Electrosynthesis of 4-chloropyrazolecarboxylic acids*

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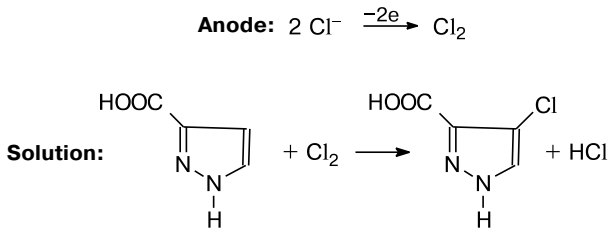
4-Chlorosubstituted pyrazolecarboxylic acids were synthesized *via* chlorination of the corresponding acids at the Pt anode in NaCl aqueous solutions under conditions of divided galvanostatic electrolysis. The efficiency of the process depends on the structures of the initial pyrazolecarboxylic acids, particularly, on the donor-acceptor properties of the substituents and on their position in the pyrazole ring. The yields of the 4-chlorosubstituted products of chlorination of pyrazole-3(5)-carboxylic acid, 1-methylpyrazole-5-carboxylic acid, 1-methylpyrazole-3-carboxylic acid, 1-ethylpyrazole-3-carboxylic acid, and 1-methyl-3-nitropyrazole-5-carboxylic acid are 92, 93, 69, 80, and 4%, respectively.

Key words: electrosynthesis, pyrazole-3(5)-carboxylic acid, 1-methylpyrazole-5-carboxylic acid, 1-methylpyrazole-3-carboxylic acid, 1-ethylpyrazole-3-carboxylic acid, 1-methyl-3-nitropyrazole-5-carboxylic acid.

The present work is aimed at the electrochemical synthesis of 4-chloropyrazolecarboxylic acids. Interest in the development of convenient methods for synthesis of such acids is due to the wide use of these compounds as by-products of synthesis of drugs[1] and herbicides.[2] When solving the stated problem, we took into account the known data on chemical chlorination of pyrazolecarboxylic acids,[3] whose electrochlorination was carried out under the conditions of galvanostatic divided electrolysis of aqueous solutions of NaCl.

Scheme 1



Results and Discussion

Already the first experiments (Table 1, entry *1*) on the electrochlorination of pyrazole-3(5)-carboxylic acid (**1**) under mild conditions at T = 15 °C (compared to the chemical chlorination[3] at T = 70 °C) allowed one to synthesize 4-chloropyrazole-3(5)-carboxylic acid (**2**) in good yield (~69% based on initial acid **1**) with 84% conversion of **1**. The process of electrochlorination of **1** can formally be described by Scheme 1.

We studied the influence of several factors on the electrochlorination with the purpose of its optimization. For example, it turned out (see Table 1, *cf.* entries *1—3*) that the increase in the temperature of the process from 15 to 50 °C decreases sharply both the yield of acid **2** (more than by 45%) and the conversion of acid **1** (more than by 25%). The decrease in the concentration of **1** from 0.5 to 0.25 mol L^{-1} (see Table 1, *cf.* entries *1* and *4*), on the contrary, increases the yield of **2** (by 10%). The still greater increase in the yield of **2** (by 47%) and a simultaneous increase in the conversion of initial **1** (by 36%) occur with an increase in the NaCl concentration in the electrolyte from 2 to 4 mol L^{-1} (see Table 1, *cf.* entries *6* and *4*). However, electrochlorination in a NaCl-saturated solution of the electrolyte (see Table 1, *cf.* entries *4* and *5*) is not already accompanied by the further increase in the yield of **2**. The variation of the current density (J_a = 0.05—0.1 A cm^{-2}) exerted almost no effect on the yield of **2** (see Table 1, *cf.* entries *4* and *7*). Thus, an increase in the NaCl concentration turned out to be the only factor that substantially affects the yield of the target product. It is most likely that with the NaCl concentration increase the concentration of electrogenerated Cl_2 in the solution bulk also increases and, as a consequence, the rate of the chlorination step increases (see Scheme 1).

