

Reactions of 3-cyclopropyl-3-oxopropionitrile anion generated by electroreduction of 5-cyclopropylisoxazole

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3-Cyclopropyl-3-oxopropionitrile anion obtained by cathodic reduction of 5-cyclopropylisoxazole in an aprotic medium was used as an example to demonstrate that cyano ketone anions show a dual reactivity. The reaction of acetyl chloride with the electrogenerated tetrabutylammonium salt of 3-cyclopropyl-3-oxopropionitrile gave *O*-acylation products, whereas the reaction with its sodium salt gives *C*-acylation products. The reactions of these salts with hydroxylamine hydrochloride follow a different route: in the case of the tetrabutylammonium salt, resinification takes place, while in the case of the sodium salt, 5-amino-3-cyclopropylisoxazole is formed. The condensation of this product with 4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dione in glacial AcOH affords 3-cyclopropyl-6-(2-thienyl)-4-(trifluoromethyl)isoxazolo[5,4-*b*]pyridine in 85% yield.

Key words: 5-cyclopropylisoxazole, cathodic deprotonation, 3-cyclopropyl-3-oxopropionitrile, *O*- and *C*-acylation, isoxazoles, isoxazolo[5,4-*b*]pyridines, cyclopropanes, organofluorine compounds.

Previously,¹ we described for the first time reductive electrolysis of 5-substituted isoxazoles and studied regularities of this process in nonaqueous media on cathodes with high (graphite) and low (ordinary steel) hydrogen overvoltage. Irrespective of the nature of the electrode, the reduction of isoxazoles **1a,b** is accompanied by proton removal from position 3 of the isoxazole ring to give carb-anions **2**, which are readily isomerized to linear enolate anions **3** (Scheme 1). Acidification of the final reaction mixture during the standard workup results in β -cyano ketone **4** as the major electrolysis products.

Compounds **4** were prepared by both direct cathodic deprotonation of isoxazoles **1** and by the alternative indirect cathodic deprotonation of these isoxazoles using methoxide and *tert*-butoxide anions as electrogenerated bases.¹

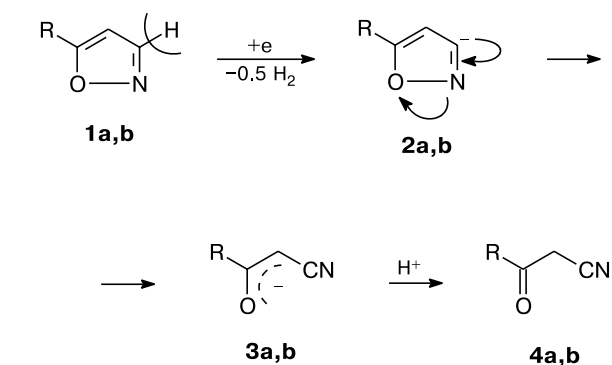
As a development of these studies, here we obtained the first information on the reactivity of enolate anions of type **3** generated by cathodic reduction (steel cathode, MeCN) of 5-cyclopropylisoxazole (**1a**), which was chosen as the model compound.

Results and Discussion

The isolation of cyano ketones **4** as the major products of electrolysis of isoxazoles **1** led to the conclusion¹ that enolate anions **3** are formed as primary products (see Scheme 1). We attempted first of all to characterize the electrogenerated species **3** by spectroscopy and thus to confirm directly their formation.

For this purpose, isoxazole **1a** was subjected to galvanostatic electrolysis in the cathodic compartment of a divided cell containing a 0.1 *M* solution of Bu₄NBr in MeCN as a supporting electrolyte using a steel cathode (ordinary steel). However, we could not record well-resolved ¹H NMR spectra of the 3-cyclopropyl-3-oxopropionitrile anion with the Bu₄N⁺ counter-cation (Bu₄N⁺**3a**). This was caused by the fact that the signals of this anion were markedly distorted and partially super-

