Electrosynthesis of pyrazole-4-carboxylic acids by oxidation of 4-formylpyrazoles on NiO(OH)-electrode in aqueous alkaline solution

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Electrochemical oxidation of di- and trisubstituted 4-formylpyrazoles on a Ni-anode in aqueous alkali led to the formation of the corresponding pyrazole-4-carboxylic acid in 60—90% yields. The yields of the target products depend on position of substituent in the pyrazole ring and are decreased in the following sequence of substituent at position 1 Me > Et > Ph, as well as when the aqueous medium was replaced with aqueous alcohol (50% Bu^{t}OH). Oxidation of 4-formylpyrazoles containing Me groups at the carbon atoms of the pyrazole ring led, to monoacids and also pyrazoledicarboxylic acids in small (1.5—14%) amounts; the latter were the oxidation products of the aldehyde and the Me groups.

Key words: electrosynthesis, undivided cell, nickel hydroxide electrode, 1,5-, 1,3-, 1,3,5-substituted 4-formylpyrazoles, 1,5-, 1,3-, 1,3,5-substituted pyrazole-4-carboxylic acids.

The interest to the search of new methods for the preparation of pyrazole-4-carboxylic acids is due to their wide use as the intermediate products in the synthesis of medicinal drugs for treatment of the Parkinson decease[1] and autoimmune diseases,[2] antibacterial agents,[3] and fungicides.[4—6]

One of the efficient approaches to the preparation of organic acids consists in the oxidation of the corresponding alcohols on a Ni-anode by galvanostatic electrolysis in aqueous alkaline medium. Under these conditions, the oxidant is NiO(OH), which is formed on the surface of the Ni-anode and self-regenerated in the course of the electrolysis. Earlier,[7] we have shown a principal possibility of the electrosynthesis of pyrazole-4-carboxylic acids in oxidation of 4-formyl-1,3,5-trimethylpyrazole to 1,3,5-trimethylpyrazole-4-carboxylic acid as an example.

Taking these data into account, in the present work we have studied the influence of the nature of substituents (Me, Et, Ph), their amount and position in the pyrazole ring on the efficiency of electrooxidation (EO) of 4-formylpyrazoles.

Results and Discussion

The process of EO of substituted 4-formylpyrazoles on the NiO(OH) electrode was performed in aqueous solution of NaOH under conditions similar to those described by us earlier.[7] Already in the first experiment, the electrolysis of 4-formyl-1,3-dimethylpyrazole (Table 1, entry *1*) led to the synthesis of 1,3-dimethylpyrazole-4-carboxylic acid in 66% yield (calculated based on the amount of the aldehyde used). A suggested mechanism of the process is given in Scheme 1.

From the data in Table 1, it follows that position of the Me group in the pyrazole ring considerably influences the yields of pyrazole-4-carboxylic acid. Thus, in the oxidation of 4-formyl-1,3-dimethylpyrazole the yield of the target product turned out to be 30% lower than that in the case of 4-formyl-1,5-dimethylpyrazole (*cf.* entries *1* and *2*). Replacement of the Me groups at the nitrogen atom of the pyrazole ring with the Et (*cf.* entries *3* and *4*) led to a slight (by ~8%) decrease in the yield of the acid. In order to verify this effect, we studied EO of 4-formyl-3,5-dimethyl-1-phenylpyrazole, which is poorly soluble in water, therefore, its electrolysis was carried out in 50% aqueous solution of Bu^{t}OH. Under the same conditions (for comparison of the data on oxidation of formylpyrazoles in aqueous and in aqueous-alcoholic media), we studied oxidation of 4-formyl-1,3,5-trimethylpyrazole. From the results of entries *5* and *6*, it follows that under comparable conditions replacement of the Me substituent at position 1 of the pyrazole ring with the Ph one decreases the yield of pyrazolecarboxylic acid nearly by one-half. It could be suggested that in this case, the increase in the electron-withdrawing properties of the pyrazole ring decreases the ability of the carbonyl group to oxidation.