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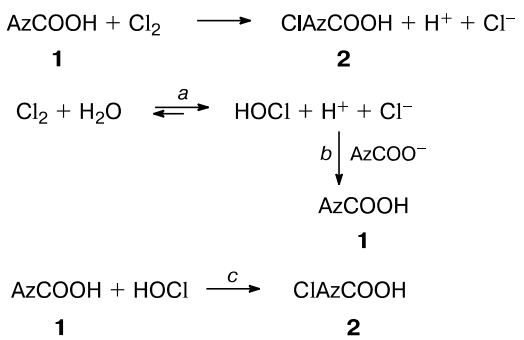
Table 1. Influence of the experimental conditions on the yield of 4-chloropyrazolecarboxylic acid (**2**) during anodic chlorination of pyrazole-3(5)-carboxylic acid (**1**) in an aqueous solution of NaCl[a]

Entry	Concentration /mol L^{-1}		T/°C	j_a/A cm^{-2}	Q/Q_{theor}	Conversion of **1** (%)	Yield[b] of **2** (%)	
	1	NaCl					I	II
1	0.5	4.0	15	0.1	1.0	84.2	69	82
2	0.5	4.0	30	0.1	1.0	71.4	57	80
3	0.5	4.0	50	0.1	1.0	58.1	22	37
4	0.25	4.0	15	0.1	1.0	84.9	78	92
5	0.25	Saturated solution	15	0.1	1.0	84.3	76	90
6	0.25	2.0	15	0.1	1.0	48.4	31	65
7	0.25	4.0	15	0.05	1.0	84.8	78	92
8[c]	0.25	4.0	15	0.1	1.0	86.8	69	79
9	0.25	4.0	15	0.1	1.5	91.9	92	100

[a] Pt anode, Cu cathode, Q_{theor} = 2 F per mole of initial acid **1**.
[b] Calculated from the ^{1}H NMR spectroscopic data for the isolated mixture of the electrolysis products: I, based on initial acid **1**; II, based on reacted acid **1**.
[c] Electrolysis of the salt of acid **1**.

At the same time, it should be mentioned that the low rate of direct interaction of **1** with electrogenerated Cl_2 (Scheme 2) results in the partial loss of unreacted Cl_2 due to its evolution to atmosphere because of its comparatively low solubility in an aqueous solution of NaCl. To avoid this, we carried out the electrochlorination approximately under the same conditions, only replacing acid **1** by its salt (see Table 1, entry *8*): it was assumed that the efficiency of electrochlorination would be enhanced due to binding of HCl capable of interacting with the NH group of the pyrazole ring to form the pyrazolium salt with resulting deactivation of the lone electron pair of the nitrogen atom. Note that equilibrium *a* exists in an electrolyte solution (see Scheme 2) and is completely shifted to the left in the absence of salt **1**. However, in the presence of salt **1**, the equilibrium shifts to the right rapidly due to the fast ion reaction in step *b*. Owing to this reaction, HCl is efficiently bound (AzCOOH is weaker than HCl). Thus, the amount of unreacted and capable of volatilizing Cl_2 decreases.

Scheme 2



In addition, the yield of **2** could be increased due to accumulation of HClO (unlike volatile Cl_2) in solution, thus increasing the chlorination rate (see Scheme 2). However, all these expectations were in vain, because the yield of **2** even somewhat decreased even for the chlorination of salt **1** (see Table 1, *cf.* entries *4* and *8*). This is most likely due to the side process leading to the partial decomposition of target **2** (see below). For this reason, we returned again to the electrochlorination of acid **1** and 1.5-fold increased the quantity of passed electricity to compensate the decrease in the efficiency of electrochlorination due to volatilization of Cl_2. As a result (see Table 1, entry *9*), both the yield of acid **2** and conversion of acid **1** increased noticeably.

Summing up this part of the study, it should be noted that the electrochlorination of **1** under the optimal conditions (aqueous solution of 0.25 *M* **1**—4 *M* NaCl as electrolyte, T = 15 °C, Pt anode, J_a = 0.05—0.1 A cm^{-2}, Q = 2—3 F per mole of **1**) makes it possible to obtain **2** with 78—92% yields based on loaded **1**. It should be indicated for comparison that the chemical[3] method for synthesis of **2** (solvent AcOH, T = 70 °C) provides a substantially lower yield of 40%.

In further studies we considered the influence of the substituent nature in pyrazolecarboxylic acids on their reactivity in electrochlorination. For this purpose, we studied the electrochlorination of pyrazolecarboxylic acids with the electron-releasing (1-methylpyrazole-5-carboxylic acid (**3**), 1-methylpyrazole-3-carboxylic acid (**4**), and 1-ethylpyrazole-3-carboxylic acid (**5**)) and electron-withdrawing (1-methyl-3-nitropyrazole-5-carboxylic acid (**6**)) substituents (Table 2) affording products **7**—**10**.

