

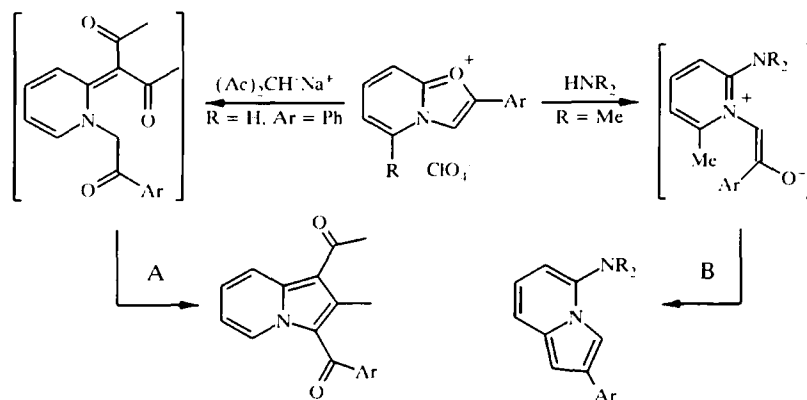
**HETEROCYCLES WITH A BRIDGED  
NITROGEN ATOM. 12\*. RECYCLIZATION  
OF 5-METHYLOXAZOLO[3,2-*a*]PYRIDINIUM  
CATION IN THE PRESENCE OF ACETYLACETONE.  
CRYSTAL STRUCTURE OF 1-ACETYL-  
2,5-DIMETHYLINDOLIZINE\*<sup>2</sup>**

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*Reaction of 5-methyl-2-(*p*-nitrophenyl)oxazolo[3,2-*a*]pyridinium perchlorate with acetylacetone gives 1-acetyl-2,5-dimethylindolizine, the structure of which was proved by X-ray analysis.*

**Keywords:** indolizine, pyridine, pyrrole, X-ray diffraction analysis.

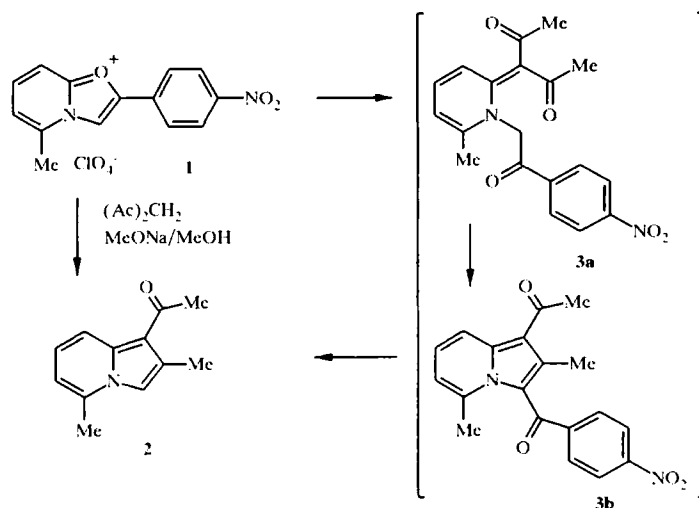
We have previously reported two novel strategies for building up the indolizine skeleton by the recyclization of oxazolo[3,2-*a*]pyridinium salts. In the first case (strategy A) the pyrrole ring is formed by two carbon atoms of acetylacetone and the C<sub>11</sub>NC<sub>10</sub> sequence in the starting cation [2]. In the second case (strategy B) the pyrrole ring is present in a hidden form in the skeleton of the starting bicycle as the C<sub>12</sub>C<sub>11</sub>NC<sub>15</sub> sequence and the methyl group at position 5 [3]. It was of interest to study such a combination of reagents in which these two strategies can occur together. If oxazolopyridinium cation containing 5-CH<sub>3</sub> group is introduced into the reaction with acetylacetone then both strategies A and B become equally likely.



\* For communication 11 see [1].

\*<sup>2</sup> Dedicated to the anniversary of Professor M. A. Yurovskaya.

We have found that the reaction of 5-methyl-2-(*p*-nitrophenyl)oxazolo[3,2-*a*]pyridinium perchlorate (**1**) with acetylacetone in methanol solution of sodium methylate gives 1-acetyl-2,5-dimethylindolizine (**2**). The structure of the compound obtained was proved by X-ray analysis (see Fig. 1).



This reaction is accompanied, not altogether obviously, by the elimination of an aryl residue from the starting structure. The probable mechanism of this process includes formation of the open form **3a**, in which closing of the pyrrole ring to indolizine **3b** occurs with elimination of the *p*-nitrobenzoyl group to form indolizine **2**. The driving force for the elimination is apparently the steric interaction between the *p*-nitrobenzoyl group at position 3 and the 5-CH<sub>3</sub> group of intermediate **3b**. We note that deacylation of 3-acylindolizines [4] (in particular 3-acyl-5-methyl derivatives [5]) under the action of base is well known. Hence, in the example studied, the scheme A is realized and the pyrrole ring is built up from oxazole with one basic difference, i. e., elimination of acyl fragment and this is, in fact, due to the presence of the methyl group in the starting substrate.