The use of 50% aqueous solution of Bu^{t}OH decreases both the conversion of 4-formyl-1,3,5-trimethylpyrazole and the yield of the target product (*cf.* entries *3* and *5*), which was apparently due to the lower reaction temperatures (because of volatility of Bu^{t}OH) and lower concentrations of alkali (because of its lower solubility in

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Scheme 1

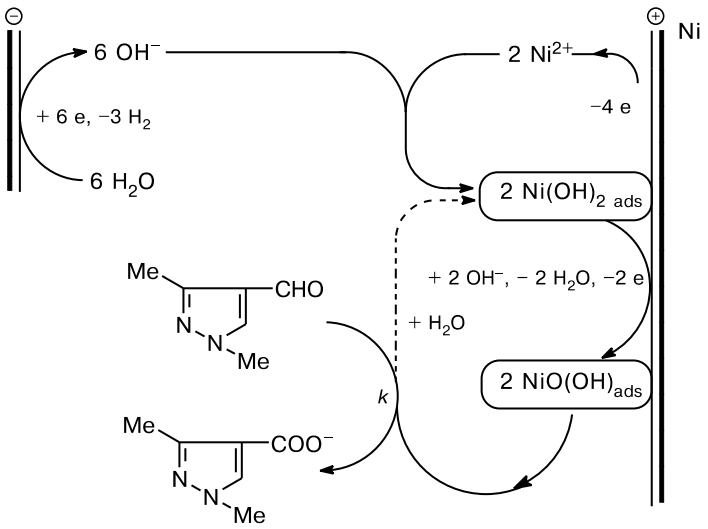
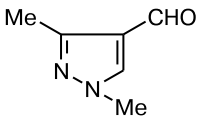
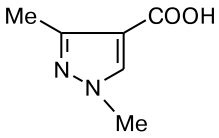
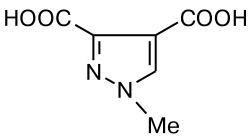
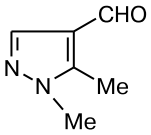
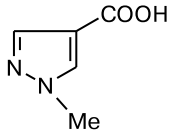
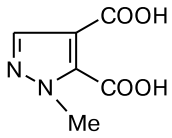
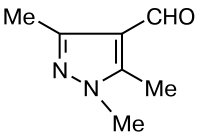
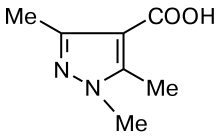
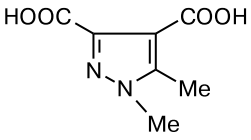
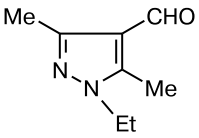
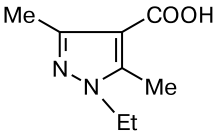
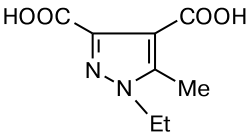
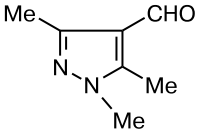
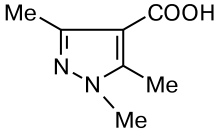
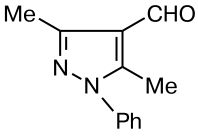
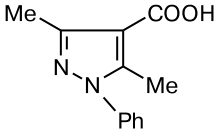
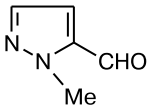
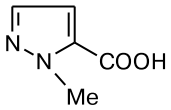


Table 1. Dependence of yields of pyrazolecarboxylic acids from the nature of formylpyrazoles in their anodic oxidation[a]

Entry	Starting formylpyrazole	Conversion of formylpyrazole (%)	Formed acid	Yield[b] of acid (%)	
				I	II
1		97.0		66.2	68.2
				4.8	4.9
2		100.0		97.5	97.5
				1.5	1.5
3		82.4		77.4	93.9
				1.7	2.1

(*to be continued*)

Table 1 (*continued*)

Entry	Starting formylpyrazole	Conversion of formylpyrazole (%)	Formed acid	Yield[b] of acid (%)	
				I	II
4		74.4		60.0	80.9
				14.1	19.0
5[c]		27.5		22.0	80.0
6[c]		14.2		14.0	98.6
7		100.0		97.8	97.8

[a] Conditions: Ni-anode, Ti-cathode, $C_{pyrazole}$ = 0.2 mol L^{-1}, C_{NaOH} = 1.0 mol L^{-1}, j_a = 6 mA cm^{-2}, T = 70 °C, $Q = 2\ F$ (mol of the starting formylpyrazole)$^{-1}$.