It turned out that the replacement of H by Me at the nitrogen atom of the pyrazole ring on going from **1** to

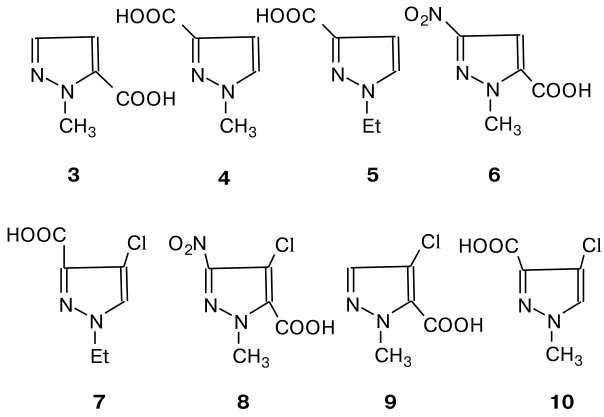


Table 2. Influence of the experimental conditions on the yield of 4-chloropyrazolecarboxylic acids during anodic chlorination of *N*-substituted pyrazolecarboxylic acids in an aqueous solution of NaCl[a]

Entry	Initial acid	Q/Q_{theor}	Conversion of acid (%)	Product	Yield[b] (%)	
					I	II
1	**3**	1.0	96.2	**9**	93	97
2	**4**	1.0	69.8	**10**	69	99
3	**5**	1.0	85.6	**7**	84	98
4	**5**	1.2	86.1	**7**	80	93
5	**5**	2.0	87.8	**7**	69	78
6[c]	**5**	1.0	89.6	**7**	77	86
7[c,d]	**5**	1.0	46.3	**7**	34	73
8[e]	**6**	1.0	23.8	**8**	4	16

[a] Pt anode, Cu cathode, Q_{theor} = 2 F per mole of the initial acid, acid concentration 0.25 mol L^{-1}, C_{NaCl} = 4 mol L^{-1}, T = 15 °C, j_a = 0.1 A cm^{-2}.
[b] Calculated from the ^{1}H NMR spectroscopic data for the isolated mixture of the electrolysis products: I, based on the initial acid; II, based on the reacted acid.
[c] Electrolysis of the salt of acid **5**.
[d] Electrolysis at 50 °C.
[e] The concentration of the acid is 0.125 mol L^{-1}.

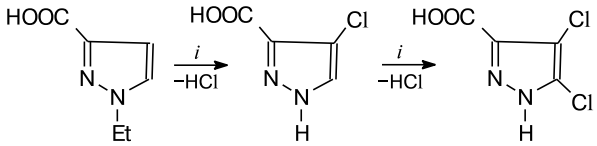
acids **3** and **4** increases* the yield of 4-chloropyrazolecarboxylic acids by ~20% (*cf.* Table 2, entries *1* and *2* and Table 1, entry *4*). Consequently, the introduction of an electron-releasing substituent into the pyrazole cycle facilitates electrochlorination. This conclusion agrees essentially (*cf.* Table 2, entry *3* and Table 1, entry *4*) with the data on electrochlorination of 1-ethylpyrazole-3-carboxylic acid **5**, although the regularities of this process have some specific features.

* The lower (69.4%) yield of 4-chloro-1-methylpyrazole-3-carboxylic acid is evidently due to its insufficient solubility in the electrolyte. In addition, this acid is a surfactant, most likely, which impedes electrochlorination by foaming of the solution during electrolysis.

Since published data on chemical chlorination of acid **5** are lacking, we specially studied this process. It turned out that the chlorination of acid **5** in AcOH at T = 70 °C, *i.e.*, under the conditions analogous to those of chlorination of acids **3** and **4**,[3] gives 4-chloro-1-ethylpyrazole-3-carboxylic acid (**7**). However, this process does not cease at the formation of the monochloro derivative (74% yield). According to the ^{1}H NMR spectroscopic data, the reaction mixture also contained 4,5-dichloro-1-ethylpyrazole-3-carboxylic acid (22% yield), which is the product of further chlorination of acid **7** with an excessive (compared to stoichiometry) amount of chlorine.

