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Rearrangement of oxazolo[3,2-*a*]pyridines as an approach of synthesizing aza[3.3.2]cyclazines

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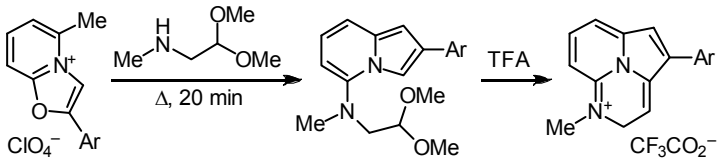


5-Methyloxazolo[3,2-*a*]pyridinium salts were shown to react with (methylamino)acetaldehyde dimethyl acetal leading to the formation of functionalized 5-aminoindolizines, which in turn are capable of closing the pyrimidine ring in acidic media forming aza[3.3.2] cyclazines.

Keywords: 5-aminoindolizines, oxazolo[3,2-*a*]pyridines, pyrimido[6,1,2-*cd*]indolizines, cyclization, NMR spectroscopy, rearrangement.

Evolution of the theory of aromaticity has raised interest in the synthesis of pericondensed indolizines such as cyclazines **1** and their analogs.[1] Yet, chemistry of hetero counterparts of such structures, including antiaromatic ones, are still poorly understood. Figure 1 shows the currently known representatives of [3.3.2]cyclazine series **1a-i**.[2]

The synthesis of such cyclazines includes addition of a five- and/or six-membered ring,[2] in accordance with cylization schemes shown in Figure 2.

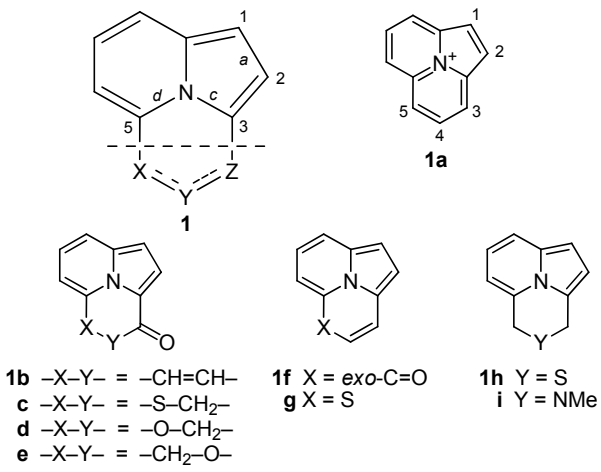


Figure 1. [3.3.2]cyclazines described in literature.

Theoretically, indolizines **2** containing a heteroatom at position 5 could serve as precursors of [3.3.2]cyclazines, but these compounds are not readily available. Our research group has developed a new strategy for the synthesis of 5-substituted indolizines by recyclization of oxazolopyridinium salts **3** by the action of nucleophiles (amines and alkoxides).[3] The use of bifunctional reagents (Nu – a nucleophilic heteroatom, E – an electrophilic carbon atom) in such a reaction could lead to indolizines **2**, potentially capable of cyclization into cyclazine **1** analogs *via* attack by an electrophilic atom on the π-excessive pyrrole moiety (Scheme 1).

Amine derivatives having a carbonyl group at the chain end could serve as suitable reagents. Of course, such agents must be stable under recyclization conditions (high temperature and concentration of the reagents). Of secondary amines, *N*-methylaminoacetaldehyde (acetal

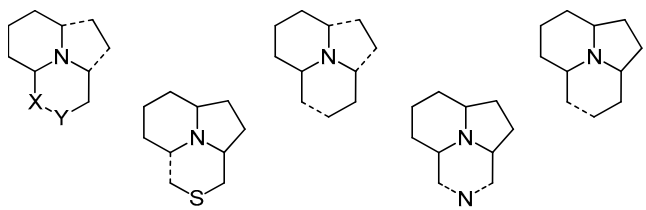
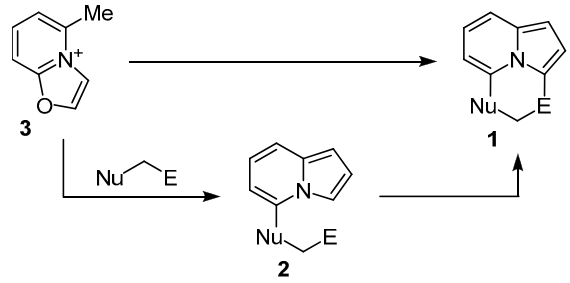
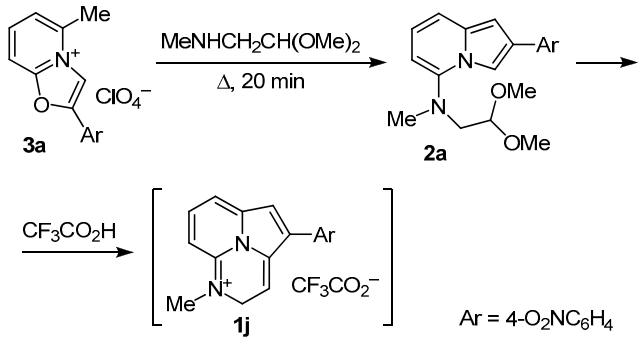