[b] Calculated based on the reacted formylpyrazole and the starting formylpyrazole, using the ^{1}H NMR spectroscopic data for the isolated mixture of the electrolysis products.

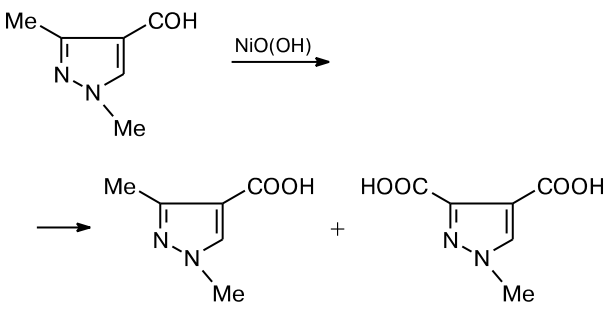
[c] Electrolysis was performed in 0.3 *M* KOH in 50% aqueous Bu^{t}OH, $C_{pyrazole}$ = 0.05 mol L^{-1}, j_a = 2.4 mA cm^{-2}, T = 50 °C.

Bu^{t}OH).* It cannot be excluded either that EO of aldehyde hindered the formation of associates of the aldehyde with the added organic solvent.[9] As a result, the major amount of the electricity passed was spent on the discharge of OH^- ions.

As to the position of the aldehyde group in the pyrazole ring, this factor, apparently, did not essentially influence the efficiency of EO of formylpyrazole (*cf.* entries *2* and *7*).

It is extremely interesting that the EO of 4-formylpyrazoles with Me group at the carbon atom of the pyrazole ring leads, besides the monoacids, to small amounts (2—14%) of pyrazoledicarboxylic** acids (see entries *1*—*4*), which are the oxidation products of both the aldehyde and the Me groups. For example, the EO of 4-formyl-1,3-dimethylpyrazole, probably, proceeds according to Scheme 2.

Scheme 2



However, it should be underscored that under these conditions the EO of 3,5-dimethylpyrazole did not lead to

* Earlier,[8] a decrease in the yields of the target acids when aqueous media were replaced with 50% aqueous Bu^{t}OH was observed by us in the electrooxidation of arylalkanols.

** According to the revised data, the formation of small amounts of pyrazoledicarboxylic acid (yield ~2%) was observed earlier during the EO studies[7] of 4-formyl-1,3,5-trimethylpyrazole. These results are given in Table 1 for comparison (entry *3*).

the formation of even trace amounts of the corresponding acids, whereas the similar electrolysis of 3(5)-methylpyrazole-5(3)-carboxylic acid was accompanied by the formation of pyrazole-3,5-dicarboxylic acid (the yield was 16% calculated based on the starting product).

Comparing these results with the data of entries *1—4* (see Table 1), we suppose that the oxidation of the Me group at position 3(5) of the ring occurs only in such a case, when a COOH group is formed in the first step of the oxidation of 4-formylpyrazole. This was a nontrivial observation, since until now the oxidation of organic compounds under such conditions was believed[10] to take place only at the groups capable of being adsorbed on the NiO(OH)-electrode (of the type —OH, —CHO, or $—NH_2$, but not a Me group at all).

In conclusion, a convenient method was suggested for the electrochemical preparation of pyrazole-4-carboxylic acids starting from 4-formylpyrazoles, which allows one to obtain the target products with higher yields than under chemical usual oxidation procedure (for example, the use of $KMnO_4$ gave 1,3-dimethyl- and 1,5-dimethylpyrazole-4-carboxylic acids[11] in 52 and 62% yields, respectively).