Using the ^{1}H NMR data, we could show that the chlorination of acid **5** proceeded following strictly successive mechanism. Passing of a precisely stoichiometric amount of chlorine through the solution resulted in the formation of product **7**, and 4,5-dichloro-1-thylpyrazole carboxylic acid was formed only after the complete conversion of the starting acid **5** (Scheme 3).

Scheme 3



Reagents and conditions: *i.* Cl_2, AcOH, T = 70 °C.

We somewhat improved the described[3] chemical chlorination of pyrazolecarboxylic acids. As a result, this process carried out in the presence of NaOAc allowed one to perform exact dosage of the required amount of passed Cl_2. The process was monitored through measuring the weight increase of the reaction mixture: the volatile reaction product HCl (see Scheme 1) reacted with NaOAc and transformed into NaCl. The use of NaOAc also made it possible to decrease the chlorination temperature by 10 °C. As a result, acid **7** was obtained in 80% yield, and the further chlorination of the reaction mixture afforded 4,5-dichloro-1-ethylpyrazole-3-carboxylic acid in 46% yield.

The same results were expected for the electrochlorination of acid **5** under the above presented optimal (for electrochlorination of **1**) conditions. However, the result was unexpected. After the theoretical quantity of electricity was passed, acid **7** was obtained (see Table 2, entry *3*) in 84% with a conversion of acid **3** of ~86%. An increase in the quantity of passed electricity by 1.2 and 2 times (see Table 2, *cf.* entries *3—5*) resulted only in an insignificant (by 1—2%) increase in the starting acid conversion but in a noticeable (by ~15%) decrease in the yield of product **7**. It should be emphasized that under these conditions, in spite of electrogenerated Cl_2 excess (in excess of passed

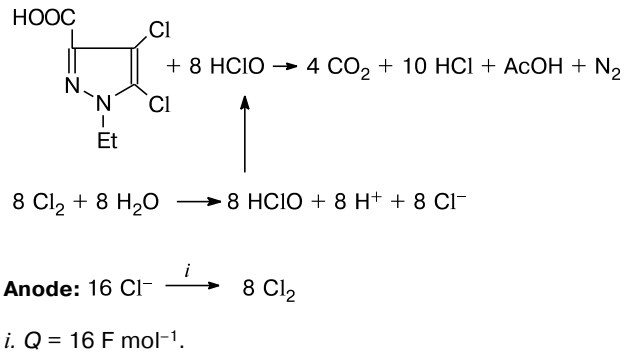
electricity), no 4,5-dichloro-1-ethylpyrazole-3-carboxylic acid is formed, unlike chemical chlorination. Using in electrochlorination of the salt instead of acid **5** (hoping to increase noticeably the conversion of acid **5** and yield of acid **7**) gave no desirable result (see Table 2, *cf.* entries *6* and *3*), although the conversion of the starting acid somewhat increased. Also, contrary to expectations, an increase in the temperature of the process from 15 to 50 °C (see Table 2, *cf.* entries *7* and *3*) decreased sharply both the conversion of acid **5** (by 40%) and the yield of acid **7** (by 50% based on the starting acid or by 25% based on the reacted acid).

An analysis suggests that upon the electrochlorination of acid **5**, along with the target process yielding product **7**, the side process of its pyrazole cycle destruction occurs. The destruction proceeds with lower or higher efficiency depending on the experimental conditions. Judging by the examples described,[4] the destruction of the pyrazole cycle could occur due to oxidation. Moreover, it is known[5] that *N*-halogenazoles (*N*-chloropyrazoles) have rather high oxidative ability. In our case, the corresponding *N*-chloro derivative is intermediately formed upon the electrochlorination of acid **5**. However, taking into account that in an aqueous medium the *N*-chloro derivative of acid **5** can easily be hydrolyzed to form HClO, this is the latter compound that seems to be the most probable oxidant.

The regularities of electrochlorination of acid **5** can be explained assuming that 4,5-dichloro-1-ethylpyrazole-3-carboxylic acid is formed along with product **7** *via* both chemical and electrochemical chlorination. However, under the electrochlorination conditions, the acid completely decomposes with the destruction of the pyrazole cycle under the action of HClO as an oxidant. It seems that acid **7** also partially undergoes this process, depending on the experimental conditions.

We wrote the assumed equation of decomposition of 4,5-dichloro-1-ethylpyrazole-3-carboxylic acid (Scheme 4) by HClO and estimated the amount Cl_2 required for this process to occur and the equivalent quantity of electricity (see Scheme 4) for the generation of the oxidant (HClO).