Scheme 1

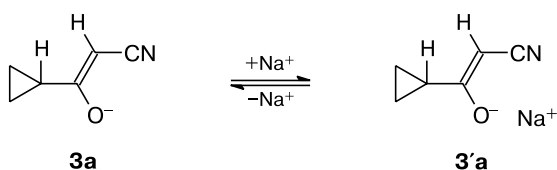


R = cyclo-C₃H₅ (**a**), Ph (**b**)

imposed by the signals from the Bu_4N^+ cation. The Bu_4N^+ salt of cyano ketone **4a** prepared by exchange reaction from the corresponding Na^+ salt of this ketone (which we synthesized by a known procedure²) showed an equally poorly resolved spectrum. In order to avoid the adverse effect of the Bu_4N^+ cation, electrolysis of isoxazole **1a** was carried out under above-described conditions but using NaClO_4 as the supporting electrolyte. In this case, the ^1H NMR spectrum of salt $\text{Na}^+\text{3a}$ isolated from the final reaction mixture was well resolved and fully corresponded to the spectrum of the Na^+ salt of cyano ketone **4a** synthesized by a chemical procedure.

It is known³ that in enolate anions of type **3a** the negative charge density is mainly concentrated on oxygen as the most electronegative (hard) atom. When the ion pair **3'a** is formed, association with the hard Na^+ cation occurs exactly through this atom (Scheme 2).

Scheme 2



It is of interest that the ^1H NMR spectrum of salt $\text{Na}^+\text{3a}$ contains two signals of CH-group protons at the double bond as singlets (δ 3.40 and 3.05) and two signals for the CH-group protons of the cyclopropyl fragment as multiplets (δ 1.90 and 1.25). This indicates that, unlike MeCN, in $\text{DMSO}-d_6$ used to record ^1H NMR spectra in which salts readily dissociate, ion pair **3'a** exists in equilibrium with free anion **3a**; the CH proton signals at δ 3.05 and 1.25 correspond apparently to species **3a**, while the CH proton signals at δ 3.40 and 1.90 correspond to **3'a**.

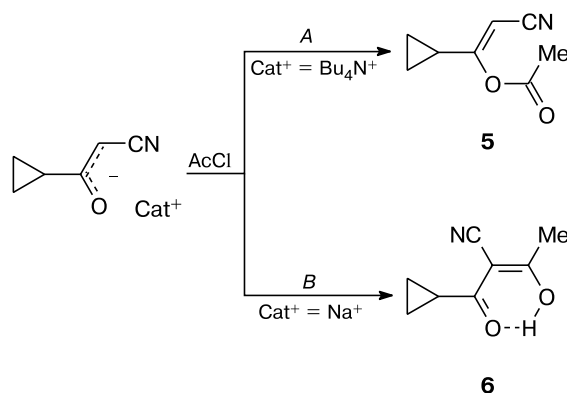
In line with published data,¹ acidification of the final reaction mixture obtained after electrolysis of isoxazole **1a** in MeCN followed by standard workup furnished cyano ketone **4a** in 71 and 77% yields for electrolysis in 0.1 M solutions of NaClO_4 and Bu_4NBr , respectively.

Even the first experiments dealing with the reactivity of anion **3a** generated by electrochemical deprotonation of isoxazole **1a** demonstrated that the experimental results depend on the nature of the counterion and differ considerably for the Na^+ and Bu_4N^+ cations. This is in good agreement with the concept of dual reactivity of enolate anions of type **3**, which is exhibited in an aprotic medium giving, for example, C- or O-alkylation products depending on the nature of the salt added.³ In aprotic medium, the formation of ion pair **3'a** considerably decreases the nucleophilicity of the oxygen atom, this coordination of the anion being preferable for C-alkylation. Conversely, the Bu_4N^+ cation having a large ionic radius

does not tend to form ion pairs; therefore, electrochemical generation in MeCN gives an enolate anion existing in a free form **3a**, which results in O-alkylation.

