

UNEXPECTED RING OPENING OF OXAZOLO[3,2-a]PYRIDINIUM CATION IN REACTION WITH MeONa. CRYSTAL STRUCTURE OF 2-PHENYLOXAZOLO[3,2-a]PYRIDINIUM PERCHLORATE AND 1-[1,1-DIMETHOXY-1-PHENYLETHYL-2]-2-PYRIDONE

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Dedicated to the late Professor Gerrit L'abbé

ABSTRACT

Selectivity of ring opening reactions of the oxazolo[3,2-a]pyridinium cation in reactions with nucleophiles (cleavage of either C₃-N bond or C_{8a}-O bond) is reviewed, and the novel direction of ring opening (cleavage of C₂-O bond) is discovered. 2-Phenyloxazolo[3,2-a]pyridinium perchlorate in reaction with MeONa is transformed to 1-[1,1-dimethoxy-1-phenylethyl-2]-2-pyridone. Crystal structures of the final ketal and the starting material are reported, and the clear alternation of length of C-C bonds in both molecules is observed.

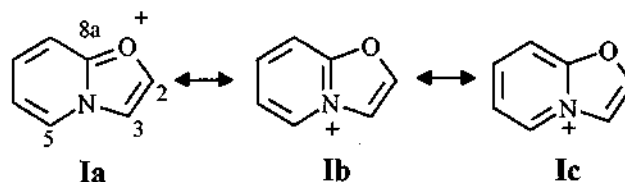
Keywords: Oxazolo[3,2-a]pyridinium perchlorate, ambident properties, ring opening, synthesis of ketals, 1-[1,1-dimethoxyethyl-1-phenyl-2]pyridone-2.

INTRODUCTION

The structure and reactivity of the aromatic system of oxazolo[3,2-a]pyridinium cation I (first obtained long ago [1]) is still poorly investigated. There may be few resonance structures (Ia-c, Scheme 1) for the cation I, and it

is still unclear whether the 6-membered ring follows a delocalized pattern (as in the pyridinium salts) or the double bonds are localized (as in the pyridone-2). There are still no experimental data on the geometry of this cation.

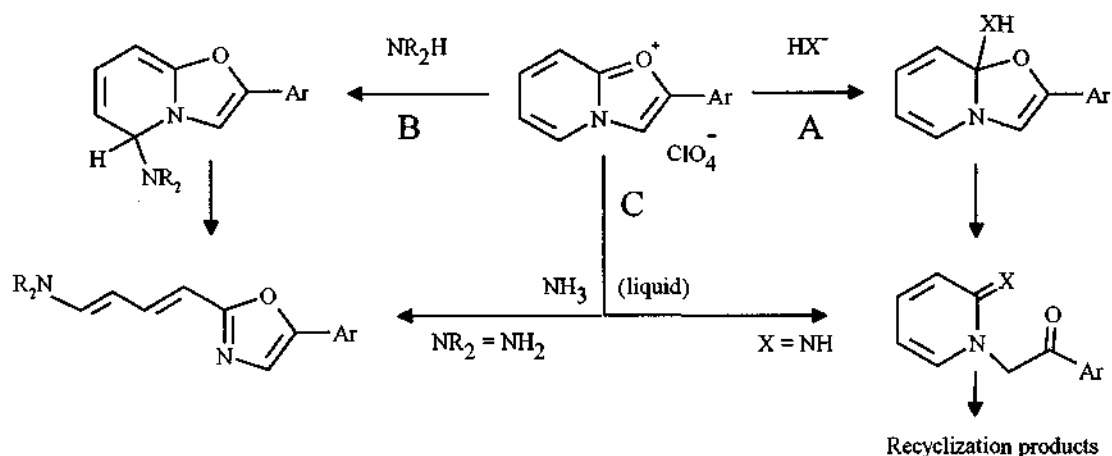
Scheme 1.



Another specific problem is related to the reactivity of the cation I toward nucleophiles. As it was considered for a long time, the nucleophiles may attack only the bridgehead carbon atom C_{8a}, causing ring opening of the oxazole fragment. Thus, in reaction with alkali [2], primary amines [3], some P- and As-nucleophiles [4], sodium hydrosulfide [5], and carbanions [6,7] only the cleavage of 5-membered ring of bicycle I was observed, and the products may undergo further

recyclizations, Scheme 2, A. However, as we proved very recently [8], the action of secondary amines causes cleavage of the pyridinium fragment of the cation I, Scheme 2, B. Finally, in the reaction of the cation I with NH₃ [5] (namely, if liquid ammonia was used as the reaction media) the mixture of two products was obtained (Scheme 2, C), confirming that both possibilities of 5- and 6-membered rings cleavage can be realized

Scheme 2. Overview of known ring opening reactions for derivatives of the cation I.



simultaneously. Therefore, the cation I should be regarded as an ambident system toward nucleophilic attack with the possibility of cleavage either of the C_{8a}-O bond (opening of the oxazolium fragment) or the C₅-N₄ bond (opening of the pyridinium fragment). Both bonds broken in this reaction are adjacent to either of two bridgehead atoms, C_{8a} or N.