Scheme 4



i. Q = 16 F mol^{-1}.

Then a mixture of 4,5-dichloro-1-ethylpyrazole-3-carboxylic acid and acid **5** (83 and 17 mol.%, respectively) was subjected to electrochlorination (under the conditions of electrochlorination of acid **5**) with passing the one-fourth part of the quantity of electricity found from Scheme 4. It turned out that 55% (based on the taken mixture of acids) of 4,5-dichloro-1-ethylpyrazole-3-caboxylic acid remained after electrolysis under these conditions. Thus, the experimental results do not contradict the hypothesis explaining the regularities of electrochlorination of acid **3** in an aqueous solution.

Thus, the electrochlorination of pyrazole-3- and pyrazole-5-carboxylic acids with N-centered donor substituents occurs under considerably milder conditions compared to their chemical chlorination. Therefore, it seemed interesting to study the electrochlorination of pyrazolecarboxylic acids containing an acceptor substituent, whose chemical chlorination is impossible.* For this purpose, we studied the electrochlorination of 1-methyl-3-nitropyrazole-5-carboxylic acid **6**. It turned out that this process is principally possible and gives 4-chloro-1-methyl-3-nitropyrazole-5-carboxylic acid (**8**) (see Table 2, entry *8*) in 4% yield based on the starting acid **6**.

Summing up the work performed, we can say that we developed a convenient electrochemical method for preparation of 4-chloropyrazolecarboxylic acids. As compared to the chemical synthesis, this method provides the formation of target products under milder conditions (water as solvent, T = 15 °C) and in higher yields.

Experimental

Electrolysis was carried out in the galvanostatic regime using the B-5-8 dc source and a temperature-controlled glass cell with a porous glass membrane; Pt anode (S = 30 cm^2), Cu cathode. The coulometer designed at the Specialized Design Bureau (Institute of Organic Chemistry, Russian Academy of Sciences) was fitted in the electric circuit. A magnetic stirrer was used for stirring solution during electrolysis.

The starting substances pyrazole-3(5)-carboxylic acid (**1**), 1-methylpyrazole-3-carboxylic acid (**4**), and 1-methylpyrazole-5-carboxylic acid (**3**) were synthesized using known procedures[3]; 1-methyl-3-nitropyrazole-5-carboxylic acid **6** was synthesized according to a procedure described in Ref. 6, and 1-ethylpyrazole-3-carboxylic acid (**5**) was synthesized using the procedure described below.

The compounds synthesized by pyrazole electrochlorination were identified by ^{1}H NMR spectroscopy using the spectra of earlier synthesized reference samples for comparison (4-chloro-1-ethylpyrazole-3-carboxylic (**7**) and 4,5-dichloro-1-ethylpyrazole-3-carboxylic acids) or the spectra described[3] for compounds **10**, **8**, and **9**. The spectra were recorded with a Bruker AC-300 instrument, using DMSO-d_6 as a solvent, and chemical shifts were measured in the δ scale.

* Our attempts of chemical chlorination of 1-methyl-3-nitropyrazole-5-carboxylic acid with gaseous chlorine under the literature conditions[3] gave no corresponding chloro derivative.

Synthesis of 4-chloropyrazole-3(5)-carboxylic acid (2) by electrochlorination of pyrazole-3(5)-carboxylic acid (1) (Table 1, entry *4*). A 4 *M* aqueous solution of NaCl (100 mL), and compound **1** (2.80 g, 0.025 mol) were placed in the anodic compartment of the cell. Electrolysis was carried out with a current of 3 A at 15 °C, and Cl_2 slipped into the space above the anolyte during electrolysis (detected qualitatively by darkening of the paper impregnated with an aqueous solution of KI). After 2 F electricity per mole of the starting substance (Q = 4824 C) passed, the electrolysis was stopped, the reaction mixture was stored with stirring for 1 h, and the precipitate was filtered off, washed with water (2S20 mL), and dried at 100 °C. A white powder (2.49 g) obtained was a **2**—**1** (5 : 1) mixture according to the data (integral intensities of signals) of ^{1}H NMR spectroscopy: δ 7.9 (s, 1 H, H5(3)) and 6.7 (s, 1 H, H(4)), respectively. After the **2**—**1** mixture was separated, water was distilled off from the mother liquor, and the precipitate formed was extracted with Me_2CO (4×20 mL) and EtOH (4×20 mL). The product representing (according to the ^{1}H NMR data) a **2**—**1** (5.95 : 1.0) mixture was isolated additionally (0.8 g). The yield of acid **2** was 78% at the 84.9% conversion of **1**.