Figure 2. Principles of construction of [3.3.2]cyclazine system.

Scheme 1



Scheme 2



form) and *N*-methylglycine (sarcosine) esters, for instance, satisfy our requirements. This strategy, however, has not yet been employed in the synthesis of cyclazine hetero analogs. The purpose of this study was to investigate this approach.

As demonstrated in our laboratory, 5-substituted indolizines are unstable compounds which are readily oxidized in air. One example of a stable system is a 5-substituted indolizine possessing a *p*-nitrophenyl group at position 2.[3] Therefore, we chose this model compound, the synthesis of which is described in the literature, for further studies.

Oxazolopyridinium perchlorate **3a** was reacted with *N*-(methylamino)acetaldehyde dimethyl acetal. The reaction proceeded in the presence of the amine by heating under reflux for 20 min, whereupon the color changes first to a bright-cherry color before turning brown. Formation of new compound was registered by TLC which gave blue color by Ehrlich's reagent (qualitative reaction to a free position 3 and/or 1 of the indolizine system). Oily product **2a** was isolated by chromatography, but the yield was low (30%) (Scheme 2). In ^{1}H NMR spectrum of the obtained compound, the signals of the aromatic protons of indolizine are observed at 6.19-8.06 ppm, the doublet of the CH_2 group protons is at 3.25 ppm, while the triplet of the acetal CH proton is at 4.69 ppm. Acetal methoxy protons appear as a singlet at 3.42 ppm (Table 1).

Compound **2a** was quite unstable and easily oxidized in air which complicated further work. Upon an attempt to cyclize the obtained indolizine **2a** by heating with hydrochloric acid (for 20 min), a mixture of difficult to identify products formed. Likewise, processing of compound **2a** with trifluoroacetic acid under argon led to the formation of a new compound as shown by TLC, but the reaction mixture decomposed upon evaporation.

An identical reaction of indolizine **2a** with CF_3COOH was carried out in $CDCl_3$ solution at 20°C in an NMR ampoule. Initially, the disappearance of the signal of the proton H-3 and the emergence of a new signal of a CH_2 group at 5.63 ppm was observed, which corresponds to the protonated form of indolizine.[4] After one day, however, the color of the solution changed to bright-red, and signals of the starting indolizine were no longer observed in the ^{1}H NMR spectrum. Proton signals of the dimethyl acetal group at 3.74 ppm had disappeared; the characteristic signals of protons of cleaved methanol appeared instead. In the spectrum of the resulting compound, signals of a new CH_2 group at 5.10 ppm and of a new CH group at 6.27 ppm were conspicuously evident. One of the proton signals of indolizine cycle had disappeared while others had shifted upfield that appears to indicate the formation of a benzylidene structure. On the basis of these data, we assumed that the structure of the resulting compound corresponds to the structure **1j**. Full interpretation of spectra is difficult because of the presence of degradation products of the starting compound **2a** in the mixture.