In the present communication we discover the third, quite unexpected, possibility of ring opening for the cation I, namely the example of cleavage of the C₂-O bond (that is not adjacent to a bridgehead atom). We also report the crystal structures of the product and of the starting material — 2-phenyloxazolo[3,2-a]pyridinium perchlorate.

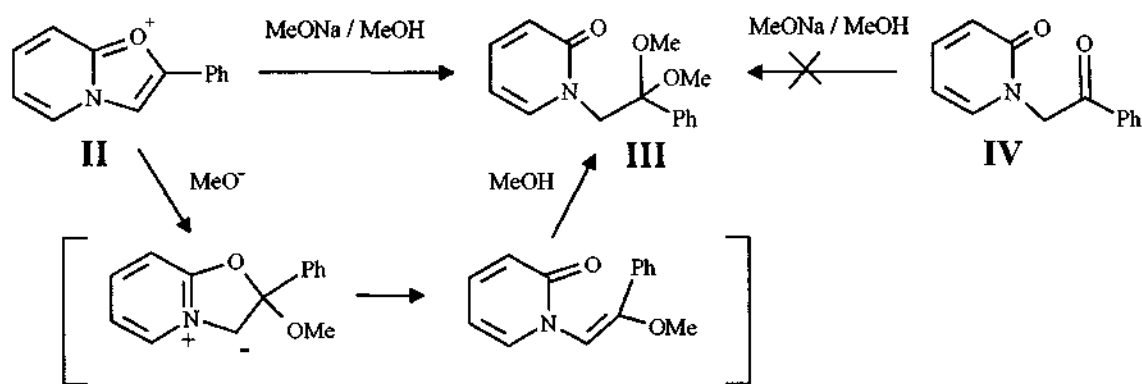
We found that 2-phenyloxazolo[3,2-a]pyridinium perchlorate (II) in reaction with MeONa in methanol is almost quantitatively transformed to 1-[1,1-dimethoxy-1-phenylethyl-2]pyridone-2 (III), Scheme 3.

Mass spectral and elemental analysis data for the product III confirm its molecular formula to be a formal adduct of two MeO-groups to the cation II. In the ¹H and ¹³C NMR spectra the signals in the aromatic region correspond to the fragments of pyridone-2 and phenyl group, and the signals of two equivalent methoxy groups and of CH₂-group appear in the region expected for ketals.

The result should be regarded as the first example of cleavage of the C₂-O bond in the cation I

RESULT AND DISCUSSION

Scheme 3.



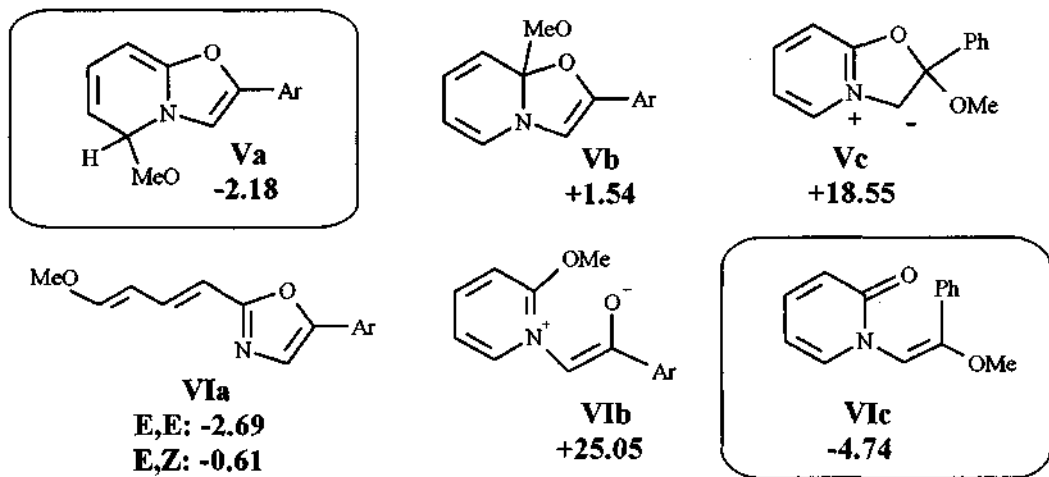
(possible intermediates are shown in brackets in Scheme 3). The hypothesis that ring opening occurs via an alternative way should be rejected. Thus, if one assumes that the initial nucleophilic attack occurs at the bridgehead position C_{8a} , the intermediate formation of 1-phenacyl-pyridone-2 (IV) would be expected. (Dealkylation of N-alkyl-2-methoxypyridinium salts to N-alkylpyridones-2 is well known [1].) However, even after prolonged keeping in the reaction conditions (MeONa/MeOH) the pyridone IV was not transformed to the ketal III.