Experimental

Electrolysis was performed under galvanostatic conditions, using a B5-8 source of the direct current, in an undivided cell with a coating for thermostating, Ni-anode (S = 45 cm^2) and Ti-cathode (S = 20 cm^2). A coulometer constructed in the Design Office of the N. D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences was included into the electric circuit. In the course of the electrolysis, the reaction mixture was stirred with a magnetic stirrer, the temperature was maintained by a U-1 thermostat. Before starting the experiments, Ni-anode was activated according to the known procedure;[12] a preliminary electrolysis was performed in the solution containing 0.1 *M* $NiSO_4$, 0.1 *M* NaOAc, and 0.005 *M* NaOH, at j_a = 1 mA cm^{-2}, with a periodical alternation of polarization of the electrodes. This procedure is required for the formation on the surface of the Ni-anode of multi-layered coating containing NiO(OH).

4-Formyl-1,3-dimethyl- and 4-formyl-1,5-dimethylpyrazoles,[13] 4-formyl-1,3,5-trimethyl- and 4-formyl-1-ethyl-3,5-dimethylpyrazoles,[14] 4-formyl-3,5-dimethyl-1-phenylpyrazole,[15] 5-formyl-1-methylpyrazole,[16] and 3(5)-methylpyrazole-5(3)-carboxylic acid were synthesized according to the procedures described earlier.[17] The acids obtained were identified using ^{1}H NMR spectroscopy by comparison their spectra with the spectra of the authentic samples: the described in the literature 1-methylpyrazole-3,4-dicarboxylic acid and 1-methylpyrazole-4,5-dicarboxylic acid,[18] 1-ethyl-5-methylpyrazol- and 1,5-dimethylpyrazole-3,4-dicarboxylic acids[19] or obtained according to the known procedures 1,3-dimethylpyrazole- and 1,5-dimethylpyrazole-4-carboxylic acids,[11] 1,3,5-trimethylpyrazol-, 1-ethyl-3,5-dimethylpyrazol-, and 3,5-dimethyl-1-phenylpyrazole-4-carboxylic acids,[20] 1-methylpyrazole-5-carboxylic acid,[21] and pyrazole-3,5-dicarboxylic acid.[22]

^{1}H NMR spectra were recorded on a Bruker AC-300 spectrometer using DMSO-d_6 as a solvent.

1. **Electrooxidation of 4-formyl-1,3-dimethylpyrazole.** 4-Formyl-1,3-dimethylpyrazole (2.48 g, 0.02 mol) and 1 *M* aq. solution of NaOH (100 mL) were placed into a cell, the electrolysis was carried out using a 270 mA current at 70 °C. After 2 *F* (mol of the starting compound)$^{-1}$ (3860 C) of electricity was passed, the electrolysis was stopped, the reaction mixture was stirred for 0.5 h, then cooled to ~20 °C, and acidified with concentrated HCl (to pH 1). A precipitate formed was filtered off, washed with water (2×15 mL), and dried at 100 °C to obtain 1,3-dimethylpyrazole-4-carboxylic acid (1.72 g, 61.4%), which was identified by the m.p. 188 °C (*cf.* Ref. 11: m.p. 188—189 °C) and the ^{1}H NMR spectral characteristics. The mother liquor left after filtration off the precipitate was combined with the washings of the precipitate, water was evaporated under reduced pressure. The residue was extracted with Me_2CO (4×25 mL) and the solvent was evaporated to obtain a white powder (0.37 g), which, according to the ^{1}H NMR spectroscopic data was a mixture of 4-formyl-1,3-dimethyl-, 1,3-dimethylpyrazole-4-carboxylic acid and 1-methylpyrazole-3,4-dicarboxylic acid. Their molar ratio, 1 : 1.56 : 1.61, was determined from the integral intensities of the signals in the ^{1}H NMR spectrum for 4-formyl-1,3-dimethylpyrazole at δ 8.10 (s, 1 H, H(5)), 1,3-dimethylpyrazole-4-carboxylic acid at δ 7.90 (s, 1 H, H(5)), and 1-methylpyrazole-3,4-dicarboxylic acid at δ 8.44 (s, 1 H, H(5)). Based on these data, the yields of 1,3-dimethylpyrazole-4-carboxylic and 1-methylpyrazole-3,4-dicarboxylic acids were found to be 66.2 and 4.8%, respectively, the conversion of 4-formyl-1,3-dimethylpyrazole was 97%.

