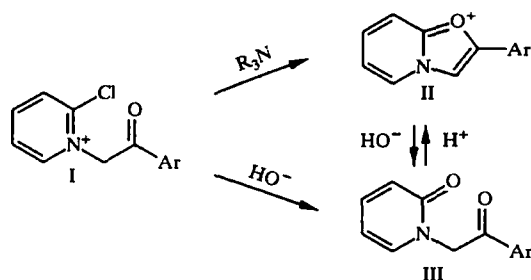


**HETEROCYCLES CONTAINING A BRIDGE  
NITROGEN ATOM. 10.\* UNEXPECTED CLOSURE  
OF OXAZOLE RING DURING THE REACTION  
OF 2-CHLORO-1-PHENACYLPYRIDINIUM SALT  
WITH POTASSIUM CYANATE. CRYSTAL  
STRUCTURE OF 2-(*p*-NITROPHENYL)OXAZOLO-  
[3,2-*a*]PYRIDINIUM BROMIDE AND  
N-(*p*-NITROPHENACYL)PYRID-2-ONE**

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*Reaction of 2-chloro-N-(p-nitrophenacyl)pyridinium bromide with potassium cyanate in acetonitrile produces 2-(p-nitrophenyl)oxazolopyridinium bromide. Performing the same reaction in methanol N-(p-nitrophenacyl)pyrid-2-one was isolated. The structures of the obtained products were proved by X-ray structural data.*

2-Halo-1-phenacylpyridinium (I) salts are useful intermediates in the synthesis of various heterocycles, in particular bridged imidazo[1,2-*a*]pyridines [2], thiazolo[3,2-*a*]pyridines [3], indolizines [4], oxazolylbutadienes [5], and some other systems. A key feature of the reactivity of I salts is the ability to easily replace the halogen atom in the 2 position via nucleophilic substitution. This process can occur not only intermolecularly but also intramolecularly. Thus, under the action of sterically hindered amines the phenacyl group of salts I is enolized and the resulting enol betaines undergo intramolecular cyclization (with displacement of the halogen atom at C<sub>(2)</sub>) into oxazolo[3,2-*a*]pyridinium cations II [6]. Bases transform I salts (as well II salts) into phenacylpyridones III. Pyridones III, in turn, are convenient precursors for the preparation of oxazolopyridinium salts II. The interrelations of compounds I, II, and III are shown in the scheme below.

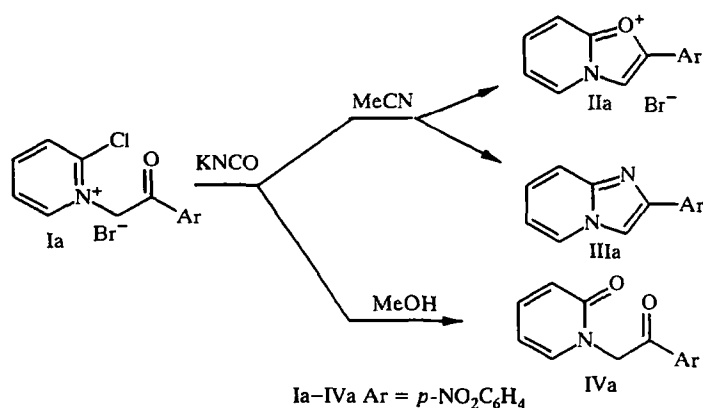


\* For No. 9, see [1].

In continuation of our investigation of the reactivity of I salts with nucleophiles, we studied the reaction of 2-chloro-1-(*p*-nitrophenacyl)pyridinium bromide (Ia) with potassium cyanate. We hypothesized that the ambident cyanate anion might act as a nucleophile by replacing the halogen atom in the pyridinium salt with possible subsequent heterocyclization involving the cyanate and phenacyl groups.

A yellow crystalline compound was isolated from the reaction between Ia salt and KNCO in acetonitrile. According to X-ray structural data, the selected single crystal corresponded to 2-(*p*-nitrophenyl)oxazolo[3,2-*a*]pyridinium bromide (IIa).

