the investigated 1,4-ylide favor structure (IX) with delocalization of the negative and positive charges in the $\text{NC-C-COOC}_2\text{H}_5$ and Py^+ fragments, respectively. A characteristic feature of the IR spectra of the ylide (IX) is the exceptionally high intensity of the absorption band for the stretching vibrations of the nitrile group at 2165 cm^{-1} . Here, as a result of the strong conjugation in the cyanoacetate fragment, due to the presence of the free electron pair at the central carbon atom, there is an unusually strong decrease in the above-mentioned absorption band of the $\text{C}\equiv\text{N}$ group by 110 cm^{-1} compared with malononitrile [15], by $92\text{-}95\text{ cm}^{-1}$ compared with 1,5-ketonitriles [16], and by $40\text{-}60\text{ cm}^{-1}$ compared with unsaturated nitriles conjugated with electron-withdrawing substituents [10, 16]. Delocalization of the negative charge in the $\text{NC-C-COOC}_2\text{H}_5$ fragment also leads to a reduction in the frequency of the vibrations of the ester group to 1693 cm^{-1} with a simultaneous increase in intensity compared with the intensity of the aliphatically bonded COOC_2H_5 group, which has an absorption band in the region of $1735\text{-}1745\text{ cm}^{-1}$ [17]. It is clear that other characteristic bands for the unconjugated cyano and ester groups would be observed in the IR spectra of the ylide (XI) [10, 15-18].

The PMR spectrum of the pyridinium ylide (I) contains two doublets for the protons of the CHAr and CHPy^+ groups in the regions of 3.95 and 5.08 ppm, respectively, with $^3J = 11.2\text{ Hz}$. Here the position of the signal for the protons of the CHPy^+ group is typical of pyridinium salts and pyridinium ylides [19] and is in practice unlikely for the protons of the CHCN group of structure (XI). The chemical shift of the signals for the methylene protons of malononitrile is shifted upfield and lies at 3.56 ppm [15]. On this basis it must be supposed that the products from the reaction of (Ib) and (IIIId) can be represented by the structure (IX) and not by the structure (XI). If the signals for the protons at 3.95 and 5.08 ppm are assigned to the CHCN and CHAr groups, respectively, of compound (XI), exchange of the proton of the CHCN group by deuterium would be expected. However, the proton with a signal at 5.08 ppm undergoes deuterioexchange. With a small concentration of D_2O in the solution the intensity of the signal for this proton is reduced, and a singlet appears in the center of the doublet at 3.95 ppm. Thus, the general pattern of this signal is represented by a triplet. Increase in the concentration of D_2O leads to complete deuterioexchange of the proton with a signal in the region of 5.08 ppm and to the appearance of a single singlet at 3.95 ppm. Consequently, the presented data confirm the existence of the structure (IX) and the presence of the equilibrium $(\text{IXA}) \rightleftharpoons (\text{IXB})$.



Taking account of the spin-spin coupling constants of the ethane fragment of the molecule (IX), we calculated the dihedral angle φ of 156° by means of the Karplus-Conroy equation [20]. With this value of the angle the existence of two conformers (IXC) and (IXD) with the syn- and anticlinal arrangement of the reaction centers COOCH_3 and $\text{NC-C-COOC}_2\text{H}_5$ is possible. The possible existence of the two conformers (IXC) and (IXD) is due to the steric strain created by the adjacent bulky groups.

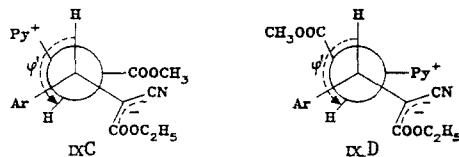


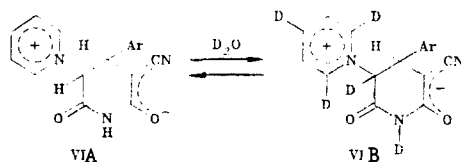
TABLE 1. The Spectral Characteristics and Elemental Analyses of the Synthesized Betaines (VIa-f)