In view of the foregoing, consider the possible reaction routes between salts of cyano ketone **4a** and acetyl chloride, which is a fairly strong electrophile. Salts $\text{Na}^+\text{3a}$ and $\text{Bu}_4\text{N}^+\text{3a}$ reacted readily, the reaction route being fully determined, as expected, by the nature of the counterion. Indeed, the reaction of anion **3a** electrogenerated in the presence of Bu_4NBr (salt $\text{Bu}_4\text{N}^+\text{3a}$) with acetyl chloride gives O-acylation product **5** in 65% yield (Scheme 3, pathway A). The ^1H NMR spectrum of the product exhibits signals at δ 2.25 (m, 1 H, cyclopropyl CH), 0.90 and 1.25 (both m, 2 H each, cyclopropyl CH_2), 2.10 (s, 3 H, Ac), and 5.40 (s, 1 H, enol CH). This outcome is also supported by the fact that the constant $^1J_{\text{C,H}}$ for the reaction product is 177.2 Hz, which corresponds to a spin-spin coupling constant for a CH group at a double bond. Note that the above-given spectrum of the O-acylation product is in good agreement with the spectrum of enol acetate **5** simulated using the AcD Labs program.

Scheme 3



The reaction of anion **3a** electrogenerated in the presence of NaClO_4 (salt $\text{Na}^+\text{3a}$) with acetyl chloride affords C-acylation product (see Scheme 3, pathway B). This is confirmed by the ^1H NMR spectrum of the product, which contains the following signals: δ 17.20 (s, 1 H, hydrogen-bonded OH group), 2.35 (s, 3 H, Me), 2.25 (m, 1 H, CH cyclopropyl), 1.25 and 1.15 (both m, 2 H each, cyclopropyl CH_2). Thus, C-acylation of anion **3a** yields 2-cyano-1-cyclopropylbutane-1,3-dione (**6**), the experimental ^1H NMR spectrum of this compound being in good agreement with the spectrum of this diketone simulated by the AcD Labs program.

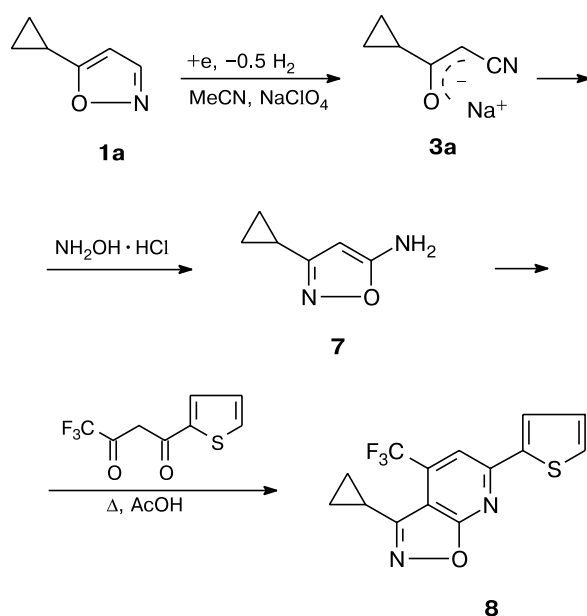
The formation of product **6** was also confirmed by its reaction with an aqueous solution of copper acetate (typical of β -dicarbonyl compounds⁴), resulting in an insoluble copper chelate. This complex was destroyed only in con-

centrated HCl. The yield of product **6** purified in this way was 21%.

We compared the results described above with the data on the acylation of chemically generated Na^+ and Bu_4N^+ salts of cyano ketone **4a** and concluded that, irrespective of the preparation method of these salts (electrochemical and chemical), the products of their acylation are fully identical, judging by the ^1H NMR spectra.

It is of interest that salts $\text{Na}^+\mathbf{3a}$ and $\text{Bu}_4\text{N}^+\mathbf{3a}$ react in different ways also with hydroxylamine hydrochloride but the reasons are not entirely clear. The reaction of electrochemically generated salt $\text{Bu}_4\text{N}^+\mathbf{3a}$ (or the same salt but obtained chemically) with hydroxylamine hydrochloride is accompanied by resinification of the reaction mixture giving unidentified products. Conversely, the reaction of electrochemically (chemically) obtained salt $\text{Na}^+\mathbf{3a}$ with hydroxylamine hydrochloride affords 5-amino-3-cyclopropylisoxazole (**7**) in 48% yield (Scheme 4). The structure of this product was confirmed ^1H , ^{13}C , and $^1\text{H}-^{15}\text{N}$ 2D NMR spectroscopy, and elemental analysis.