The PMR spectrum of the obtained product indeed contained the expected signals for oxazolo[3,2-*a*]pyridinium [7]. Furthermore, the spectrum also contained additional signals for aromatic protons at stronger field (6.8-7.6 ppm). The position and multiplicity of these additional peaks corresponded to a CH=CH-CH=CH moiety, which is typical, for example, of the pyridine moiety of uncharged azolopyridines containing a bridge nitrogen atom. This suggested that a minor neutral impurity was present in the mixture along with IIa bromide. By extraction of the product crystals by ethyl acetate a compound with properties identical to those of 2-(*p*-nitrophenyl)-imidazo[1,2-*a*]pyridine (IIIa) was isolated. According to spectral data, the IIa:IIIa ratio was 5:1. The transformation degree of the initial salt is very high, the yields of compounds IIa and IIIa are 83 and 16%, respectively.



The analogous reaction of Ia with KNCO in methanol produces a single product representing N-(*p*-nitrophenacyl)pyrid-2-one (IVa) according to X-ray structural data.

Figures 1 and 2 show the geometries of molecules IIa and IVa. The atomic coordinates and bond lengths and angles are listed in Tables 1-6. The molecule of IIa (bromide) is a crystal hydrate. The oxazolopyridinium nucleus in molecule of IIa is planar, the phenyl group lying practically in the plane of the heterocycle whereas the twist angle of the nitro group is only 9°. The carbonyl group in phenacylpyridone IVa molecule lies in the plane of the phenyl ring whereas the nitro group is inclined to this plane by 13°. The plane of the phenacyl group is situated practically orthogonal to that of the pyridone moiety.

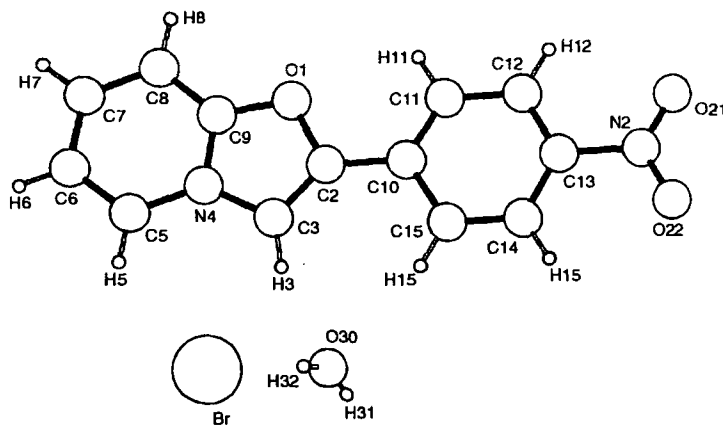


Fig. 1. Structure and numbering of atoms in molecule of compound IIa.

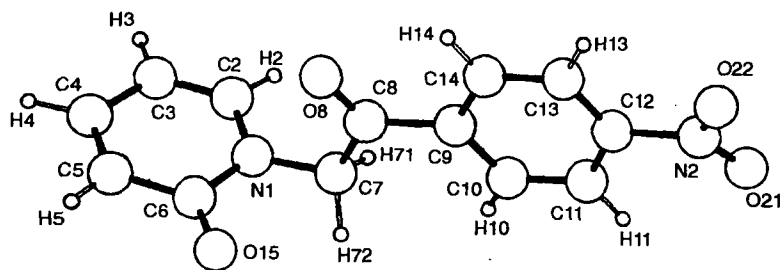


Fig. 2. Structure and numbering of atoms in molecule of compound IVa.

The following feature in the structure of IIa should be noticed. Three resonance structures A, B, and C can be drawn for the condensed cations II:

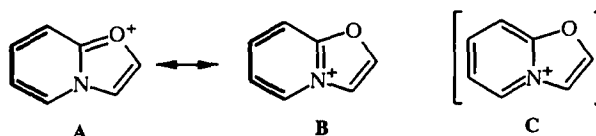


TABLE 1. Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Parameters ( $U_{eq} \times 10^3$ ) in Structure of IIa