It is known that 5-amino-substituted indolizines are unstable compounds, easily oxidized in air.[5] The most stable compounds of the series contain electron-withdrawing groups in the pyridine ring, therefore, it is necessary to use the appropriate pyridine derivatives for their synthesis.[6,7] In the current work, we utilized the easily accessible homolog 3-cyanopyridin-2-one, which we succeeded in turning into an oxazolopyridinium salt **3b** by phenacylation and subsequent

Table 1. ^{1}H NMR spectra of ($CDCl_3$) indolizines **2a**–**c**

Com-pound	Chemical shifts, δ, ppm (*J*, Hz)									
	H-1 (1H, s)	Ar (2H, m)	H-3 (1H, s)	H-8 (1H)	NCH_3 (3H, s)	CH_2 (2H)	CH (1H)	OAlk	7-CH_3 (3H, s)	ArCH_3 (3H, s)
2a*	6.79	7.83–7.85; 8.25–8.27	8.06	7.19 (d, *J* = 8.8)	2.97	3.25 (d, *J* = 4.8)	4.69 (t, *J* = 4.8)	3.42 (6H, s, $2CH_3$)	–	–
2b	6.66	7.15–7.17; 7.54–7.56	7.72	7.03 (s)	3.19	3.44 (d, *J* = 5.3)	4.63 (t, *J* = 5.3)	3.31 (6H, s, $2CH_3$)	2.41	2.42
2c	6.69	7.22–7.24; 7.57–7.59	7.83	7.01 (s)	3.21	4.05 (s)	–	1.51 (9H, s, $C(CH_3)_3$)	2.41	2.43

* Other signals: 6.19 (1H, d, *J* = 8.8, H-6); 6.74–6.76 (1H, m, H-7).

cyclocondensation by a method developed by us previously.[7]

Using the sodium salt of the precursor cyanopyridone (promotes alkylation at the nitrogen atom), and carrying out the reaction in an ion-solvating solvent (e.g., DMF) was expected to increase the yield of *N*-alkylated isomer **4b**. Despite the low yield of compound **4b** (and the formation of the *O*-alkylation by-product **4a**) in the first step, we found this method convenient since it does not require the use of chromatography and can be done in a larger scale. *N*-Phenacylpyridone **4b** underwent cyclization to oxazolopyridinium salt **3b** by the action of an acid (Scheme 3). The hydrolysis of the cyano group is possible in this case; however, the cyclization proceeded to completion by the action of the acid for 30 min and no hydrolysis was observed (as in the case of a *p*-bromophenyl derivative).[7]

For recyclization of salt **3b**, *N*-(methylamino)acetaldehyde dimethyl acetal and an ester of sarcosine were selected as the secondary amines. Recyclization was conducted by heating under reflux with an excess of the amine (Scheme 3). Structures of the obtained compounds **2b**,**c** were confirmed by IR, NMR spectroscopy and elemental analysis.

Reaction of perchlorate **3b** with *N*-(methylamino) acetaldehyde dimethyl acetal by heating in acetonitrile led to only trace amounts of the recyclization product **2b**. However, by heating under reflux without solvent in an excess of the amine, target indolizine **2b** was obtained in 25% yield (Scheme 3). ^{1}H NMR spectrum of dimethyl acetal derivative **2b** is in good agreement with the spectrum of the previously obtained compound **2a** (Table 1).

When indolizine **2b** was treated with CF_3COOH, the reaction solution turned bright-red after a day of the experiment, and the starting material had completely converted to pyrimidoindolizinium trifluoroacetate **1k** (Scheme 3). The formation of indolizine **2b** degradation products was not observed, allowing acquisition and interpretation of ^{1}H and ^{13}C NMR spectra of the cyclization product **1k** (Fig. 3). An attempt to convert the salt **1k** to the base form by the action of a base (alkali or triethylamine) led to its decomposition. Probably, the instability of the bases corresponding to cations **1j**,**k** stems from anti-aromaticity of these systems.

Sarcosine was used in the form of its *tert*-butyl ester in order to prevent self-condensation. While compound **2c** obtained in this case was quite stable, it was formed in low yield (20%) and required chromatographic purification. In the ^{1}H NMR spectrum of compound **2c**, indolizine proton signals are visible (Table 1), including protons H-1, H-8, and H-3 at 6.69, 7.01, and 7.83 ppm, respectively. Also, signals of sarcosine *tert*-butyl ester fragment are observed: CH_2 group proton singlets at 4.05 ppm, *N*-methyl group at 3.21 ppm, and those of *tert*-butyl group at 1.51 ppm.