Electrochlorination of 1-methylpyrazole-5-carboxylic acid (3) (Table 2, entry *1*). A 4 *M* aqueous solution of NaCl (100 mL) and compound **3** (3.15 g, 0.025 mol) were placed in the anodic compartment of the cell. The electrolysis and isolation of products were carried out as for the electrochlorination of acid **1**. A white powder (3.24 g) was obtained, representing a mixture of acids **9**—**3** (25.3 : 1.0) according to the ^{1}H NMR data: δ 7.65 (s, 1 H, H(5)) and 6.80 (s, 1 H, H(4)), respectively. After the major product was separated, water was distilled off from the mother liquor, extraction was carried out (see the previous experiment), and the product, representing (^{1}H NMR data) a **9**—**3** (20.4 : 1.0) mixture, was additionally isolated (0.63 g). The yield of 4-chloro-1-methylpyrazole-5-carboxylic acid (**9**) was 93% at the 96.2% conversion of acid **3**.

Electrochlorination of 1-methylpyrazole-3-carboxylic acid (4) (Table 2, entry *2*). A 4 *M* aqueous solution of NaCl (100 mL) and compound **4** (3.15 g, 0.025 mol) were placed in the anodic compartment of the cell. The electrolysis and isolation of the products were carried out as for the electrochlorination of acids **1** and **3**. A finely dispersed white powder (2.47 g) was obtained. The powder represented a mixture of compounds **10**—**4** (10.0 : 1.0) according to the ^{1}H NMR data: δ 8.05 (s, 1 H, H(5)) and 6.70 (s, 1 H, H(4)), respectively. After the **10**—**4** mixture was isolated, water was distilled off from the mother liquor. The extraction gave additional 0.63 g of a mixture of compounds **10**—**4** (0.43 : 1.0) (^{1}H NMR data). The yield of product **5** was 69%, and the conversion of acid **4** was 69.3%.

Synthesis of 1-ethylpyrazole-3-carboxylic acid (5). Diethyl sulfate (48.8 g, 0.32 mol) was added with stirring to a solution of acid **1** (33.6 g, 0.3 mol) in a 20% aqueous solution of NaOH (140 mL) for 1 h at 30—35 °C. The reaction mixture was heated for 2 h at 80—85 °C and then cooled to room temperature and acidified with concentrated HCl to pH 1. A precipitate formed (1-ethylpyrazole-5-carboxylic acid) was filtered off, and the filtrate was extracted with $CHCl_3$ (4×100 mL). The organic phase was dried over $MgSO_4$, the solvent was distilled off under reduced pressure, and compound **3** (18.5 g) was obtained with an admixture of 1-ethylpyrazole-5-carboxylic acid. The product was recrystallized from Pr^iOH, and 1-ethylpyrazole-3-carboxylic acid was obtained (9.8 g, 23%), m.p. 176—177 °C. Found (%): C, 51.52; H, 5.65; N, 20.11. $C_6H_8N_2O_2$. Calculated (%): C, 51.43; H, 5.71; N, 20.00. ^{1}H NMR, δ: 1.38 (t, 3 H, CH_3, J = 7.0 Hz); 4.18 (q, 2 H, CH_2, J = 7.2 Hz); 6.71 (d, 1 H, H(4), J = 1.9 Hz); 7.81 (d, 1 H, H(5), J = 1.9 Hz). ^{13}C NMR, δ: 15.35 (qt, CH_3, J = 131.0 Hz, J = 4.0 Hz); 47.00 (tq, CH_2, J = 141.0 Hz, J = 4.7 Hz); 143.10 (dd, C(3), J = 11.0 Hz, J = 3.0 Hz); 108,34 (dd, C(4), J = 180.0 Hz, J = 8.8 Hz); 130.92 (ddt, C(5), J = 193.0 Hz, J = 9.0 Hz, J = 2.6 Hz) 163.32 (s, COOH).