Atom	x	y	z	$U_{eq}$
Br	8831(1)	8069(1)	6870(1)	49(1)
O <sub>(1)</sub>	13698(2)	6006(1)	8186(2)	38(1)
C <sub>(2)</sub>	11950(3)	6216(1)	6796(3)	36(1)
C <sub>(3)</sub>	12478(3)	6604(1)	6258(3)	37(1)
N <sub>(4)</sub>	14593(2)	6644(1)	7340(3)	32(1)
C <sub>(5)</sub>	15949(4)	6978(1)	7422(4)	42(1)
C <sub>(6)</sub>	17950(4)	6923(1)	8645(4)	51(1)
C <sub>(7)</sub>	18639(4)	6539(1)	9807(4)	48(1)
C <sub>(8)</sub>	17309(3)	6210(1)	9739(3)	40(1)
C <sub>(9)</sub>	15271(3)	6278(1)	8497(3)	34(1)
C <sub>(10)</sub>	10031(3)	5970(1)	6264(3)	35(1)
C <sub>(11)</sub>	10043(3)	5561(1)	7029(4)	49(1)
C <sub>(12)</sub>	8189(4)	5335(1)	6553(4)	51(1)
C <sub>(13)</sub>	6429(3)	5525(1)	5258(3)	43(1)
C <sub>(14)</sub>	6368(3)	5937(1)	4441(4)	42(1)
C <sub>(15)</sub>	8182(3)	6159(1)	4916(3)	36(1)
N <sub>(2)</sub>	4459(3)	5282(1)	4776(4)	59(1)
O <sub>(21)</sub>	4560(4)	4906(1)	5358(4)	95(1)
O <sub>(22)</sub>	2855(3)	5473(1)	3771(4)	82(1)
O <sub>(30)</sub>	18693(3)	7258(1)	13630(3)	58(1)
H <sub>(3)</sub>	11657(34)	6808(7)	5404(35)	33(6)
H <sub>(5)</sub>	15519(34)	7232(7)	6650(35)	39(7)
H <sub>(6)</sub>	18858(37)	7149(9)	8705(36)	50(7)
H <sub>(7)</sub>	19974(36)	6498(7)	10623(35)	49(7)
H <sub>(8)</sub>	17741(37)	5962(7)	10427(35)	45(7)
H <sub>(11)</sub>	11178(37)	5433(8)	7933(34)	46(7)
H <sub>(12)</sub>	8207(32)	5071(8)	7080(36)	47(7)
H <sub>(14)</sub>	5189(35)	6063(7)	3619(34)	36(6)
H <sub>(15)</sub>	8126(34)	6423(8)	4410(34)	36(6)
H <sub>(31)</sub>	8066(40)	7264(8)	2837(38)	57(8)
H <sub>(32)</sub>	8824(36)	7450(7)	4396(37)	40(7)

TABLE 2. Bond Lengths in Molecule of Compound IIa

Bond	<i>l</i> , Å	Bond	<i>l</i> , Å
O <sub>(1)</sub> -C <sub>(9)</sub>	1,333(3)	C <sub>(8)</sub> -H <sub>(8)</sub>	0,89(2)
O <sub>(1)</sub> -C <sub>(2)</sub>	1,393(2)	C <sub>(10)</sub> -C <sub>(11)</sub>	1,355(3)
C <sub>(2)</sub> -C <sub>(3)</sub>	1,338(3)	C <sub>(10)</sub> -C <sub>(15)</sub>	1,401(3)
C <sub>(2)</sub> -C <sub>(10)</sub>	1,462(3)	C <sub>(11)</sub> -C <sub>(12)</sub>	1,397(4)
C <sub>(3)</sub> -N <sub>(4)</sub>	1,391(3)	C <sub>(11)</sub> -H <sub>(11)</sub>	0,89(2)
C <sub>(3)</sub> -H <sub>(3)</sub>	0,90(2)	C <sub>(12)</sub> -C <sub>(13)</sub>	1,351(3)
N <sub>(4)</sub> -C <sub>(9)</sub>	1,350(3)	C <sub>(12)</sub> -H <sub>(12)</sub>	0,88(2)
N <sub>(4)</sub> -C <sub>(5)</sub>	1,382(3)	C <sub>(13)</sub> -C <sub>(14)</sub>	1,371(4)
C <sub>(5)</sub> -C <sub>(6)</sub>	1,348(3)	C <sub>(13)</sub> -N <sub>(2)</sub>	1,492(3)
C <sub>(5)</sub> -H <sub>(5)</sub>	0,92(2)	C <sub>(14)</sub> -C <sub>(15)</sub>	1,368(3)
C <sub>(6)</sub> -C <sub>(7)</sub>	1,398(4)	C <sub>(14)</sub> -H <sub>(14)</sub>	0,89(2)
C <sub>(6)</sub> -H <sub>(6)</sub>	0,93(3)	C <sub>(15)</sub> -H <sub>(15)</sub>	0,88(2)
C <sub>(7)</sub> -C <sub>(8)</sub>	1,359(4)	N <sub>(2)</sub> -O <sub>(21)</sub>	1,211(3)
C <sub>(7)</sub> -H <sub>(7)</sub>	0,90(2)	N <sub>(2)</sub> -O <sub>(22)</sub>	1,223(3)
C <sub>(8)</sub> -C <sub>(9)</sub>	1,376(3)		