In order to understand the abnormal direction of cleavage of the C_2 -O bond in the cation II we performed semiempirical quantum-chemical MNDO calculations of the isomeric intermediates of ring opening. The energy of isomeric adducts Va-c (between cation II and MeO-anion) and possible isomeric products of ring cleavage VIa-c are presented in Scheme 4. As it is evident, the formation of the C_5 adduct Va is the most favorable from thermodynamical viewpoint. (By contrast, the zwitter-ionic intermediate Vc has the highest energy.) However, the process of the nucleophilic addition may be reversible. In turn, the cleavage of

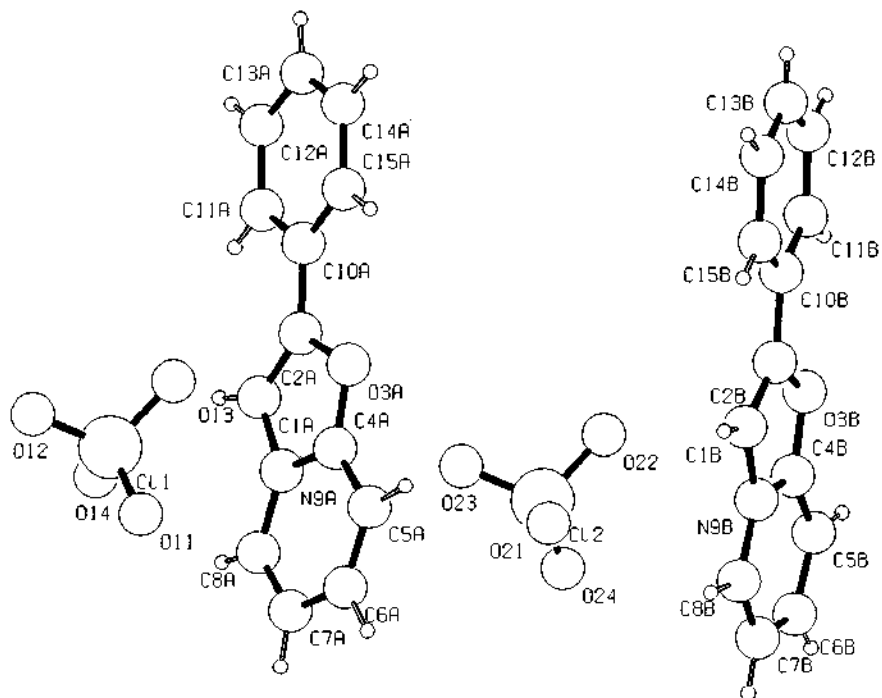
the C_2 -O bond results in the most stable product of reaction VIc, that is the evident precursor of the experimentally observed ketal III. Therefore, the experimentally observed ring opening (II to III involving intermediate VIc) may be treated in terms of the thermodynamically controlled reaction, whereas in the other ring opening reactions (Scheme 2) the kinetic control may play an important role.

X-ray data completely confirm the ketal structure assigned to the product III. In Schemes 5,6 the crystal structures of the starting material II and the product III are presented. The observed geometry of the molecule II provides a clear answer to the question, which of resonance structures (Ia-c) would better represent the structure of the cation I. With evidence, there is pronounced alternation of bonds' length along the six-membered fragment in the structure II, so that it closely resembles a butadiene-like pattern in the pyridone III (cf. Tables 1 - 4). Therefore, the contribution of the structure Ic may be neglected, and the geometry of the cation I would be better regarded as the superimposition of the oxazolium ring and butadiene fragment (contribution of the structures Ia and Ib).

Scheme 4. Energy (MNDO, kcal/mol) of the isomeric adducts Va-c of the cation II and MeO-anion and of the ring opening products VIa-c. The most stable intermediates are Va and VIc.



Scheme 5. View of the molecule II and atom numbering [10]



Scheme 6. View of the molecule III and atom numbering [10].