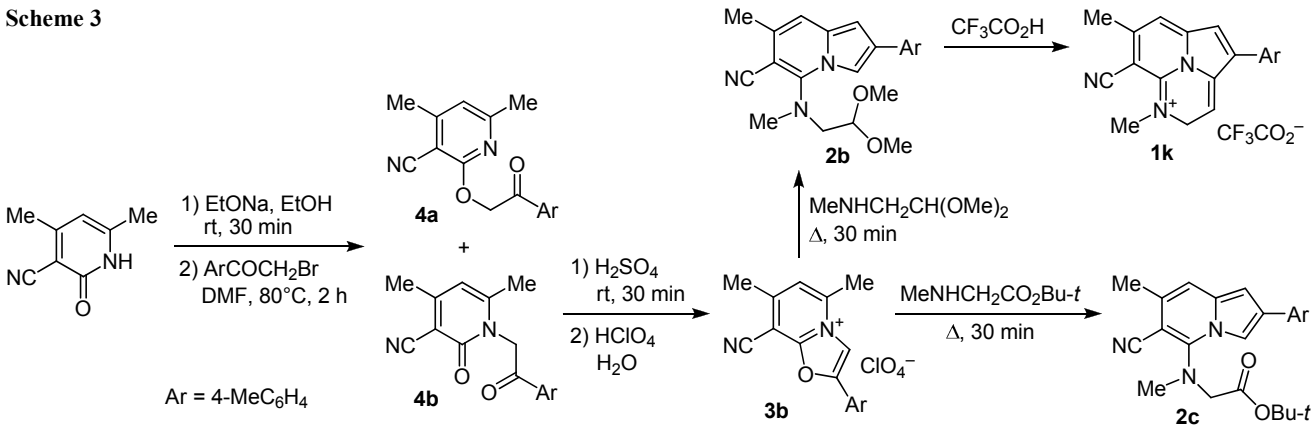
Notably, sarcosine *tert*-butyl ester was obtained by the reaction of *tert*-butyl chloroacetate with aqueous methylamine in the presence of KI in only 7% yield. Therefore, in order to reduce the required amounts of sarcosine ester and increase recyclization product **2c** yield, we attempted to optimize the recyclization conditions. Heating compound **3b** in acetonitrile or DMF with 3 equiv of a base (4-dimethylaminopyridine, triethylamine) and 1 equiv of sarcosine *tert*-butyl ester did not lead to the expected derivative **2c**. In all cases, the dimerization product was the only product isolated from the reaction mixture. Thus, although indolizine **2c** possessing an amino acid residue has been synthesized (and its structure unequivocally proved), the low yield and time-consuming purification did not allow us to synthesize the compound in amounts necessary for further transformations.

To conclude, indolizines substituted at position 5 with sarcosine *tert*-butyl ester and *N*-methyl-2,2-dimethoxyethanamine moieties have been obtained for the first time. Derivatives of the previously unknown 2*H*-pyrimido[6,1,2-*cd*]indolizinium heterocyclic system have been synthesized and studied by NMR spectroscopy.

Experimental

IR spectra were registered on a UR-20 spectrometer in petroleum jelly. ^{1}H and ^{13}C NMR spectra were acquired on a Bruker AM 400 (400 and 100 MHz, respectively) in DMSO-d_6 (^{1}H NMR spectra of salts **3b**, **4a**,**b**) and in $CDCl_3$ (remaining NMR spectra) with TMS as internal standard. Elemental analysis was performed on a Vario multi cube analyzer. Melting points were determined on an Electrothermal IA910 apparatus. Refractive indices of obtained liquid products were measured on a IRF-22 apparatus. Silufol plates were used for thin-layer chromatography (visualization with UV light); Acros (0.04 –0.06 mm) silica gel was used for column chromatography. All used solvents were purified by distillation.