The X-ray structural data of IIa unambiguously indicate that the six-membered bicyclic moiety of II contains a butadiene fragment, i.e., it is "pyridonium" and not "pyridinium." In other words, the resonance structure C is unimportant. Therefore, it is more correct to view the geometry of II as a superposition of the two structures A and B with a distinct alternation of essentially single and essentially double bonds. Thus, "resonance" occurs exclusively between N<sup>+</sup>=C-O and N-C=O<sup>+</sup> fragment of the five-membered ring. A comparison of the bond lengths in the "pyridonium" fragment N-C=C-C=C-O of IIa and pyridone IVa molecules is even more instructive:

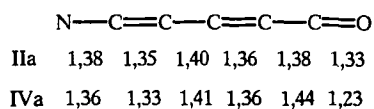


TABLE 3. Bond Angles in Molecule of Compound IIa

Angle	$\omega$ , deg.	Angle	$\omega$ , deg.
C <sub>(9)</sub> -O <sub>(1)</sub> -C <sub>(2)</sub>	106,6(2)	O <sub>(1)</sub> -C <sub>(9)</sub> -C <sub>(8)</sub>	127,5(2)
C <sub>(3)</sub> -C <sub>(2)</sub> -O <sub>(1)</sub>	109,5(2)	N <sub>(4)</sub> -C <sub>(9)</sub> -C <sub>(8)</sub>	122,9(2)
C <sub>(3)</sub> -C <sub>(2)</sub> -C <sub>(10)</sub>	135,4(2)	C <sub>(11)</sub> -C <sub>(10)</sub> -C <sub>(15)</sub>	120,3(2)
O <sub>(1)</sub> -C <sub>(2)</sub> -C <sub>(10)</sub>	115,2(2)	C <sub>(11)</sub> -C <sub>(10)</sub> -C <sub>(2)</sub>	120,4(2)
C <sub>(2)</sub> -C <sub>(3)</sub> -N <sub>(4)</sub>	106,3(2)	C <sub>(15)</sub> -C <sub>(10)</sub> -C <sub>(2)</sub>	119,4(2)
C <sub>(2)</sub> -C <sub>(3)</sub> -H <sub>(3)</sub>	128(2)	C <sub>(10)</sub> -C <sub>(11)</sub> -C <sub>(12)</sub>	119,7(2)
N <sub>(4)</sub> -C <sub>(3)</sub> -H <sub>(3)</sub>	125(2)	C <sub>(10)</sub> -C <sub>(11)</sub> -H <sub>(11)</sub>	123(2)
C <sub>(9)</sub> -N <sub>(4)</sub> -C <sub>(3)</sub>	120,2(2)	C <sub>(12)</sub> -C <sub>(11)</sub> -H <sub>(11)</sub>	117(2)
C <sub>(9)</sub> -N <sub>(4)</sub> -C <sub>(5)</sub>	108,1(2)	C <sub>(13)</sub> -C <sub>(12)</sub> -C <sub>(11)</sub>	118,8(2)