Com- pound	Molecular formula	mp, °C (decomp.)	IR spectrum (KBr), ν , cm^{-1}				PMR spectrum, δ , ppm							Yield, %					
			NH	CH	C \equiv N	C=O	CONH	NH	$\Delta\tau$	3-H	4-II	3J	Py ⁺ protons			A	B	C	
													2-H, 6-H (a)	4-H (r)	3-H, 5-H (r)				
VIa	$\text{C}_{17}\text{H}_{13}\text{N}_3\text{O}_2$	233...235	3420	2855, 2963	2174	1703	1634	9.88	7.14	5.98	4.47	13.1	8.86	8.51	8.03	70	68	59	
VIb	$\text{C}_{17}\text{H}_{12}\text{FN}_3\text{O}_2$	242...245	3428	2840, 2968	2180	1694	1638	9.94	7.09	5.96	4.50	13.4	8.85	8.48	8.03	78	75	64	
VIc	$\text{C}_{17}\text{H}_{12}\text{FN}_3\text{O}_2$	240...243	3429	2853, 2945	2170	1706	1632	9.92	7.15	5.97	4.49	13.1	8.84	8.46	8.02	86	80	82*	
VI d	$\text{C}_{17}\text{H}_{12}\text{FN}_3\text{O}_2$	236...240	3418	2832, 2963	2174	1702	1637	9.79	7.12	5.95	4.61	13.4	8.83	8.48	8.03	81	75	75	
VIe	$\text{C}_{17}\text{H}_{12}\text{ClN}_3\text{O}_2$	245...248	3426	2836, 2975	2172	1705	1635	9.87	7.23	5.96	4.57	13.2	8.84	8.45	8.02	83	—	75	
VI f	$\text{C}_{18}\text{H}_{17}\text{N}_3\text{O}_3$	237...240	3420	2830, 2910, 2929	2172	1700	1635	9.85	7.13 d**; $^3J = 8.6 \text{ Hz}$	5.98	4.43	12.8	8.82	8.48	8.02	97	—	88	

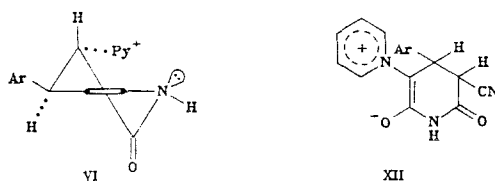
*The yield by method D was 62%.

**CS (C_2H_5): 3.84 (2H, q, CH_2 , $^3J = 7.2 \text{ Hz}$); 1.20 ppm (3H, t, CH_3).

Of the two presented conformers the conformer (IXC) with the almost coplanar arrangement of the reaction centers is evidently realized under the reaction conditions. It is this fact which favors the retention of the trans arrangement of the proton and the aryl substituent during the cyclization of the adduct (IX) to the corresponding pyridin-6-olate (VI). In addition, the data on the structure of the betaines (VIa-f) indicate indirectly that the conformer (IXC) is formed. The stabilization of the molecule of compound (VI) takes place as a result of the separation of the negative and positive charges and their delocalization in the Py^+ and $\text{O}\dots\text{C}^2\dots\text{C}^3\dots\text{C}\dots\text{N}$ fragments of the molecule of (VI). Here the high-intensity absorption band of the $\text{C}=\text{N}$ group of compounds (VI) is shifted toward lower frequencies to $2170\text{-}2180\text{ cm}^{-1}$, similarly to the hydrogenated salts 3-cyanopyridin-2-thiolate [21, 22]. In addition, in the IR spectra of compounds (VI) a high-frequency absorption band for the $\text{C}=\text{O}$ group appears at $1694\text{-}1706\text{ cm}^{-1}$, and the absorption bands of the other functional groups appear (Table 1). In the PMR spectra of compounds (VI), in addition to the signals for the protons of the NH , Py^+ , and Ar groups, there are doublets for the 4-H and 3-H protons in the regions of 4.43-4.61 and 5.95-5.98 ppm with $^3J = 12.8\text{-}13.4\text{ Hz}$. With partial deuterioexchange of the 3-H proton the signal of the 4-H proton is complicated and appears in the form of a triplet. Complete deuterioexchange takes place when D_2O is added to solutions of compounds (VI) in DMSO-d_6 . Here there is also partial deuterioexchange of the α - and γ -protons in the pyridinium cation and complete exchange of the NH proton. During investigation of the dependence of the spin-spin coupling constant of compounds (VI) on the torsion angle $\varphi_{\text{H-C}(4)\text{-C}(5)\text{-H}}$ [20] it can be seen that its value is $\geq 173^\circ$.