Scheme 3



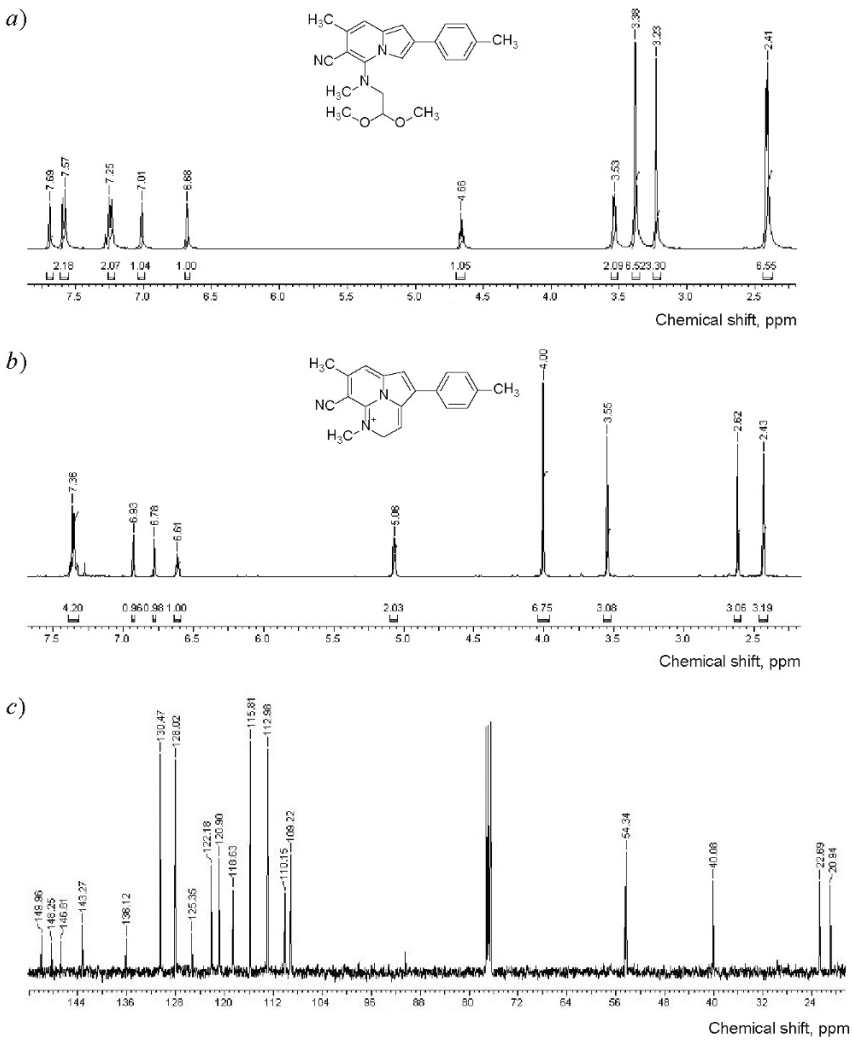


Figure 3. Spectroscopic study of the reaction of compound **2b** with CF_3COOH in an NMR ampoule: *a*) ^{1}H NMR spectrum of precursor **2b**; *b*) ^{1}H NMR spectrum of compound **1k**; *c*) ^{13}C NMR spectrum of compound **1k**.

5-Methyl-2-(4-nitrophenyl)oxazolo[3,2-*a*]pyridinium perchlorate (3a)[3] (yield 69%), **3-cyano-4,6-dimethylpyridin-2(1*H*)-one**[8] (yield 98%), and ***tert*-butyl chloroacetate**[9] (yield 53%) were prepared using known methods.

Oxazolopyridinium salt 3a recyclization. *N*-(Methylamino)acetaldehyde dimethyl acetal (6 ml) was added to oxazolopyridinium perchlorate **3a** (0.4 g, 1.13 mmol) and the reaction mixture heated under reflux for 20 min. The starting perchlorate quickly dissolves, the color of the solution changes from yellow to cherry-red that stays for 10 min; then the solution turns brown. The reaction mixture was cooled to room temperature and poured into H_2O (10 ml). The formed emulsion was extracted with PhH (2×10 ml), and the organic phase concentrated. The oily residue was purified by column chromatography (eluent $CHCl_3$, R_f 0.6) to give ***N*-(2,2-dimethoxyethyl)-*N*-methyl-2-(4-nitrophenyl)indolizin-5-amine (2a)**. Yield 0.12 g (30%), yellow oil that decomposes in air. ^{13}C NMR spectrum, δ, ppm: 146.0; 144.7; 142.7; 139.3; 135.7; 126.1; 124.2; 119.0; 114.4; 108.3; 102.5; 99.7; 97.6; 55.0; 53.9; 40.4.

Indolizine 2a cyclization reaction by the action of CF_3COOH (in NMR ampoule). ^{1}H NMR spectrum of indolizine **2a** (20 mg) solution in $CDCl_3$ was acquired. Subsequently, 1 drop of CF_3COOH was added, the mixture stirred, and ^{1}H NMR spectrum acquired repeatedly after 1 h and 1 day. Spectra can be found in the Supporting information file.