C <sub>(5)</sub> -N <sub>(4)</sub> -C <sub>(3)</sub>	131,7(2)	C <sub>(13)</sub> -C <sub>(12)</sub> -H <sub>(12)</sub>	122,0(14)
C <sub>(6)</sub> -C <sub>(5)</sub> -N <sub>(4)</sub>	118,2(2)	C <sub>(11)</sub> -C <sub>(12)</sub> -H <sub>(12)</sub>	119,2(14)
C <sub>(6)</sub> -C <sub>(5)</sub> -H <sub>(5)</sub>	120,1(14)	C <sub>(12)</sub> -C <sub>(13)</sub> -C <sub>(14)</sub>	122,9(2)
N <sub>(4)</sub> -C <sub>(5)</sub> -H <sub>(5)</sub>	121,7(14)	C <sub>(12)</sub> -C <sub>(13)</sub> -N <sub>(2)</sub>	118,2(2)
C <sub>(5)</sub> -C <sub>(6)</sub> -C <sub>(7)</sub>	121,0(2)	C <sub>(14)</sub> -C <sub>(13)</sub> -N <sub>(2)</sub>	118,9(2)
C <sub>(5)</sub> -C <sub>(6)</sub> -H <sub>(6)</sub>	118,0(14)	C <sub>(15)</sub> -C <sub>(14)</sub> -C <sub>(13)</sub>	118,3(2)
C <sub>(7)</sub> -C <sub>(6)</sub> -H <sub>(6)</sub>	120,9(14)	C <sub>(15)</sub> -C <sub>(14)</sub> -H <sub>(14)</sub>	120(2)
C <sub>(8)</sub> -C <sub>(7)</sub> -C <sub>(6)</sub>	121,0(2)	C <sub>(13)</sub> -C <sub>(14)</sub> -H <sub>(14)</sub>	122(2)
C <sub>(8)</sub> -C <sub>(7)</sub> -H <sub>(7)</sub>	117(2)	C <sub>(14)</sub> -C <sub>(15)</sub> -C <sub>(10)</sub>	120,0(2)
C <sub>(6)</sub> -C <sub>(7)</sub> -H <sub>(7)</sub>	122(2)	C <sub>(14)</sub> -C <sub>(15)</sub> -H <sub>(15)</sub>	117,7(14)
C <sub>(7)</sub> -C <sub>(8)</sub> -C <sub>(9)</sub>	116,7(2)	C <sub>(10)</sub> -C <sub>(15)</sub> -H <sub>(15)</sub>	122,2(14)
C <sub>(7)</sub> -C <sub>(8)</sub> -H <sub>(8)</sub>	122(2)	O <sub>(21)</sub> -N <sub>(2)</sub> -O <sub>(22)</sub>	124,4(2)
C <sub>(9)</sub> -C <sub>(8)</sub> -H <sub>(8)</sub>	122(2)	O <sub>(21)</sub> -N <sub>(2)</sub> -C <sub>(13)</sub>	117,8(2)
O <sub>(1)</sub> -C <sub>(9)</sub> -N <sub>(4)</sub>	109,6(2)	O <sub>(22)</sub> -N <sub>(2)</sub> -C <sub>(13)</sub>	117,8(2)

TABLE 4. Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Parameters ( $U_{eq} \times 10^3$ ) in Structure of IVa