Synthesis of 4-chloro-1-ethylpyrazole-3-carboxylic acid (7) by chemical chlorination of 1-ethylpyrazole-3-carboxylic acid (5). ***A (in the presence of NaOAc).*** Gaseous Cl_2 was passed through a solution of compound **5** (18.8 g, 0.134 mol) and NaOAc (12.1 g) in AcOH (200 mL) at 60 °C with stirring until the weight was increased to 9.5 g. Then the reaction mixture was cooled to room temperature, and the precipitate formed was filtered off. The filtrate was concentrated by evaporation under reduced pressure to dryness, the residue was joined with the precipitate from filtration, and NaCl was washed off with water (2×40 mL). The product was dried at 100 °C. Compound **7** (18.6 g, 80%) was obtained, m.p. 176—177 °C. Found (%): C, 41.35; H, 4.11; Cl, 20.27; N, 16.09. $C_6H_7ClN_2O_2$. Calculated (%): C, 41.26; H, 4.01; Cl, 20.34; N, 16.04. ^{1}H NMR, δ: 1.38 (t, 3 H, CH_3, J = 7.1 Hz); 4.18 (q, 2 H, CH_2, J = 7.5 Hz); 8.10 (s, 1 H, H(5).). ^{13}C NMR, δ: 14.82 (qt, CH_3, J = 125.0 Hz, J = 3.6 Hz); 47.79 (tq, CH_2, J = 142.0 Hz, J = 4.4 Hz); 139.29 (d, C(3), J = 6.9 Hz); 110.69 (d, C(4), J = 5.7 Hz); 129.99 (dt, C(5), J = 195.8 Hz, J = 2.3 Hz); 161.80 (s, COOH).

B (in the absence of NaOAc). Gaseous Cl_2 was passed for 2 h through a solution of compound **5** (14.0 g, 0.1 mol) in AcOH (150 mL) at 70 °C with stirring. The products were isolated as indicated above (see item ***A***). A white powder obtained (17.55 g) was a mixture of compound **5** and 4,5-dichloro-1-ethylpyrazole-3-carboxylic acid (1 : 0.3) according to the ^{1}H NMR data: δ 8.10 (s, 1 H, H(5)) and 4.20—4.15 (q, 2 H, CH_2) for the total signals of 4-chloro-1-ethylpyrazole-3-carboxylic acid and 4,5-dichloro-1-ethylpyrazole-3-carboxylic acids, respectively. The yield of compound **7** was 74%, and that of 4,5-dichloro-1-ethylpyrazole-3-carboxylic acid was 22.2%.

Synthesis of 4,5-dichloro-1-ethylpyrazole-3-carboxylic acid by chemical chlorination of 4-chloro-1-ethylpyrazole-3-carboxylic acid (7). Gaseous Cl_2 was passed through a solution of compound **5** (1.74 g, 0.01 mol) and NaOAc (1.23 g) in AcOAc (20 mL) at 60—70 °C with stirring until the weight increase reached 0.71 g. The reaction mixture was stirred for 0.5 h more and cooled, and the solvent was distilled off under reduced pressure. The residue was washed with water (2×3 mL) and dried. 4,5-Dichloro-1-ethylpyrazole-3-carboxylic acid was obtained (1.44 g) with a minor admixture of 4-chloro-1-ethylpyrazole-3-carboxylic acid (according to the ^{1}H NMR data). The product was recrystallized from 36% aqueous Pr^iOH. 4,5-Dichloro-1-ethylpyrazole-3-carboxylic acid was obtained (0.86 g). The yield was 69%, m.p. 165—166 °C. Found (%): C, 34.37; H, 2.91; Cl, 33,85; N, 13.45. $C_6H_6Cl_2N_2O_2$. Calculated (%): C, 34.45; H, 2.86; Cl, 33,97; N, 13.40. ^{1}H NMR, δ: 1.32 (t, 3 H, CH_3, J = 7.0 Hz); 4.20 (q, 2H, CH_2, J = 7.0 Hz). ^{13}C NMR, δ: 14.08 (qt, CH_3, J = 125.0 Hz, J = 4.4 Hz); 45.96 (tq, CH_2, J = 138.0 Hz, J = 4.3 Hz); 138.36 (s, C(3)); 109.70 (s, C(4)); 125.78 (t, C(5), $^3J_{C(5)-NCH_2}$ = 2.7 Hz); 161.10 (s, COOH).