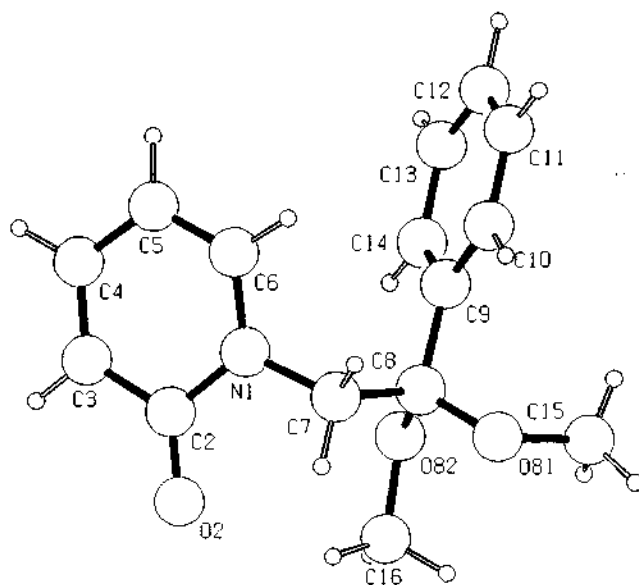


Table 1. Structure of the molecule II. Atomic coordinates ($\times 10^4$) and equivalent temperature factors U_{eq} ($\text{\AA}^2 \times 10^3$) defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	X	Y	Z	U_{eq}
Cl(1)	3939(2)	514(1)	3020(1)	42(1)
Cl(2)	8872(2)	5607(1)	3208(1)	50(1)
O(11)	2177(7)	1121(3)	3677(2)	92(2)
O(12)	3406(7)	-511(3)	2744(3)	77(1)
O(13)	4057(6)	801(3)	2280(2)	63(1)
O(14)	6158(6)	647(3)	3348(2)	64(1)
O(21)	6392(7)	5668(3)	3431(3)	84(1)
O(22)	9319(7)	5900(3)	2479(3)	86(1)
O(23)	9613(8)	4603(3)	2933(3)	104(2)
O(24)	9890(10)	6270(4)	3911(3)	131(2)
C(1A)	9410(8)	2081(3)	2403(3)	37(1)
C(1B)	3912(9)	-2962(4)	2251(3)	42(1)
C(2A)	8569(7)	2101(3)	1697(3)	32(1)
C(2B)	5269(7)	-2947(3)	1559(3)	36(1)
O(3A)	6456(5)	2669(2)	1964(2)	38(1)
O(3B)	7169(5)	-2366(2)	1850(2)	42(1)
C(4A)	6069(8)	2986(3)	2842(3)	37(1)
C(4B)	6878(8)	-2027(3)	2730(3)	39(1)
C(5A)	4232(9)	3580(3)	3405(3)	46(1)
C(5B)	8270(11)	-1405(4)	3313(4)	56(2)
C(6A)	4307(10)	3797(4)	4273(3)	52(1)
C(6B)	7520(13)	-1174(5)	4179(4)	67(2)
C(7A)	6124(10)	3456(4)	4580(4)	54(1)
C(7B)	5465(12)	-1535(4)	4449(4)	65(2)
C(8A)	7921(10)	2883(4)	4007(3)	47(1)
C(8B)	4163(11)	-2129(4)	3863(4)	57(2)
N(9A)	7846(6)	2647(2)	3131(2)	36(1)
N(9B)	4894(6)	-2377(3)	2996(2)	39(1)
C(10A)	9346(7)	1662(3)	764(3)	31(1)
C(10B)	5168(8)	-3401(3)	617(3)	35(1)
C(11A)	11540(8)	1157(3)	462(3)	39(1)
C(11B)	7018(9)	-3359(4)	21(3)	42(1)
C(12A)	12257(9)	704(3)	-416(3)	44(1)
C(12B)	6901(10)	-3827(4)	-868(3)	49(1)
C(13A)	10833(9)	748(3)	-1015(3)	44(1)
C(13B)	4958(11)	-4330(4)	-1160(4)	53(2)
C(14A)	8691(10)	1243(4)	-735(3)	44(1)
C(14B)	3080(10)	-4370(4)	-580(4)	49(1)
C(15A)	7953(9)	1701(3)	153(3)	39(1)
C(15B)	3193(9)	-3905(3)	308(3)	44(1)
H(1A)	684(80)	1734(33)	2450(28)	52(14)
H(1B)	2724(80)	-3220(33)	2306(29)	43(15)
H(5A)	3049(72)	3772(29)	3150(25)	33(12)
H(5B)	9452(85)	-1163(35)	3084(30)	51(16)
H(6A)	3189(84)	4216(34)	4700(31)	56(15)
H(6B)	8250(116)	-768(48)	4523(42)	102(25)
H(7A)	6178(80)	3677(33)	5173(31)	52(14)
H(7B)	5038(74)	-1338(31)	5031(30)	41(13)
H(8A)	9211(92)	2629(38)	4150(32)	70(18)
H(8B)	7120(79)	2422(33)	5998(28)	43(14)
H(11A)	2372(84)	1129(34)	882(31)	57(16)
H(11B)	8193(78)	-3000(32)	216(28)	43(14)
H(12A)	13738(84)	348(34)	-608(29)	57(15)
H(12B)	11910(70)	3792(28)	1256(26)	30(11)
H(13A)	11280(68)	448(29)	-1570(27)	29(11)
H(13B)	4832(83)	-4609(34)	-1671(30)	48(16)
H(14A)	7837(80)	1295(33)	-1107(30)	48(15)
H(14B)	1716(84)	-4715(34)	-801(30)	55(15)
H(15A)	6627(69)	2021(28)	328(24)	21(11)
H(15B)	2038(81)	-3931(33)	699(29)	48(15)

Bond lengths [Å] and angles [deg].