Atom	x	y	z	$U_{eq}$
N <sub>(1)</sub>	-1588(2)	-1158(2)	10214(2)	40(1)
C <sub>(2)</sub>	-3110(3)	-2162(3)	9752(2)	49(1)
C <sub>(3)</sub>	-4458(3)	-2319(3)	10420(2)	54(1)
C <sub>(4)</sub>	-4342(3)	-1405(3)	11616(2)	53(1)
C <sub>(5)</sub>	-2846(3)	-389(3)	12078(2)	52(1)
C <sub>(6)</sub>	-1344(3)	-223(3)	11394(2)	46(1)
C <sub>(7)</sub>	-209(3)	-965(3)	9403(2)	46(1)
C <sub>(8)</sub>	-875(3)	304(2)	8311(2)	40(1)
O <sub>(8)</sub>	-2299(2)	1067(2)	8244(2)	62(1)
C <sub>(9)</sub>	275(3)	542(3)	7279(2)	39(1)
C <sub>(10)</sub>	1963(3)	-278(3)	7351(2)	49(1)
C <sub>(11)</sub>	3008(3)	-31(3)	6412(2)	56(1)
C <sub>(12)</sub>	2319(3)	1089(3)	5386(2)	48(1)
C <sub>(13)</sub>	673(3)	1928(3)	5292(2)	55(1)
C <sub>(14)</sub>	-350(3)	1647(3)	6234(2)	47(1)
N <sub>(2)</sub>	3466(2)	1473(4)	4390(2)	75(1)
O <sub>(21)</sub>	4625(3)	499(4)	4285(2)	123(1)
O <sub>(22)</sub>	3106(3)	2667(3)	3732(2)	82(1)
O <sub>(15)</sub>	70(2)	649(2)	11774(2)	61(1)
H <sub>(2)</sub>	-3133(27)	-2808(28)	8981(21)	50(6)
H <sub>(3)</sub>	-5494(31)	-3112(34)	10143(25)	72(8)
H <sub>(4)</sub>	-5346(24)	-1477(25)	12131(19)	42(5)
H <sub>(5)</sub>	-2652(31)	151(31)	12855(23)	70(8)
H <sub>(71)</sub>	-213(31)	-1868(34)	8867(24)	71(8)
H <sub>(72)</sub>	1159(25)	-739(29)	10116(21)	47(6)
H <sub>(10)</sub>	2365(35)	-1000(38)	8018(25)	92(10)
H <sub>(11)</sub>	4209(29)	-576(30)	6471(22)	60(7)
H <sub>(13)</sub>	217(33)	2696(34)	4560(24)	80(8)
H <sub>(14)</sub>	-1572(34)	2269(37)	6147(27)	90(9)

Clearly the numerical values of the bond lengths in the N–C=C–C fragments of the both molecules are practically identical.

TABLE 5. Bond Lengths in Molecule of IVa

Bond	<i>l</i> , Å	Bond	<i>l</i> , Å
N <sub>(1)</sub> –C <sub>(2)</sub>	1,364(3)	C <sub>(8)</sub> –C <sub>(9)</sub>	1,502(3)
N <sub>(1)</sub> –C <sub>(6)</sub>	1,388(3)	C <sub>(9)</sub> –C <sub>(10)</sub>	1,386(3)
N <sub>(1)</sub> –C <sub>(7)</sub>	1,453(3)	C <sub>(9)</sub> –C <sub>(14)</sub>	1,384(3)
C <sub>(2)</sub> –C <sub>(3)</sub>	1,328(3)	C <sub>(10)</sub> –C <sub>(11)</sub>	1,370(3)
C <sub>(2)</sub> –H <sub>(2)</sub>	0,94(2)	C <sub>(10)</sub> –H <sub>(10)</sub>	0,89(3)
C <sub>(3)</sub> –C <sub>(4)</sub>	1,405(3)	C <sub>(11)</sub> –C <sub>(12)</sub>	1,386(3)
C <sub>(3)</sub> –H <sub>(3)</sub>	0,99(3)	C <sub>(11)</sub> –H <sub>(11)</sub>	0,97(2)
C <sub>(4)</sub> –C <sub>(5)</sub>	1,357(3)	C <sub>(12)</sub> –C <sub>(13)</sub>	1,365(3)
C <sub>(4)</sub> –H <sub>(4)</sub>	1,00(2)	C <sub>(12)</sub> –N <sub>(2)</sub>	1,495(3)
C <sub>(5)</sub> –C <sub>(6)</sub>	1,436(3)	C <sub>(13)</sub> –C <sub>(14)</sub>	1,365(3)
C <sub>(5)</sub> –H <sub>(5)</sub>	0,87(2)	C <sub>(13)</sub> –H <sub>(13)</sub>	0,97(3)
C <sub>(6)</sub> –O <sub>(15)</sub>	1,230(3)	C <sub>(14)</sub> –H <sub>(14)</sub>	1,01(3)
C <sub>(7)</sub> –C <sub>(8)</sub>	1,519(3)	N <sub>(2)</sub> –O <sub>(22)</sub>	1,217(4)
C <sub>(7)</sub> –H <sub>(71)</sub>	0,95(3)	N <sub>(2)</sub> –O <sub>(21)</sub>	1,216(4)
C <sub>(7)</sub> –H <sub>(72)</sub>	1,03(2)	C <sub>(8)</sub> –O <sub>(8)</sub>	1,202(3)