Scheme 4

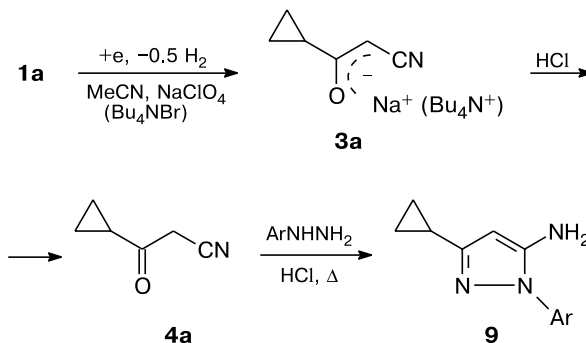


Compound **7** shows a broad spectrum of reactivity as it can react both at the NH_2 group^{5,6} and at position 4 of the isoxazole ring.^{7,8} For example, it is known⁹ that 5-aminoisoxazoles react with 1,3-diketones to give isoxazolopyrimidines. The condensation of compound **7** with 4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dione in glacial AcOH occurs regioselectively (see Ref. 9) to give 3-cyclopropyl-6-(2-thienyl)-4-(trifluoromethyl)isoxazolo[5,4-*b*]pyridine (**8**) in 85% yield (see Scheme 4).

5-Amino-3-cyclopropyl-1-(4-fluorophenyl)pyrazole (**9**) with a structure similar to that of **7** was synthesized

from isoxazole **1a** in ~70% yield (Scheme 5). The intermediate cyano ketone **4a** was refluxed for 4 h in acid medium with an equimolar amount of 4-fluorophenylhydrazine hydrochloride and the subsequent alkalification of the reaction mixture yielded product **9**. The steps **3a** \rightarrow **4a** \rightarrow **9** occur in a highly acidic medium and the nature of the counterion for anion **3a** does not affect the course of the reaction.

Scheme 5



Ar = 4- FC_6H_4

In chemical properties pyrazole **9** resembles isoxazole **7**. In particular, it reacts with 1,3-diketones,⁹ giving rise to pyrazolopyridines.

Experimental

Products of electrolysis were identified by ^1H NMR spectroscopy on a Bruker AC-300 instrument by comparison with the spectra of reference samples prepared by chemical procedures outlined below.

The starting 5-cyclopropylisoxazole (**1a**) was prepared by a known procedure.¹ Hydroxylamine hydrochloride, 4-fluorophenylhydrazine hydrochloride, acetyl chloride, and 4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dione were commercial chemicals (Acros), which were used as purchased. Acetonitrile was purified by a published procedure,¹⁰ and MeOH was dried as described previously.¹¹

The product yields both in electrochemical and in chemical experiments are related to the starting compound taken.

Chemical synthesis of reference compounds

Sodium salt of 3-cyclopropyl-3-oxopropionitrile ($\text{Na}^+\mathbf{3a}$).

A solution of 5-cyclopropylisoxazole (**1a**) (1.09 g, 10 mmol) in MeOH (10 mL) was added dropwise over a period of 10 min to a solution of NaOMe obtained from Na (0.25 g, 11 mmol) and anhydrous MeOH (20 mL) and the mixture was stirred for 30 min at 40 °C. Evaporation of the solvent under reduced pressure gave 1.3 g (97%) of the salt. Found (%): C, 54.95; H, 4.60; N, 10.70. $\text{C}_6\text{H}_6\text{NNaO}$. Calculated (%): C, 54.96; H, 4.58; N, 10.69. ^1H NMR ($\text{DMSO}-d_6$), δ : 3.40 (s); 3.05 (s); 1.90 (m); 1.25 (m); 0.60, 0.25 (both m, 2 H each, cyclopropyl CH_2).