Cl(1)-O(12)	1.418(4)
Cl(1)-O(11)	1.418(4)
Cl(1)-O(14)	1.431(3)
Cl(1)-O(13)	1.433(3)
Cl(2)-O(24)	1.386(4)
Cl(2)-O(23)	1.397(4)
Cl(2)-O(22)	1.426(4)
Cl(2)-O(21)	1.428(4)
C(1A)-C(2A)	1.330(6)
C(1A)-N(9A)	1.392(5)
C(1B)-C(2B)	1.319(6)
C(1B)-N(9B)	1.387(6)
C(1B)-H(1B)	0.79(4)
C(2A)-O(3A)	1.399(5)
C(2A)-C(10A)	1.445(6)
C(2B)-O(3B)	1.393(5)
C(2B)-C(10B)	1.455(6)
O(3A)-C(4A)	1.340(5)
O(3B)-C(4B)	1.341(5)
C(4A)-N(9A)	1.348(5)
C(4A)-C(5A)	1.378(6)
C(4B)-N(9B)	1.344(5)
C(4B)-C(5B)	1.377(7)
C(5A)-C(6A)	1.357(7)
C(5A)-H(5A)	0.94(4)
C(5B)-C(6B)	1.362(8)
C(5B)-H(5B)	0.88(5)
C(6A)-C(7A)	1.386(7)
C(6A)-H(6A)	0.92(5)
C(6B)-C(7B)	1.388(9)
C(6B)-H(6B)	0.80(6)
C(7A)-C(8A)	1.356(7)
C(7A)-H(7A)	0.92(5)
C(7B)-C(8B)	1.331(8)
C(7B)-H(7B)	0.90(4)
C(8A)-N(9A)	1.367(6)
C(8A)-H(8A)	0.92(5)
C(8B)-N(9B)	1.357(6)
C(10A)-C(15A)	1.382(6)
C(10A)-C(11A)	1.402(6)
C(10B)-C(15B)	1.385(6)
C(10B)-C(11B)	1.389(6)
C(11A)-C(12A)	1.362(6)
C(11B)-C(12B)	1.377(7)
C(11B)-H(11B)	0.87(4)
C(12A)-C(13A)	1.379(7)
C(12A)-H(12A)	0.95(5)
C(12B)-C(13B)	1.367(7)
C(13A)-C(14A)	1.369(7)
C(13A)-H(13A)	0.86(4)
C(13B)-C(14B)	1.379(7)
C(13B)-H(13B)	0.80(4)
C(14A)-C(15A)	1.379(6)
C(14A)-H(14A)	0.86(4)
C(14B)-C(15B)	1.375(7)
C(14B)-H(14B)	0.96(5)
C(15A)-H(15A)	0.86(4)
C(15B)-H(15B)	0.89(4)
O(12)-Cl(1)-O(11)	110.6(3)
O(12)-Cl(1)-O(14)	109.0(2)
O(11)-Cl(1)-O(14)	110.4(2)
O(12)-Cl(1)-O(13)	108.9(2)
O(11)-Cl(1)-O(13)	108.7(2)
O(14)-Cl(1)-O(13)	109.3(2)

Table 2. Structure of the molecule II.

O(24)-C(2)-O(23)	115.4(4)
O(24)-C(2)-O(22)	109.2(3)
O(23)-C(2)-O(22)	108.3(3)
O(24)-C(2)-O(21)	109.5(3)
O(23)-C(2)-O(21)	107.6(3)
O(22)-C(2)-O(21)	106.6(3)
C(2A)-C(1A)-N(9A)	107.1(4)
C(2B)-C(1B)-N(9B)	107.9(4)
C(2B)-C(1B)-H(1B)	133(3)
N(9B)-C(1B)-H(1B)	119(3)
C(1A)-C(2A)-O(3A)	108.8(4)
C(1A)-C(2A)-C(10A)	134.0(4)
O(3A)-C(2A)-C(10A)	117.2(4)
C(1B)-C(2B)-O(3B)	108.4(4)
C(1B)-C(2B)-C(10B)	133.8(4)
O(3B)-C(2B)-C(10B)	117.7(4)
C(4A)-O(3A)-C(2A)	107.0(3)
C(4B)-O(3B)-C(2B)	107.0(3)
O(3A)-C(4A)-N(9A)	109.1(4)
O(3A)-C(4A)-C(5A)	128.5(4)
N(9A)-C(4A)-C(5A)	122.4(4)
O(3B)-C(4B)-N(9B)	109.1(4)
O(3B)-C(4B)-C(5B)	128.6(5)
N(9B)-C(4B)-C(5B)	122.3(5)
C(6A)-C(5A)-C(4A)	115.8(5)
C(6A)-C(5A)-H(5A)	127(3)
C(4A)-C(5A)-H(5A)	117(3)
C(6B)-C(5B)-C(4B)	115.6(6)
C(6B)-C(5B)-H(5B)	128(3)
C(4B)-C(5B)-H(5B)	116(3)
C(5A)-C(6A)-C(7A)	122.5(5)
C(5A)-C(6A)-H(6A)	122(3)
C(7A)-C(6A)-H(6A)	116(3)
C(5B)-C(6B)-C(7B)	121.7(6)
C(5B)-C(6B)-H(6B)	116(5)
C(7B)-C(6B)-H(6B)	122(5)
C(8A)-C(7A)-C(6A)	120.1(5)
C(8A)-C(7A)-H(7A)	120(3)
C(6A)-C(7A)-H(7A)	119(3)
C(8B)-C(7B)-C(6B)	120.6(6)
C(8B)-C(7B)-H(7B)	122(3)
C(6B)-C(7B)-H(7B)	117(3)
C(7A)-C(8A)-N(9A)	117.9(5)
C(7A)-C(8A)-H(8A)	126(3)
N(9A)-C(8A)-H(8A)	116(3)
C(7B)-C(8B)-N(9B)	118.5(6)
C(4A)-N(9A)-C(8A)	121.3(4)
C(4A)-N(9A)-C(1A)	108.1(4)
C(8A)-N(9A)-C(1A)	130.6(4)
C(4B)-N(9B)-C(8B)	121.1(4)
C(4B)-N(9B)-C(1B)	107.5(4)
C(8B)-N(9B)-C(1B)	131.3(4)
C(15A)-C(10A)-C(11A)	118.6(4)
C(15A)-C(10A)-C(2A)	121.7(4)
C(11A)-C(10A)-C(2A)	119.7(4)
C(11B)-C(10B)-C(15B)	119.4(4)
C(11B)-C(10B)-C(2B)	121.4(4)
C(15B)-C(10B)-C(2B)	119.2(4)
C(12A)-C(11A)-C(10A)	120.4(5)
C(12B)-C(11B)-C(10B)	119.9(5)
C(12B)-C(11B)-H(11B)	121(3)
C(10B)-C(11B)-H(11B)	119(3)
C(11A)-C(12A)-C(13A)	120.1(5)
C(11A)-C(12A)-H(12A)	119(3)
C(13A)-C(12A)-H(12A)	121(3)
C(13B)-C(12B)-C(11B)	119.9(5)
C(14A)-C(13A)-C(12A)	120.5(5)
C(14A)-C(13A)-H(13A)	120(3)
C(12A)-C(13A)-H(13A)	120(3)
C(12B)-C(13B)-C(14B)	121.2(5)
C(12B)-C(13B)-H(13B)	123(4)