Phenacylation of 4,6-dimethyl-2-oxo-1,2-dihydropyridine-3-carbonitrile and separation of the isomer mixture (according to a literature method)[7]. 4,6-Dimethyl-2-oxo-1,2-dihydropyridine-3-carbonitrile (20.0 g, 0.135 mol) was added to a solution of EtONa prepared from Na (3.1 g, 0.135 mol) and EtOH (50 ml); the mixture was stirred for 30 min, and the solvent evaporated to dryness. 4-Methylphenacyl bromide (28.8 g, 0.135 mol) and dry DMF (100 ml) was added to the resulting salt. The reaction mixture was heated on water bath at 80°C for 2 h, cooled to room temperature, poured into ice water, and the formed precipitate was filtered off. The mixture of *N*- and *O*-alkylated isomers obtained in this way could be

separated by two methods. Method I is based on difference in solubility of these substances (isomer **4b** is less soluble in $CHCl_3$ and EtOAc than isomer **4a**). To separate the isomers, the obtained precipitate was placed on a Schott filter and washed with $CHCl_3$–EtOAc, 1:1, several times. The substance remaining on the filter was recrystallized from EtOH. Method II involves the use of column chromatography (gradient eluting through SiO_2, eluent $CHCl_3$ followed by EtOAc).

4,6-Dimethyl-2-[2-(4-methylphenyl)-2-oxoethoxy]nicotinonitrile (4a). Yield 12.0 g (31%, method II), colorless crystals, mp 133–135°C, R_f 0.5 ($CHCl_3$). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.87 (2H, d, *J* = 7.9, H Ar); 7.32 (2H, d, *J* = 7.9, H Ar); 6.86 (1H, s, 5-CH); 5.73 (2H, s, CH_2); 2.48 (3H, s, CH_3); 2.44 (3H, s, CH_3); 2.31 (3H, s, CH_3).

4,6-Dimethyl-1-[2-(4-methylphenyl)-2-oxoethyl]-2-oxo-1,2-dihydropyridine-3-carbonitrile (4b). Yield 9.3 g (25%, method I), colorless crystals, mp 182–183°C, R_f 0.2 ($CHCl_3$). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.98 (2H, d, *J* = 7.9, H Ar); 7.37 (2H, d, *J* = 7.9, H Ar); 6.28 (1H, s, 5-CH); 5.59 (2H, s, CH_2); 2.46 (3H, s, CH_3); 2.40 (3H, s, CH_3); 2.30 (3H, s, CH_3). ^{13}C NMR spectrum, δ, ppm: 191.1; 160.7; 158.7; 150.9; 145.4; 132.0; 129.6; 128.2; 115.2; 109.3; 101.3; 50.3; 21.7; 20.9 (2C). Found, %: C 72.64; H 5.93; N 10.13. $C_{17}H_{16}N_2O_2$. Calculated, %: C 72.84; H 5.75; N 9.99.

8-Cyano-5,7-dimethyl-2-(4-methylphenyl)oxazolo[3,2-*a*]-pyridin-4-ium perchlorate (3b). Conc. H_2SO_4 (5 ml) was added to *N*-phenacylpyridone **4b** (0.6 g, 2 mmol); the mixture was stirred at room temperature for 30 min, poured into H_2O (50 ml), and 70% $HClO_4$ added (2 ml). The formed precipitate was filtered off, washed with PhH, and dried in air. Yield 0.7 g (90%), colorless crystals, mp 249–250°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 9.49 (1H, s, H-3); 7.96 (2H, d, *J* = 7.9, H Ar); 7.47 (2H, d, *J* = 7.9, H Ar); 2.95 (3H, s, CH_3); 2.87 (3H, s, CH_3); 2.49 (3H, s, CH_3). Found, %: C 56.10; H 4.11; N 7.80. $C_{17}H_{15}N_2O_5Cl$. Calculated, %: C 56.29; H 4.17; N 7.72.