Tetrabutylammonium salt of 3-cyclopropyl-3-oxopropionitrile ($\text{Bu}_4\text{N}^+\text{3a}$). A solution of Bu_4NBr (3.22 g, 10 mmol) in anhydrous MeOH (20 mL) was added to a solution of the Na^+ salt of cyano ketone **4a** prepared as described previously. The mixture was stirred for 30 min at -20°C . The solvent was evaporated, dry MeCN (100 mL) was added, and the mixture was refluxed for 40 min to complete extraction of the salt $\text{Bu}_4\text{N}^+\text{3a}$. The NaBr precipitate was filtered off and MeCN was evaporated on a rotary evaporator. Yield 3.46 g (99%). Found (%): C, 75.45; H, 12.01; N, 7.97. $\text{C}_{22}\text{H}_{42}\text{N}_2\text{O}$. Calculated (%): C, 75.43; H, 12.00; N, 8.00. ^1H NMR (CDCl_3), δ : 3.25 (m, NCH_2); 1.65, 1.40 (both m, CH_2); 1.00 (m, Me).

Electrochemical experiments

Electrolysis was carried out in the galvanostatic mode ($I = 0.1\text{ A}$) in the cathodic compartment of a glass cell with a ceramic diaphragm with a thermostatic jacket, a thermometer, and an N_2 bubbling device. A B5-49 direct current source and a coulometer (production of the N. D. Zelinsky Institute of Organic Chemistry workshop) were incorporated in an electric circuit. During electrolysis, the reaction mixture was stirred by a magnetic stirrer. A stainless-steel plate ($S = 47\text{ cm}^2$) was used as the cathode. A glass carbon plate served as the anode. Prior to electrolysis, the steel cathode was kept for 3 min in dilute aqueous HCl (1 : 4) for activation, washed with distilled water, and dried. As supporting electrolytes, 0.1 M solutions of Bu_4NBr or NaClO_4 were used. The supporting salts (chemically pure) were dried prior to use by heating for 2 h on a water bath under reduced pressure. The electrolysis was carried out until the starting isoxazole was completely consumed. The process was monitored by TLC using Silufol UV-254 plates (elution with $\text{CCl}_4\text{--AcOEt}$, 10 : 4).

Electrosynthesis of $\text{Na}^+\text{3a}$ and its transformation into cyano ketone **4a.** A 0.1 M solution of NaClO_4 (100 mL) and isoxazole **1a** (1 g, 9 mmol) were placed into the cathodic compartment of the cell and a 0.1 M solution of NaClO_4 in MeCN (40 mL) was placed into the anodic compartment. After deaeration of the catholyte for 10 min, electrolysis at $I = 0.1\text{ A}$, $T = 20^\circ\text{C}$ and continuous purging with nitrogen was carried out. After 1.5 F of electricity per mole of the starting compound (1300 Q) was passed, the electrolysis was stopped because isoxazole **1a** was completely consumed (TLC data). The cathode was washed with MeOH ($2 \times 10\text{ mL}$) to remove the stuck salt, the washing was combined with the catholyte, and the solvent was evaporated under reduced pressure until a dry residue formed. The ^1H NMR spectrum of salt $\text{Na}^+\text{3a}$ obtained in this way coincided with the spectrum of chemically synthesized sample (see above).

The precipitate of salt $\text{Na}^+\text{3a}$ was acidified with a 0.1 M aqueous HCl (50 mL) and extracted with ether ($3 \times 50\text{ mL}$). The ether extracts were dried over Na_2SO_4 (anhydr.) and concentrated *in vacuo*. The residual yellowish oil (0.71 g) was almost pure cyano ketone **4a** (^1H NMR, *cf.* Ref. 1). The substance yield of 3-cyclopropyl-3-oxopropionitrile (**4a**) was 71% and the current yield was 48%.

Electrosynthesis of the salt $\text{Bu}_4\text{N}^+\text{3a}$ and its transformation into cyano ketone **4a.** A 0.1 M solution of Bu_4NBr (100 mL) and isoxazole **1a** (1 g, 9 mmol) were placed into the cathodic compartment and a 0.1 M solution of Bu_4NBr in MeCN (40 mL) was placed into the anodic compartment. The electrolysis was

carried out as described above by passing 1.1 F of electricity per mole of the starting compound (960 Q) until compound **1a** was fully consumed (TLC data). Then the solvent was evaporated from the catholyte under reduced pressure. The ^1H NMR spectrum of the residue was fully identical to the spectrum of the chemically prepared sample of the salt $\text{Bu}_4\text{N}^+\text{3a}$ (see above).