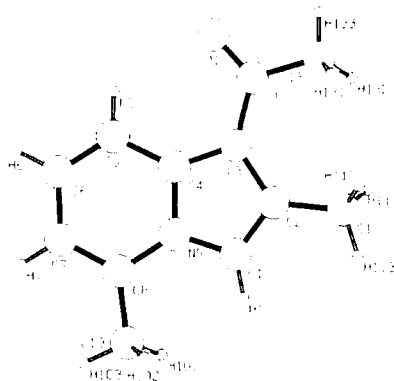


Fig. 1. Numbering of the atoms and the structure of compound **2**.

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

Atom	x	y	z	$U_{eq}$
C <sub>(1)</sub>	3112(4)	5729(2)	6215(2)	53(1)
C <sub>(2)</sub>	2336(4)	5145(2)	6982(2)	53(1)
C <sub>(3)</sub>	510(3)	5512(2)	6770(2)	50(1)
C <sub>(4)</sub>	266(3)	6329(2)	5854(2)	47(1)
C <sub>(5)</sub>	-1156(4)	7016(3)	5261(3)	57(1)
C <sub>(6)</sub>	-945(4)	7760(3)	4400(3)	64(1)
C <sub>(7)</sub>	702(4)	7839(3)	4066(3)	60(1)
C <sub>(8)</sub>	2108(4)	7185(2)	4616(2)	52(1)
N <sub>(9)</sub>	1886(3)	6456(2)	5511(2)	47(1)
C <sub>(10)</sub>	3880(5)	7186(4)	4295(4)	69(1)
C <sub>(11)</sub>	3329(5)	4278(4)	7830(3)	72(1)
C <sub>(12)</sub>	-907(4)	5149(3)	7331(2)	60(1)
C <sub>(13)</sub>	-564(7)	4302(5)	8329(4)	86(1)
O <sub>(1)</sub>	-2433(3)	5529(2)	6993(2)	79(1)
H <sub>(1)</sub>	4252(44)	5706(25)	6096(23)	69(9)
H <sub>(5)</sub>	-2203(42)	6944(24)	5535(24)	69(9)
H <sub>(6)</sub>	-1946(42)	8200(25)	3962(24)	68(8)
H <sub>(7)</sub>	817(39)	8368(26)	3425(25)	75(9)
H <sub>(10)</sub>	4219(45)	6348(33)	4144(26)	95(11)
H <sub>(102)</sub>	4790(51)	7474(32)	4975(30)	101(12)
H <sub>(103)</sub>	3848(50)	7712(35)	3622(35)	111(13)
H <sub>(11)</sub>	3270(39)	4477(25)	8636(27)	69(9)
H <sub>(12)</sub>	2799(46)	3489(31)	7716(27)	83(11)
H <sub>(13)</sub>	4638(59)	4237(33)	7834(30)	113(13)
H <sub>(131)</sub>	302(59)	4644(34)	8929(36)	113(15)
H <sub>(132)</sub>	-10(70)	3532(45)	8177(39)	156(20)
H <sub>(133)</sub>	-1652(62)	4228(36)	8570(34)	116(14)

TABLE 2. Bond Lengths ( $d$ ) in the Molecule of the Investigated Compound

Bond	$d, \text{Å}$	Bond	$d, \text{Å}$
C <sub>(1)</sub> -C <sub>(2)</sub>	1.353(4)	C <sub>(5)</sub> -C <sub>(6)</sub>	1.349(4)
C <sub>(1)</sub> -N <sub>(9)</sub>	1.386(3)	C <sub>(6)</sub> -C <sub>(7)</sub>	1.410(4)
C <sub>(2)</sub> -C <sub>(3)</sub>	1.439(4)	C <sub>(7)</sub> -C <sub>(8)</sub>	1.357(4)
C <sub>(2)</sub> -C <sub>(11)</sub>	1.487(4)	C <sub>(8)</sub> -N <sub>(9)</sub>	1.373(3)
C <sub>(3)</sub> -C <sub>(1)</sub>	1.398(4)	C <sub>(8)</sub> -C <sub>(10)</sub>	1.493(4)
C <sub>(3)</sub> -C <sub>(12)</sub>	1.450(4)	C <sub>(12)</sub> -O <sub>(1)</sub>	1.238(4)
C <sub>(3)</sub> -N <sub>(9)</sub>	1.399(3)	C <sub>(12)</sub> -C <sub>(13)</sub>	1.493(5)
C <sub>(4)</sub> -C <sub>(5)</sub>	1.403(4)		