Preparation of sarcosine *tert*-butyl ester. A mixture of *tert*-butyl chloroacetate (30 ml, 0.21 mol), KI (34.9 g, 0.21 mol), and 40% aqueous $MeNH_2$ (1 l) was stirred at room temperature for 1 day. The reaction mixture was then extracted with CH_2Cl_2 (3×100 ml), the extract washed with H_2O, dried over Na_2SO_4, filtered, and concentrated on a rotary evaporator. The residue was distilled *in vacuo*. Yield 2.3 g (7%), colorless liquid, bp 74–75°C (26 mmHg), n_D^{19} 1.4164 (bp 76.5–78°C (40 mmHg), n_D^{23} 1.4148).[10]

Recyclization of oxazolopyridinium perchlorate 3b by the action of sarcosine *tert*-butyl ester. Sarcosine *tert*-butyl ester (0.7 ml, 4.50 mmol) was added to perchlorate **3b** (0.1 g, 0.27 mmol), and the mixture heated under reflux for 30 min. The color of the mixture turns from yellow to cherry-red, then turns brown. The mixture was cooled, poured into H_2O (20 ml), and the formed emulsion extracted with EtOAc (2×10 ml). The organic extract was evaporated, the residue extracted several times with petroleum ether, and the extract evaporated. The obtained ***tert*-butyl (2-{(methyl)-[6-cyano-7-methyl-2-(4-methylphenyl)indolizin-5-yl]-amino})acetate (2c)** was recrystallized from EtOH. Yield 20 mg (20%), yellow crystals, mp 132–133°C. IR spectrum, ν, cm^{-1}: 1625, 1715 (C=O), 2225 (C≡N). ^{13}C NMR spectrum, δ, ppm: 168.8; 148.7; 136.9; 134.5; 131.5; 129.6; 127.1; 126.2; 124.6; 117.4; 114.1; 107.9; 98.7; 82.2; 76.7; 55.4; 39.7; 28.1; 21.2; 20.0. Found, %: C 74.02; H 7.21; N 10.39. $C_{24}H_{27}N_3O_2$. Calculated, %: C 74.01; H 6.99; N 10.79.

Recyclization of oxazolopyridinium perchlorate 3b by the action of *N*-(methylamino)acetaldehyde dimethyl acetal. *N*-(Methylamino)acetaldehyde dimethyl acetal (2 ml) was added to oxazolopyridinium perchlorate **3b** (0.2 g, 0.55 mmol), and the mixture heated under reflux for 30 min. The color of the mixture turns from yellow to cherry-red, then turns brown. The mixture was cooled, poured into H_2O, and the formed precipitate filtered off. The product was separated by column chromatography (eluent $CHCl_3$, R_f 0.7). The obtained **5-[(2,2-dimethoxyethyl)(methyl)amino]-7-methyl-2-(4-methylphenyl)indolizine-6-carbonitrile (2b)** was recrystallized from EtOH. Yield 50 mg (25%), colorless crystals, mp 107–108°C. IR spectrum, ν, cm^{-1}: 1625, 2225 (C≡N). ^{13}C NMR spectrum, δ, ppm: 147.1; 137.0; 133.4; 131.4; 129.6; 127.0; 126.2; 124.5; 117.4; 114.1; 107.5; 102.7; 98.7; 91.2; 54.5; 54.0; 40.4; 21.2; 20.0. Found, %: C 72.79; H 7.07; N 11.35. $C_{22}H_{25}N_3O_2$. Calculated, %: C 72.70; H 6.93; N 11.56.

8-Cyano-1,7-dimethyl-4-(4-methylphenyl)-2*H*-pyrimido[6,1,2-*cd*]indolizin-1-ium trifluoroacetate (1k). A drop of CF_3COOH was added to a solution of compound **2b** in $CDCl_3$, agitated, and kept in dark. ^{1}H NMR spectrum was acquired right after adding the acid, as well as after 1 h and 1 day. The last spectrum corresponds to complete transformation of starting compound **2b** into a mixture of pyrimidoindolizinium salt **1k** and methyl trifluoroacetate. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.34-7.36 (4H, m, H Ar); 7.35 (4H, dd, *J* = 4.0, *J* = 8.3, H Ar); 6.93 (1H, s, H 5); 6.78 (1H, s, H-6); 6.61 (1H, t, *J* = 4.0, 3-CH); 5.07 (2H, d, *J* = 4.0, 2-CH_2); 4.00 (6H, s, $CF_3CO_2CH_3$); 3.55 (3H, s, 1-CH_3); 2.62 (3H, s, CH_3); 2.43 (3H, s, CH_3).

Supporting information file with data of the NMR study of the cyclization reaction of indolizine **2a** by the action of CF_3COOH is available for authorized users.

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