In view of the fact that the $\text{O}\dots\text{C}(2)\dots\text{C}(3)\dots\text{C}\dots\text{N}^-$ fragment is planar with the adjacent atom in compounds (V) it can be seen that the pyridin-6-olates exist in the half-chair conformation similar to cyclohexene [23] and the hydrogenated 3-cyanopyridin-2-thiolate salts [21, 24]. Here the 4-H and 3-H protons are in the trans-pseudodiaxial arrangement, and the substituents Ar and Py^+ are in the trans-pseudodiequatorial arrangement.



In this conformation the $\text{C}(2)=\text{O}$ group projects from the plane of conjugation with the π -electrons of the ring nitrogen atom, and this leads to a significant increase in the frequency of the vibrations of the $\text{C}=\text{O}$ group in the IR spectra of (VI) (Table 1) compared with the frequency of the absorption band of the cyclic amide group in substituted pyridin-2-ones [21]. On the basis of the possibility of the formation of structure (XI) it would be logical to suppose that the betaine (XII) is also formed during its heterocyclization. However, it could be expected for the structure (XII) that the band for the $\text{C}=\text{N}$ group in the IR spectrum would lie in the high-frequency region of $2250\text{-}2260\text{ cm}^{-1}$, and its intensity would be low (leading to complete disappearance) and similar to the intensity in substituted 4-aryl-3-cyano-3,4-dihydro-2(1H)-pyridinethiones [21, 22, 24]. In addition, the signals for the protons of the CHCN and CHAr groups in the PMR spectra of the indicated thiones [21, 22, 24] lie in the regions of ~ 4.20 and 4.40 ppm, respectively, with $^3J = 2.7\text{-}3.2\text{ Hz}$. A similar pattern was to be expected for the structure (XII). However, on the basis of the foregoing the products from the reaction of the pyridinium ylides with α,β -unsaturated nitriles must be assigned the structure of (VI) and not (XII).

On the basis of conformational analysis of compounds (VI, IX) it can be seen that the nucleophilic addition of pyridinium ylides to unsaturated nitriles takes place stereoselectively with the formation of the anti conformers of the Michael adducts. Heterocyclization of the adducts (XI) to the tetrahydropyridin-6-olates also takes place stereoselectively.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 instrument for tablets with potassium bromide. The PMR spectra were obtained on a Bruker WM-250 instrument in DMSO-d₆ with TMS as internal standard. The reactions and the individualities of the obtained compounds were monitored by TLC on Silufol UV-254 plates in the 4:1:1 butanol-acetone-hexane system.

The results from elemental analysis of the compounds for C, H, N, and Hal agree with the calculated data.

6-Hydroxy-4-phenyl-3-cyanopyridin-2(1H)-one (V). A. A mixture of 5 mmole of (Ia), 5 mmole of the unsaturated nitrile (IIIa), and 10 mmole of ammonium acetate in 20 ml of acetic acid was boiled for 3 h and was then poured onto 50 g of ice. The precipitate was filtered off and washed with water, ethanol, and hexane. After recrystallization from acetic acid we obtained 0.45 g (43%) of (V) identical in its physicochemical constants with the pyridone obtained by the method in [25].

B. The pyridone (V) was obtained similarly from (Ib) and (IIIa). The yield was 0.43 g (41%).

C. A mixture of 5 mmole of (VIa) and 8 mmole of ammonium acetate in 15 ml of acetic acid was boiled for 3 h and poured onto 50 g of ice. The precipitate was separated and recrystallized twice from acetic acid. The yield was 0.64 g (60%).