Compound **4a** was prepared by the standard workup of the precipitate of salt $\text{Bu}_4\text{N}^+\text{3a}$ (see above). This gave 0.77 g of a yellowish oil, whose ^1H NMR spectrum was identical to the spectrum of the reference sample. The substance yield of compound **4a** was 77% and the current yield was 72%.

Syntheses based on salts of cyano ketone **4a**

3-Acetoxy-3-cyclopropylacrylonitrile (5**).** The salt $\text{Bu}_4\text{N}^+\text{3a}$ was electrogenerated (see above). After electrolysis, dry CHCl_3 (30 mL) was added to the catholyte pre-concentrated to dryness, then a solution of AcCl (1.57 g, 20 mmol) in dry CHCl_3 (20 mL) was slowly added with stirring over a period of 5 min; the mixture spontaneously warmed-up to 45°C . After 24 h, the reaction mixture was washed with water ($2 \times 20\text{ mL}$), the organic solution was dried over Na_2SO_4 (anhydr.), and the volatile components were distilled off to give 0.98 g (65%) of a yellow oil, b.p. 120°C (15 Torr). Found (%): C, 63.50; H, 5.90; N, 9.31. $\text{C}_8\text{H}_9\text{NO}_2$. Calculated (%): C, 63.58; H, 5.96; N, 9.27. ^1H NMR (CDCl_3), δ : 0.90, 1.25 (both m, 2 H each); 2.10 (s, 3 H); 2.25 (m, 1 H); 5.40 (s, 1 H).

Enol acetate **5** was synthesized from the chemically generated salt $\text{Bu}_4\text{N}^+\text{3a}$ (see above) using the same procedure. The reaction of $\text{Bu}_4\text{N}^+\text{3a}$ (3.5 g) gave 0.91 g (60%) of the target product.

2-Cyano-1-cyclopropylbutane-1,3-dione (6**).** The salt $\text{Na}^+\text{3a}$ was prepared by electrosynthesis as described above. After electrolysis, dry CHCl_3 (30 mL) was added to the catholyte pre-concentrated to dryness, then a solution of AcCl (1.57 g, 20 mmol) in dry CHCl_3 (20 mL) was slowly added with stirring over a period of 5 min; the mixture warmed-up to 40°C . After 24 h, the reaction mixture was washed from NaCl, the volatile components were distilled off on a rotary evaporator under reduced pressure. The residue was purified *via* the synthesis of copper chelate. For this purpose, the residue was dissolved in EtOH (10 mL) and this solution was added with vigorous stirring to a saturated solution of $\text{Cu}(\text{OAc})_2$ (30 mL). After stirring for 4 h, the precipitate was filtered off and washed on the filter with EtOH. Then the wet complex was decomposed by adding concentrated HCl (10 mL) (to dissolve the precipitate) followed by extraction with CH_2Cl_2 ($3 \times 20\text{ mL}$). The extract was dried over Na_2SO_4 (anhydr.) and the solvent was evaporated under reduced pressure. The yield of thus purified product **6** was 0.317 g (21%), m.p. 56°C . Found (%): C, 63.29; H, 6.05; N, 9.23. $\text{C}_8\text{H}_9\text{NO}_2$. Calculated (%): C, 63.58; H, 5.96; N, 9.27. ^1H NMR (CDCl_3), δ : 17.20 (s, 1 H, OH); 2.30 (s, 3 H, Ac); 2.20 (m, 1 H, cyclopropyl CH); 1.25, 1.10 (both m, 2 H each, cyclopropyl CH_2).

Compound **6** was obtained from chemically prepared salt $\text{Na}^+\text{3a}$ and purified as described above. Yield 22%.