2. **Electrooxidation of 4-formyl-1,5-dimethylpyrazole.** 4-Formyl-1,5-dimethylpyrazole (2.48 g, 0.02 mol) and 1 *M* aq. solution of NaOH (100 mL) were placed into a cell and the electrolysis was carried out as indicated above. After the electrolysis and the product isolation were complete (see above), 1,5-dimethylpyrazole-4-carboxylic acid (0.20 g, 7.1%) was obtained. The acid was identified based on the m.p. 185 °C (*cf.* Ref. 11: m.p. 184—185 °C) and the ^{1}H NMR spectral characteristics. From the mother liquor (after separation of the main product), additional 2.70 g of the product was isolated (see above), which was (the ^{1}H NMR spectroscopic data) a mixture of 1,5-dimethylpyrazole-4-carboxylic acid and 1-methylpyrazole-4,5-dicarboxylic acid. Their molar ratio, 60 : 1, was determined based on the integral intensities of the signals for 1.5-dimethylpyrazole-4-carboxylic acid at δ 3.70 (s, 3 H, Me) and 1-methylpyrazole-4,5-dicarboxylic acid at δ 4.08 (s, 3 H, Me). Based on these data, the yields of 1.5-dimethylpyrazole-4-carboxylic and 1-methylpyrazole-4,5-dicarboxylic acid were 97.5 and 1.5%, respectively, with the conversion of 4-formyl-1,5-dimethylpyrazole being quantitative.

3. **Electrooxidation of 4-formyl-1,3,5-trimethylpyrazole.** 4-Formyl-1,3,5-trimethylpyrazole (2.76 g, 0.02 mol) and 1 *M* aq. solution of NaOH (100 mL) were placed into a cell and the electrolysis was carried out as indicated above. After the electrolysis and the product isolation were complete (see above), 1,3,5-trimethylpyrazole-4-carboxylic acid (2.17 g, 70.4%) was obtained. The acid was identified based on the m.p. 219 °C (*cf.* Ref. 20: m.p. 217.5 °C) and the ^{1}H NMR spectral characteristics. From the mother liquor (after isolation of the main product), additional 0.69 g of a white powder was isolated as indicated above, which according to the ^{1}H NMR spectroscopic data

was a mixture of 4-formyl-1,3,5-trimethylpyrazole, 1,3,5-trimethylpyrazole-4-carboxylic acid and 1,5-dimethylpyrazole-3,4-dicarboxylic acid. Their molar ratio, 7.8 : 4.6 : 1.0, was determined from the integral intensities of the signals for the starting aldehyde at δ 9.70 (s, 1 H, CHO), the overlapped signals of the aldehyde and 1,3,5-trimethylpyrazole-4-carboxylic acid at δ 3.65 (m, 3 H, Me), and the signal for 1,5-dimethylpyrazole-3,4-dicarboxylic acid at δ 3.84 (s, 3 H, Me). Based on these data, the yields of 1,3,5-trimethylpyrazole-4-carboxylic and 1,5-dimethylpyrazole-3,4-dicarboxylic acids were 77.4 and 1.7%, respectively, the conversion of 4-formyl-1,3,5-trimethylpyrazole was 82.4%.