TABLE 6. Bond Angles in Molecule of IVa

Angle	$\omega$ , deg.	Angle	$\omega$ , deg.
C(2)-N(1)-C(6)	122,9(2)	O(8)-C(8)-C(9)	120,8(2)
C(2)-N(1)-C(7)	119,7(2)	O(8)-C(8)-C(7)	121,6(2)
C(6)-N(1)-C(7)	117,2(2)	C(9)-C(8)-C(7)	117,6(2)
C(3)-C(2)-N(1)	121,7(2)	C(10)-C(9)-C(14)	118,6(2)
C(3)-C(2)-H(2)	119,9(13)	C(10)-C(9)-C(8)	122,6(2)
C(3)-C(4)-H(4)	121,4(11)	C(12)-C(11)-H(11)	120,2(14)
N(1)-C(2)-H(2)	118,2(13)	C(14)-C(9)-C(8)	118,8(2)
C(2)-C(3)-C(4)	119,3(2)	C(11)-C(10)-C(9)	121,8(2)
C(2)-C(3)-H(3)	122,2(2)	C(11)-C(10)-H(10)	119(2)
C(4)-C(3)-H(3)	119(2)	C(9)-C(10)-H(10)	119(2)
C(5)-C(4)-C(3)	119,6(2)	C(10)-C(11)-C(12)	117,3(2)
C(5)-C(4)-H(4)	119,0(11)	C(10)-C(11)-H(11)	122,5(14)
C(4)-C(5)-C(6)	122(2)	C(13)-C(12)-C(11)	122,5(2)
C(4)-C(5)-H(5)	123(2)	C(13)-C(12)-N(2)	117,8(2)
C(6)-C(5)-H(5)	115(2)	C(11)-C(12)-N(2)	119,6(2)
O(15)-C(6)-N(1)	120,2(2)	C(12)-C(13)-C(14)	119,0(2)
O(15)-C(6)-C(5)	125,5(2)	C(12)-C(13)-H(13)	121(2)
N(1)-C(6)-C(5)	114,3(2)	C(14)-C(13)-H(13)	120(2)
N(1)-C(7)-C(8)	110,9(2)	C(13)-C(14)-C(9)	120,8(2)
N(1)-C(7)-H(71)	109(2)	C(13)-C(14)-H(14)	118(2)
C(8)-C(7)-H(71)	106(2)	C(9)-C(14)-H(14)	121(2)
N(1)-C(7)-H(72)	107,9(12)	O(22)-N(2)-O(21)	126,7(2)
C(8)-C(7)-H(72)	111,4(14)	O(22)-N(2)-C(12)	118,3(2)
H(71)-C(7)-H(72)	112(2)	O(21)-N(2)-C(12)	114,8(3)

The mechanism of the somewhat unexpected cyclization of pyridine Ia into compound IIa and IIIa under the action of KNCO can be explained by supposition that a strong base is present (or appears) in the reaction mixture causing the I→II conversion *via* intramolecular cyclization of the enol betaine. Cyanate itself is clearly not sufficiently basic ( $pK_b = 10.1$ ) to deprotonate the phenacyl group of Ia salt. (It has been demonstrated that such reaction occurs only with highly basic amines [2].) Traces of moisture most likely lead to formation of an unstable carbamate, a strong base and source of ammonia. This leads to formation of both oxazolopyridinium IIa and imidazopyridine IIIa. The formation of compounds IIa and IIIa *via* nucleophilic attack of the ambident cyanate ion with replacement of chlorine atom in the 2-position is less likely. In this instance the cyclization mechanism of the formed ionic intermediates into IIa and IIIa molecules is not obvious. In the future, we intend to elucidate this problem in detail.