C(14B)-C(13B)-H(13B)	116(4)
C(13A)-C(14A)-C(15A)	119.7(5)
C(13A)-C(14A)-H(14A)	120(3)
C(15A)-C(14A)-H(14A)	120(3)
C(15B)-C(14B)-C(13B)	119.0(5)
C(15B)-C(14B)-H(14B)	121(3)
C(13B)-C(14B)-H(14B)	120(3)
C(14A)-C(15A)-C(10A)	120.7(5)
C(14A)-C(15A)-H(15A)	120(3)
C(10A)-C(15A)-H(15A)	120(3)
C(14B)-C(15B)-C(10B)	120.5(5)
C(14B)-C(15B)-H(15B)	122(3)
C(10B)-C(15B)-H(15B)	118(3)

Table 3. Structure of the molecule III. Atomic coordinates ($\times 10^4$) and equivalent temperature factors U_{eq} ($\text{\AA}^2 \times 10^3$) defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	X	Y	Z	U_{eq}
N(1)	5965(2)	3203(2)	7188(1)	38(1)
C(2)	6664(2)	2304(2)	6649(2)	44(1)
O(2)	7745(2)	1612(2)	6960(1)	59(1)
C(3)	6038(3)	2286(3)	5742(2)	56(1)
C(4)	4925(3)	3124(3)	5427(2)	65(1)
C(5)	4336(3)	4066(3)	5989(2)	61(1)
C(6)	4868(3)	4082(3)	6847(2)	48(1)
C(7)	6468(2)	3268(2)	8139(1)	37(1)
C(8)	5405(2)	2521(2)	8721(1)	34(1)
O(81)	6129(2)	2745(2)	9585(1)	42(1)
O(82)	5268(2)	1159(1)	8521(1)	41(1)
C(9)	3795(2)	3085(2)	8616(1)	33(1)
C(10)	3531(3)	4343(2)	8948(2)	43(1)
C(11)	2097(3)	4910(3)	8834(2)	52(1)
C(12)	913(3)	4229(3)	8377(2)	56(1)
C(13)	1162(3)	2988(3)	8044(2)	53(1)
C(14)	2596(2)	2410(2)	8164(2)	42(1)
C(15)	5369(4)	2165(3)	10286(2)	56(1)
C(16)	6618(3)	372(3)	8674(2)	54(1)
H(3)	6497(29)	1644(25)	5373(17)	66(8)
H(4)	4526(31)	3091(28)	4793(20)	85(9)
H(5)	3526(30)	4708(28)	5809(17)	75(8)
H(6)	4518(26)	4717(24)	7270(16)	57(7)
H(71)	6536(20)	4211(22)	8314(12)	34(5)
H(72)	7494(23)	2873(20)	8219(13)	36(5)
H(10)	4379(27)	4805(24)	9269(16)	60(7)
H(11)	1914(26)	5761(27)	9063(16)	61(7)
H(12)	-96(30)	4638(26)	8302(17)	73(8)
H(13)	363(28)	2510(26)	7700(17)	69(8)
H(14)	2804(23)	1567(22)	7915(13)	40(6)
H(151)	4460(34)	2564(31)	10326(20)	85(10)
H(152)	6062(36)	2283(32)	10847(23)	102(11)
H(153)	5254(40)	1193(39)	10228(23)	121(13)
H(161)	6296(27)	-513(30)	8477(16)	68(8)
H(162)	6962(31)	301(29)	9315(21)	88(10)
H(163)	7420(32)	693(30)	8342(19)	84(9)

Table 4. Structure of the molecule III. Bond lengths [Å] and angles [deg].