5-Amino-3-cyclopropylisoxazole (7**).** The catholyte containing the salt $\text{Na}^+\text{3a}$ (10 mmol) was concentrated to dryness. A solution of hydroxylamine hydrochloride (0.7 g, 10 mmol) in H_2O (20 mL) was added to the residue, and the mixture was

stirred for 6 h at 40–50 °C. Then the solution was rapidly cooled to ~20 °C, saturated with K₂CO₃, and extracted with ether (3×20 mL). The ether extracts were dried over Na₂SO₄ (anhydr.). Evaporation of the ether gave 0.6 g (48%) of product **7** as a poorly crystallizable yellow oil. Found (%): C, 58.16; H, 6.51; N, 22.49. C₆H₈N₂O. Calculated (%): C, 58.06; H, 6.45; N, 22.58. ¹H NMR (CDCl₃), δ: 4.75 (s, 1 H, H(4) isoxazole); 4.40 (s, 2 H, NH₂); 1.60 (m, 1 H, cyclopropyl CH); 0.90, 0.70 (both m, 2 H each, cyclopropyl CH₂). ¹³C NMR (DMSO-d₆), δ: 7.34 (cyclopropyl CH₂); 7.47 (cyclopropyl CH); 74.35 (isoxazole C(4)); 167.19 (isoxazole C(3)); 170.25 (isoxazole C(5)). In addition, the observed spin-spin coupling constant between the isoxazole ring nitrogen and the α-hydrogen of the cyclopropyl fragment in the ¹H–¹⁵N 2D NMR spectrum was 3 Hz, which attested to the cyclopropyl group position at the C–N fragment rather than at the C–O fragment. The same ³J_{H,15N} value was observed for substituted pyrazoles.

3-Cyclopropyl-6-(2-thienyl)-4-(trifluoromethyl)isoxazolo[5,4-*b*]pyridine (8). 4,4,4-Trifluoro-1-(2-thienyl)butane-1,3-dione (0.89 g, 4 mmol) was added to a solution of 5-amino-3-cyclopropylisoxazole (**7**) (0.5 g, 4 mmol) in glacial AcOH (10 mL). The resulting solution was refluxed for 15 min with thorough stirring. After cooling, the reaction mixture was poured into cold water (100 mL), the precipitate that formed was filtered off, washed with water, and dried to give 1.05 g (85%) of product **8**. Found (%): C, 54.29; H, 2.95; N, 9.23. C₁₄H₉F₃N₂OS. Calculated (%): C, 54.19; H, 2.90; N, 9.03. ¹H NMR (CDCl₃), δ: 7.90 (s, 1 H, bicyclic H(5)); 7.85 (d, 1 H, thiophene H(3), *J* = 5.2 Hz); 7.60 (d, 1 H, thiophene H(5), *J* = 3.9 Hz); 7.20 (dd, 1 H, thiophene H(4), *J* = 5.2 Hz, *J* = 3.9 Hz); 2.20 (m, 1 H, cyclopropyl CH); 1.20, 1.10 (both m, 2 H each, cyclopropyl CH₂).

5-Amino-3-cyclopropyl-1-(4-fluorophenyl)pyrazole (9). After electroreduction of 10 mmol of isoxazole **1a** (see above), the catholyte was concentrated to dryness, and a solution of 4-fluorophenylhydrazine hydrochloride (1.62 g, 10 mmol) in H₂O (20 mL) was added to the residue. After thorough stirring, concentrated HCl (20 mL) was added to the reaction mixture, and the mixture was refluxed for 2 h. Then the reaction mixture was cooled to ~20 °C and alkalified by concentrated aqueous NH₃ to pH 9–10 (warming-up should be avoided, otherwise the product is poorly crystallized). The precipitated aminopyrazole **9** was filtered off, washed with H₂O to neutral pH, and dried in air. Yield 1.54 g (71%), m.p. 127 °C. Found (%): C, 66.41;

H, 5.60; N, 19.33. C₁₂H₁₂FN₃. Calculated (%): C, 66.36; H, 5.53; N, 19.35. ¹H NMR (CDCl₃), δ: 7.50, 7.10 (both m, 2 H each, =CH arom.); 5.25 (s, 1 H, pyrazole H(4)); 3.65 (s, 2 H, NH₂); 1.90 (m, 1 H, cyclopropyl CH); 0.90, 0.65 (both m, 2 H each, cyclopropyl CH₂).

The reaction of salt Bu₄N⁺**3a** with 4-fluorophenylhydrazine hydrochloride was carried out under the same conditions as for the Na⁺ salt. The yield of product **9** was 70%.

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