## EXPERIMENTAL

### Reaction of 5-Methyl-2-(*p*-nitrophenyl)oxazolo[3,2-*a*]pyridinium Perchlorate **1** with Acetylacetone.

Acetylacetone (6 ml, 60 mmol) was added to solution of perchlorate **1** (0.1 g, 0.3 mmol) in methanol (20 ml) containing sodium methylate (4 mmol) and the product was held at room temperature. The conversion degree was monitored by TLC from the growth in intensity of the indolizine spot (developed using the Ehrlich reagent). The best yield was achieved with an extremely prolonged (100 days) holding off the reaction mixture at 20°C (brief heating leads to significant tarring and formation of a mixture of reaction products). The reaction mixture was filtered and the filtrate was evaporated and chromatographed on SiO<sub>2</sub> column with chloroform as the eluent to give 1-acetyl-2,5-dimethylindolizine **2**; mp 127°C. Monocrystals for X-ray analysis were prepared by slow

TABLE 3. Bond Angles ( $\omega$ ) in the Molecule of the Investigated Compound

Angle	$\omega$ , deg.	Angle	$\omega$ , deg.
C <sub>12</sub> -C <sub>11</sub> -N <sub>9</sub>	110.0(2)	C <sub>51</sub> -C <sub>60</sub> -C <sub>71</sub>	120.4(3)
C <sub>11</sub> -C <sub>12</sub> -C <sub>13</sub>	107.4(2)	C <sub>18</sub> -C <sub>17</sub> -C <sub>16</sub>	120.7(3)
C <sub>11</sub> -C <sub>12</sub> -C <sub>111</sub>	121.9(3)	C <sub>72</sub> -C <sub>18</sub> -N <sub>9</sub>	118.2(3)
C <sub>13</sub> -C <sub>12</sub> -C <sub>111</sub>	130.8(3)	C <sub>72</sub> -C <sub>18</sub> -C <sub>10</sub>	124.2(3)
C <sub>14</sub> -C <sub>13</sub> -C <sub>12</sub>	107.0(2)	N <sub>9</sub> -C <sub>18</sub> -C <sub>10</sub>	117.6(3)
C <sub>14</sub> -C <sub>13</sub> -C <sub>112</sub>	122.9(2)	C <sub>18</sub> -N <sub>9</sub> -C <sub>11</sub>	129.1(2)
C <sub>12</sub> -C <sub>13</sub> -C <sub>112</sub>	130.2(3)	C <sub>18</sub> -N <sub>9</sub> -C <sub>11</sub>	123.0(2)
C <sub>13</sub> -C <sub>14</sub> -N <sub>9</sub>	107.7(2)	C <sub>11</sub> -N <sub>9</sub> -C <sub>13</sub>	107.9(2)
C <sub>13</sub> -C <sub>14</sub> -C <sub>15</sub>	135.3(3)	O <sub>11</sub> -C <sub>112</sub> -C <sub>13</sub>	120.9(3)
N <sub>9</sub> -C <sub>14</sub> -C <sub>15</sub>	117.0(2)	O <sub>11</sub> -C <sub>112</sub> -C <sub>113</sub>	118.4(3)
C <sub>16</sub> -C <sub>15</sub> -C <sub>14</sub>	120.6(3)		
C <sub>11</sub> -C <sub>12</sub> -C <sub>113</sub>	120.7(3)		

evaporation of chloroform solution at 4°C. <sup>1</sup>H NMR spectrum (400 MHz, DMSO-d<sub>6</sub>): 8.14 (1H, d,  $J_{7,8}$  = 10 Hz, 8-H); 7.28 (1H, s, 3-H); 7.13 (1H, dd,  $J_{6,7}$  = 9 Hz,  $J_{7,8}$  = 10 Hz, 7-H); 6.49 (1H, d,  $J_{6,7}$  = 9 Hz, 6-H); 2.56 (3H, s, 1-COCH<sub>3</sub>); 2.50 (3H, s, 5-CH<sub>3</sub>); 2.48 ppm (3H, s, 2-CH<sub>3</sub>). For protons of the 2- and 5-CH<sub>3</sub> groups the signal assignment may be reversed.

**X-Ray Structural Investigation of Compound 2** was carried out on a CAD-4 automatic monocrystal diffractometer using  $\lambda$ MoK $\alpha$  irradiation. Unit cell parameters were determined in the range of 15-16  $\theta$  angles for 25 reflections. Crystals of the studied compound were assigned to the monoclinic syngony (space group  $P2_1/n$ ) with unit cell parameters  $a = 7.721(6)$ ,  $b = 11.096(2)$ ,  $c = 11.869(5)$  Å;  $\beta = 101.76(5)^\circ$ ;  $Z = 4$ . The structure was solved by direct methods using the SHELXS-97 complex program [6] and refined by a full-matrix, least-squares analysis via the SHELXL-97 program [7] in the anisotropic approximation for non-hydrogen atoms. All of the hydrogen atoms were localized from differential Fourier synthesis of the electron density and refined isotropically. The final R-factor was 0.0600 for 1956 independent reflections with  $I > 2\sigma(I)$ .

Positional parameters for the atoms in the investigated compound and isotropic thermal parameters equivalent to the corresponding anisotropic ones are given in Table 1 and interatomic distances and bond angles reported in Tables 2 and 3. The spatial disposition of the atoms in the molecule and their numbering are given in Fig. 1 [8].

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