4-Aryl-2-oxo-3-(1-pyridinio)-5-cyano-3,4-trans-1,2,3,4-tetrahydropyridin-6-olates (VIa-f). A. To a mixture of 5 mmole of (Ia) and 5 mmole of the unsaturated nitrile (IIIa-f) in 10-15 ml of ethanol we added 5 mmole of triethylamine in one portion. The boiling solution was quickly filtered through a fluted coarse filter. A precipitate soon separated from the hot solution. After 4-5 h it was filtered off and washed with ethanol and hexane.

B. Compounds (VI) were obtained from the indole (Ib) and the nitriles (IIIa-e) by analogy with method A.

C. A mixture of equimolar amounts of 5 mmole of compounds (Ib, VIIa-f, VIII) and triethylamine in 10-15 ml of ethanol was brought to boiling and quickly filtered through a fluted filter. After 4-5 h the precipitate was separated and washed with ethanol and with hexane.

D. To a boiling suspension of 5 mmole of the adduct (IXa) in 10 ml of ethanol we added 1 ml of a 25% solution of ammonia. The solution was filtered through a fluted filter. After 3 h the precipitate was filtered off and washed with ethanol and hexane.

The compounds (VIa-f) obtained by methods A-D were identical in their melting points and IR spectra (Table 1).

1-Ethoxycarbonyl-1-cyano-2-(2-fluorophenyl)-3-(1-pyridinio)-3-methoxycarbonyl-1-propanide (IX) (C₂₀H₁₉FN₂O₄). To a mixture of 5 mmole of (Ib) and 5 mmole of (IIIId) in 10 ml of ethanol, while stirring, we added 5 mmole of triethylamine. The reaction mixture was stirred at room temperature for 1 h. The precipitate was filtered off and washed with ethanol and hexane. The yield was 1.15 g (62%); mp 72-75°C (decomp.). IR spectrum, ν , cm⁻¹: 1693 (COOC₂H₅), 1730 (COOCH₃), 2165 cm⁻¹ (C≡N). PMR spectrum: 1.16 (3H, t, CH₃CH₂); 4.02 (2H, q, CH₃CH₂, ³J = 7.3 Hz); 3.85 (3H, s, CH₃); 3.95 (1H, d, CH-C₆H₄, ³J = 11.2 Hz, φ = 156°); 5.08 (1H, d, CH-C₅H₅N⁺); 7.24 (4H, m, 2-FC₆H₄); 7.39 (2H, q, 3-H, 5-H of pyridine, ³J₅₄ = 5.6 Hz, ³J₃₄ = 8.0 Hz); 7.80 (1H, t, 4-H of pyridine); 8.60 ppm (2H, d, 2-H,6-H of pyridine).

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STEREOCHEMICAL ASPECTS OF FORMATION OF SUBSTITUTED HYDROGENATED
 3-(1-PYRIDINIO)-6-PYRIDINETHIOLATES AND SYNTHESIS OF 4,6-DIARYL-
 3-CYANO-2(1H)-PYRIDINETHIONES ON THEIR BASIS

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 and V. K. Promonenkov

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 07:541.621.22:543.422.25

Regioselective and stereoselective methods were developed for the synthesis of 2-hydroxy-2,4-diaryl-3-(1-pyridinio)-5-cyano-3,4-trans-1,2,3,4-tetrahydropyridine-6-thiolates on the basis of the reactions of cyanothioacetamide with E-1-styrylpyridinium salts or aromatic aldehydes and 1-phenacylpyridinium bromide. The products exist in the half-chair conformation with the trans-diaxial arrangement of hydrogen atoms 3 and 4. The Michael adducts in the form of the anti conformers with the synclinal arrangement of the reaction centers act as intermediates. The obtained thiolates were converted with high yields into 4,6-diaryl-3-cyano-2(1H)-pyridinethiones.

As a result of the high polarization of the double bond by the pyridinium cation 1-styryl(vinyl)pyridinium salts enter into nucleophilic addition with amines, thiols, and CH acids [1] and also act as highly stereoselective dienophiles [2]. The ability of pyridine salts to undergo fairly ready transformation makes it possible to use them in the synthesis of the difficultly obtainable heterocycles 5-aza-3-oxatricyclo[4.2.1.0^{2,6}]non-7-enes,

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