N(1)-C(6)	1.373(3)
O(82)-C(16)	1.428(3)
N(1)-C(2)	1.398(3)
C(9)-C(14)	1.382(3)
N(1)-C(7)	1.469(3)
C(9)-C(10)	1.387(3)
C(2)-O(2)	1.236(3)
C(10)-C(11)	1.382(3)
C(2)-C(3)	1.433(3)
C(10)-H(10)	0.97(2)
C(3)-C(4)	1.345(4)
C(11)-C(12)	1.379(3)
C(3)-H(3)	0.97(3)
C(11)-H(11)	0.94(3)
C(4)-C(5)	1.403(4)
C(12)-C(13)	1.370(4)
C(4)-H(4)	0.99(3)
C(12)-H(12)	0.98(3)
C(5)-C(6)	1.342(3)
C(13)-C(14)	1.387(3)
C(5)-H(5)	0.98(3)
C(13)-H(13)	0.96(3)
C(6)-H(6)	0.97(2)
C(14)-H(14)	0.95(2)
C(7)-C(8)	1.539(3)
C(15)-H(151)	0.90(3)
C(7)-H(71)	0.98(2)
C(15)-H(152)	1.01(3)
C(7)-H(72)	0.98(2)
C(15)-H(153)	0.98(4)
C(8)-O(82)	1.403(2)
C(16)-H(161)	0.97(3)
C(8)-O(81)	1.420(2)
C(16)-H(162)	0.99(3)
C(8)-C(9)	1.522(3)
C(16)-H(163)	0.96(3)
O(81)-C(15)	1.431(3)
C(6)-N(1)-C(2)	121.8(2)
C(8)-O(82)-C(16)	116.7(2)
C(6)-N(1)-C(7)	118.6(2)
C(14)-C(9)-C(10)	118.7(2)
C(2)-N(1)-C(7)	119.5(2)
C(14)-C(9)-C(8)	122.1(2)
O(2)-C(2)-N(1)	120.3(2)
C(10)-C(9)-C(8)	119.2(2)
O(2)-C(2)-C(3)	125.0(2)
C(11)-C(10)-C(9)	120.8(2)
N(1)-C(2)-C(3)	114.7(2)
C(11)-C(10)-H(10)	121.2(14)
C(4)-C(3)-C(2)	122.3(3)
C(9)-C(10)-H(10)	118.0(14)
C(4)-C(3)-H(3)	123(2)
C(12)-C(11)-C(10)	119.9(2)
C(2)-C(3)-H(3)	115(2)
C(12)-C(11)-H(11)	119(2)
C(3)-C(4)-C(5)	120.4(3)
C(10)-C(11)-H(11)	121(2)
C(3)-C(4)-H(4)	120(2)
C(13)-C(12)-C(11)	119.7(2)
C(5)-C(4)-H(4)	120(2)
C(13)-C(12)-H(12)	121(2)
C(6)-C(5)-C(4)	118.7(3)
C(11)-C(12)-H(12)	119(2)
C(6)-C(5)-H(5)	116(2)
C(12)-C(13)-C(14)	120.5(2)
C(4)-C(5)-H(5)	125(2)
C(12)-C(13)-H(13)	121(2)

C(5)-C(6)-N(1)	121.8(3)
C(14)-C(13)-H(13)	118(2)
C(5)-C(6)-H(6)	122.8(14)
C(9)-C(14)-C(13)	120.3(2)
N(1)-C(6)-H(6)	115.3(14)
C(9)-C(14)-H(14)	117.8(12)
N(1)-C(7)-C(8)	113.3(2)
C(13)-C(14)-H(14)	121.8(12)
N(1)-C(7)-H(71)	108.2(11)
O(81)-C(15)-H(151)	110(2)
C(8)-C(7)-H(71)	109.9(11)
O(81)-C(15)-H(152)	107(2)
N(1)-C(7)-H(72)	107.1(11)
H(151)-C(15)-H(152)	111(3)
C(8)-C(7)-H(72)	109.5(12)
O(81)-C(15)-H(153)	113(2)
H(71)-C(7)-H(72)	109(2)
H(151)-C(15)-H(153)	111(3)
O(82)-C(8)-O(81)	112.1(2)
H(152)-C(15)-H(153)	104(3)
O(82)-C(8)-C(9)	106.2(2)
O(82)-C(16)-H(161)	104(2)
O(81)-C(8)-C(9)	111.8(2)
O(82)-C(16)-H(162)	112(2)
O(82)-C(8)-C(7)	113.3(2)
H(161)-C(16)-H(162)	107(2)
O(81)-C(8)-C(7)	101.8(2)
O(82)-C(16)-H(163)	112(2)
C(9)-C(8)-C(7)	111.7(2)
H(161)-C(16)-H(163)	111(2)
C(8)-O(81)-C(15)	114.8(2)
H(162)-C(16)-H(163)	111(2)

EXPERIMENTAL

2-Phenylloxazolo[3,2-a]pyridinium perchlorate (II) [1,2] was prepared according to the modified method described early [9].