Synthesis of 4-chloro-1-ethylpyrazole-3-carboxylic acid (7) by electrochlorination of 1-ethylpyrazole-3-carboxylic acid (5) (using entry *4* in Table 2 as an example). A 4 *M* aqueous solution

of NaCl (100 mL) and compound **5** (3.5 g, 0.025 mol) were placed in the anodic compartment of the cell. The electrolysis and isolation of the products were carried out as for the electrochlorination of acids **1**, **3**, and **4**. A white powder (3.53 g) obtained was a mixture of compounds **7—5** (7.2 : 1.0) according to the ^{1}H NMR data: δ 8.10 (s, 1 H, H(5)) and 6.71 (s, 1 H, H(4)), respectively. After a **7—5** mixture was isolated from the mother liquor, water was distilled off, extraction was carried out, and the product was additionally isolated (0.64 g), which represented (according to the ^{1}H NMR data) a **7—5** (2.56 : 1.0) mixture. The yield of product **7** was 69% at the 87.8% conversion of the starting acid **5**.

Electrochlorination of a mixture of 4,5-dichloro-1-ethylpyrazole-3-carboxylic acid (83 mol.%) **and 1-ethylpyrazole-3-carboxylic acid (5)** (17 mol.%)**.** A 4 *M* aqueous solution of NaCl (100 mL), 4,5-dichloro-1-ethylpyrazole-3-carboxylic acid (2.61 g, 0.0125 mol), acid **3** (0.35 g, 0.0025 mol), and Na_2CO_3 (0.8 g, 0.0075 mol) were placed in the anodic compartment of the cell. Electrolysis was carried out as indicated above (see previous experiment) at 50 °C, passing 4 F electricity per mole of 4,5-dichloro-1-ethylpyrazole-3-carboxylic acid (Q = 4825 C). After the end of electrolysis, the reaction mixture was stirred for 1 h, and the precipitate was filtered off, stirred for 1 h, washed with water (2×20 mL), and dried in air. A powder was obtained (0.46 g), which was (according to ^{1}H NMR data) 4,5-dichloro-1-ethylpyrazole-3-carboxylic acid with an admixture (7—8%) of unknown substances giving ^{1}H NMR signals at δ 4.0 and 1.3. The substances were not identified but, most likely, these signals belong to 1-(2-chloroethyl)-4,5-dichloropyrazole-3-carboxylic acid (4.0 ppm (m, 1 H, CHCl)) and 1-(2-dichloroethyl)-4,5-dichloropyrazole-3-carboxylic acid (1.3 ppm (s, 3 H, CH_3)). To exclude the influence of migration of substances on the escape of the products to the cathodic space, after isolation and washing of the precipitate, aqueous solutions were combined with a solution of the catholyte and acidified with concentrated HCl to pH 1, and water was distilled off under reduced pressure. The residue was extracted with Me_2CO (2×20 mL) and EtOH (2×20 mL). 4,5-Dichloro-1-ethylpyrazole-3-carboxylic acid (1.51 g) was obtained (^{1}H NMR data) with an admixture of 1-ethylpyrazole-3-carboxylic acid (1%) and 1-(2-chloroethyl)-4,5-dichloropyrazole-3-carboxylic and 1-(2-dichloroethyl)-4,5-dichloropyrazole-3-carboxylic acids (totally ~5%). According to the estimation by these data, after electrolysis 55% of 4,5-dichloro-1-ethylpyrazole-3-carboxylic acid remained (relative to the sum of the starting 4,5-dichloro-1-ethylpyrazole-3-carboxylic and 1-ethylpyrazole-3-carboxylic acids).

Electrochlorination of 1-methyl-3-nitropyrazole-5-carboxylic acid (6) (exemplified by entry *8* in Table 2). A 4 *M* aqueous solution of NaCl (100 mL) and compound **6** (2.14 g, 0.0125 mol) were placed in the anodic compartment of the cell. The electrolysis and isolation of products were carried out as described above, passing 2413 C of electricity (2 F per mole of the starting substance). A white powder was obtained (1.08 g), representing the starting acid **6** (^{1}H NMR data). After the product was isolated, water was distilled off from the mother liquor, extraction was carried out, and a mixture of compounds **6—8** (6.5 : 1.0) was additionally isolated (0.65 g). The molar ratio of the acids in the reaction mixture was determined from integral intensities of the signals from acid **4**: δ_H 7.30 (s, 1 H, H(4)) and total signals of **6** and **8**: δ_H 4.20 (s, 3 H, CH_3). The yield of acid **8** was 4%, and the conversion of acid **6** was 23.8%.

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