## EXPERIMENTAL

**Reaction of 2-Chloro-1-phenacylpyridinium Bromide Ia with Potassium Cyanate.** Suspension of Ia salt (0.4 g, 1.1 mmol) in acetonitrile (5 ml) is treated with ground potassium cyanate (0.17 g, 2.1 mmol) and heated for 12 h. The solid formed (0.43 g) is filtered off, recrystallized from ethanol, and used for recording the PMR spectrum and for the X-ray structural study. PMR spectrum (400 MHz, DMSO- $d_6$ ): cation IIa 9.80 (1H, s, 3-H), 9.41 (1H, d, 5-H,  $J = 7$  Hz), 8.40 (4H, m, *p*-NO<sub>2</sub>Ph), 8.02 (1H, dd, 6-H), IIIa 8.22 (4H, m, *p*-NO<sub>2</sub>Ph), 7.54 (1H, d, 8-H,  $J = 9$  Hz), 7.24 (1H, dd, 7-H,  $J = 7$  Hz), 6.87 (1H, dd, 6-H,  $J = 7$  Hz), signals from both molecules overlap in the 8.50-8.65 ppm region.

The compound isolated by filtration after boiling crystals in ethyl acetate and evaporating the solvent has properties identical to those (mp, chromatographic behavior) of 2-(*p*-nitrophenyl)imidazo[1,2-*a*]pyridine (IIIa).

If the reaction of Ia with KNCO (with the same ratio of reagents) is carried out in methanol, N-(*p*-nitrophenacyl)pyrid-2-one (IVa) is isolated in 40% yield.

**X-ray Structural Studies of Compound IIa** were performed on a CAD-4 automated single-crystal diffractometer [8] using  $\lambda$  MoK $\alpha$ -radiation. The unit cell parameters were determined and refined in the range of 14–16°  $\theta$  using 25 reflections and a crystal of dimensions 0.4×0.4×0.3 mm. The crystals belong to the monoclinic syngony (space group *Cc*) with parameters  $a = 7.034(3)$ ,  $b = 30.492(9)$ ,  $c = 6.938(4)$  Å;  $\beta = 112.50(4)^\circ$ ;  $V = 1374.8(10)$  Å<sup>3</sup>; and  $Z = 4$ . The structure was solved by direct methods using the SHELXS-97 programs [9] and 3729 reflections in the range of  $\theta = 1$ –28° and was refined by anisotropic full-matrix least-squares methods for the nonhydrogen atoms using the SHELXL-97 programs [10]. The coordinates of the hydrogen atoms were localized in a difference Fourier electron-density synthesis and were refined in isotropic approximation. The final *R*-factor was 0.0547 for 3320 independent reflections with  $I > 2\sigma(I)$ .

Table 1 contains the atomic coordinates and the isotropic thermal parameters equivalent to the corresponding anisotropic ones. Tables 2 and 3 list the interatomic distances and angles. Figure 1 shows the arrangement of the atoms and their numbering [11].

**X-ray Structural Studies of Compound IVa** were performed on a CAD-4 automated single-crystal diffractometer [8] using  $\lambda$  MoK $\alpha$ -radiation. The unit cell parameters were determined and refined in the range of 14–16°  $\theta$  using 25 reflections and a crystal of dimensions 0.5×0.3×0.3 mm. The crystals belong to the monoclinic syngony (space group *P2<sub>1</sub>*) with parameters  $a = 7.133(2)$ ,  $b = 8.778(10)$ ,  $c = 9.8333(12)$  Å;  $\beta = 107.87(1)^\circ$ ;  $V = 586.0(7)$  Å<sup>3</sup>;  $Z = 2$ . The structure was refined by direct methods using the SHELXS-97 programs [9] and 1188 reflections in the range of  $\theta = 2$ –27° and was refined by anisotropic full-matrix least-squares methods for the nonhydrogen atoms using the SHELXL-97 programs [10]. The coordinates of the hydrogen atoms were found in a difference Fourier electron-density synthesis and were refined isotropically. The final *R*-factor was 0.0525 for 1121 independent reflections with  $I > 2\sigma(I)$ .

Table 4 contains the atomic coordinates and the isotropic thermal parameters equivalent to the anisotropic ones. Tables 5 and 6 list the interatomic distances and angles. Figure 2 shows the arrangement of atoms and their numbering [11].

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