1-[1,1-dimethoxy-1-phenylethyl-2]pyridone-2 (III).

0.3 g (1 mmol) of the perchlorate II was dissolved in 15 ml of the solution of MeONa in MeOH (prepared from 0.03 g (1.3 mmol) of Na and 15 ml of MeOH). The mixture was stirred at 20°C for 2 hours and kept overnight. After evaporation of the solvent the residue was purified by column chromatography (SiO₂, CH₂Cl₂) giving 0.25 g (95%) of ketal III, M.p. 142-144°C. Calculated (%): C 69.58, H 6.61, N 5.40. C₁₅H₁₇NO₃. Found (%): C 70.15, H 6.63, N 5.43. NMR ¹H (400 MHz, CDCl₃, δ, ppm): 7.35-7.25 (5H, m, Ph), 7.11 (1H, dd, H-4, J₃₄ 9.2 Hz, J₄₅ 6.7 Hz), 6.72 (1H, d, H-6, J₅₆ 6.9 Hz), 6.33 (1H, d, H-3, J₃₄ 9.2 Hz), 5.82 (1H, dd, H-5, J₄₅ 6.7 Hz, J₄₅ 6.7 Hz, J₅₆ 6.9 Hz), 4.37 (2H, s, CH₂), 3.33 (6H, c, CH₃O). NMR ¹³C (400 Mhz, CDCl₃, δ, ppm): 162.53 (C₂=O); 139.14, 138.28 (C₄, C₆); 137.93 (C, Ph); 128.60, 128.30, 127.48 (CH, Ph); 120.74 (C₃); 104.96 (C₅), 102.60 (C, (OMe)₂); 51.34 (OMe), 49.64 (CH₂).

In the analogous conditions 1-phenacylpyridone-2 (IV) does not form the ketal III even after a week (TLC control). Only after a month of keeping some traces of III have been registered in the reaction mixture.

Crystal structure of II. $C_{13}H_{10}ClNO_5$, $M_r = 295.67$, triclinic, $P-1$, $a=5.762(1)$, $b=14.469(3)$, $c=16.598(4)A$, $\alpha=112.53(2)$, $\beta=83.35(2)$, $\gamma=90.29(2)^\circ$, $V=1268.5(5)A^3$, $Z=4$, $D_x=1.548 g/cm^3$. Prismatic crystal with dimension $0.45 \times 0.25 \times 0.25$ mm. Lattice parameters refined using 25 reflections in the range $12^\circ < \theta < 16^\circ$. CAD-4 four circle diffractometer, graphite monochromatized MoK_α radiation. 4443 measured reflections, with $\theta_{max}=25^\circ$; $-6 < h < 6$, $-17 < k < 17$, $0 < l < 19$. Two standard reflections were checked every 1 hour. Structure was solved by direct methods using SHELXS86 [11]. Anisotropic full-matrix least squares refinement (SHELXL93 [12]) using F^2 . All H atoms were located from difference Fourier synthesis. 442 parameters, $R=0.0589$, $wR_2=0.1193$ for reflection with $I > 2\sigma(I)$ and $R=0.1215$, $wR_2=0.1501$ for all data. Final maximum shift to error = 0.01. Maximum and minimum height in final difference fourier synthesis 0.405 and -0.303 $e.A^3$. Atomic coordinates are in Table 1, bond lengths and angles are in Table 2.

Crystal structure of III. $C_{15}H_{17}NO_3$, $M_r = 259.29$, monoclinic, $P2_1/c$, $a=8.812(2)$, $b=10.036(1)$, $c=15.152(2)A$, $\beta=95.32(2)^\circ$, $V=1334.2(4)A^3$, $Z=8$, $D_x=1.291 g/cm^3$. Prismatic crystal with dimension $0.35 \times 0.30 \times 0.25$ mm. Lattice parameters refined using 25 reflections in the range $12^\circ < \theta < 16^\circ$. CAD-4 four circle diffractometer, graphite monochromatized MoK_α radiation. 2713 measured reflections, with $\theta_{max}=26^\circ$; $-10 < h < 10$, $0 < k < 12$, $0 < l < 18$. Two standard reflections were checked every 1 hour. Structure was solved by direct methods using SHELXS86 [11]. Anisotropic full-matrix least squares refinement (SHELXL93 [12]) using F^2 . All H atoms were located from difference Fourier synthesis. 241 parameters, $R=0.0473$, $wR_2=0.0980$ for reflection with $I > 2\sigma(I)$ and $R=0.0813$, $wR_2=0.1164$ for all data. Final

maximum shift to error = 0.01. Maximum and minimum height in final difference fourier synthesis 0.187 and -0.164 $e.A^3$. Atomic coordinates are in Table 3, bond lengths and angles are in Table 4.

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