4. **Electrooxidation of 4-formyl-1-ethyl-3,5-dimethylpyrazole.** 4-Formyl-1-ethyl-3,5-dimethylpyrazole (3.36 g, 0.02 mol) and 1 *M* aq. solution of NaOH (100 mL) were placed into a cell and the electrolysis was carried out as indicated above. After electrolysis was complete, the reaction mixture was acidified with conc. HCl (see above), water was evaporated under reduced pressure, the residue formed was extracted with Me_2CO (2×25 mL) and EtOH (2×25 mL) to obtain a white powder (3.9 g) containing (the ^{1}H NMR spectroscopic data) a mixture of 4-formyl-1-ethyl-3,5-dimethylpyrazole, 1-ethyl-3,5-dimethylpyrazole-4-carboxylic acid, and 1-ethyl-5-methylpyrazole-3,4-dicarboxylic acid. Their molar ratio, 1.83 : 4.35 : 1.0, was determined from the integral intensities of the signals for 4-formyl-1-ethyl-3,5-dimethylpyrazole at δ 4.00 (q, 2 H, CH_2), 1-ethyl-3,5-dimethylpyrazole-4-carboxylic acid at δ 4.10 (q, 2 H, CH_2), and 1-ethyl-5-methylpyrazole-3,4-dicarboxylic acid at δ 4.25 (q, 2 H, CH_2). Based on these data, the yields of 1-ethyl-3,5-dimethylpyrazole-4-carboxylic acid and 1-ethyl-5-methylpyrazole-3,4-dicarboxylic acid were 60 and 14.1%, respectively, the conversion of 4-formyl-1-ethyl-3,5-dimethylpyrazole was 74.4%.

5. **Electrooxidation of 4-formyl-3,5-dimethyl-1-phenylpyrazole.** 4-Formyl-3,5-dimethyl-1-phenylpyrazole (1.0 g, 0.005 mol), 50% aq. solution of Bu^tOH (100 mL), and KOH (1.68 g, 0.03 mol) were placed into a cell, and the electrolysis was carried out using a 108 mA current at 50 °C. After 2 *F* (mol aldehyde)$^{-1}$ of electricity was passed, the electrolysis was stopped, Bu^tOH was salted off the reaction solution by addition of solid NaCl with subsequent separation of the aqueous and organic fractions. The alcohol was evaporated from the organic fraction under reduced pressure. The residue obtained after the evaporation (unreacted starting aldehyde with NaCl impurities) was mixed with water (5 mL) and treated with $CHCl_3$ (2×10 mL). The organic extract was dried with Na_2SO_4 and the solvent was evaporated to obtain 4-formyl-3,5-dimethyl-1-phenylpyrazole (0.81 g) (identified by ^{1}H NMR spectroscopy). The aqueous fractions (after isolation of the aldehyde) were combined, acidified with conc. HCl (to pH 1), and extracted with $CHCl_3$ (3×25 mL). The extract was dried with Na_2SO_4 and the solvent was evaporated to obtain the product (0.20 g), which was (the ^{1}H NMR spectroscopic data) a mixture of 3,5-dimethyl-1-phenylpyrazole-4-carboxylic acid and 4-formyl-3,5-dimethyl-1-phenylpyrazole. Their molar ratio, 3.24 : 1.0, was determined based on the integral intensities of the signals for 3,5-dimethyl-1-phenylpyrazole-4-carboxylic acid at δ 2.35 (s, 3 H, Me) and 4-formyl-3,5-dimethyl-1-phenylpyrazole at δ 2.43 (s, 3 H, Me). Based on these data, the yield of 3,5-dimethyl-1-phenylpyrazole-4-carboxylic acid was 14%, the conversion of 4-formyl-3,5-dimethyl-1-phenylpyrazole was 14.2%.

6. **Electrooxidation of 5-formyl-1-methylpyrazole.** 5-Formyl-1-methylpyrazole (2.2 g, 0.02 mol) and 1 *M* aq. solution of NaOH (100 mL) were placed into a cell and the electrolysis was carried out as indicated above. After the electrolysis and the product isolation were complete (see entry *1*), 1-methylpyrazole-5-carboxylic acid (2.0 g, 79%) was obtained. The acid was identified based on the m.p. 221 °C (*cf.* Ref. 21: m.p. 221—222 °C) and the ^{1}H NMR spectral characteristics. Water was evaporated from the mother liquor (after separation of the main product), the residue formed was treated with Me_2CO (4×25 mL) to additionally isolate 0.45 g of 1-methylpyrazole-5-carboxylic acid (identification based on the m.p. and the ^{1}H NMR spectral characteristics). The yield of 1-methylpyrazole-5-carboxylic acid was 97.8%, with the conversion of the starting aldehyde being quantitative.

7. **Electrooxidation of 3(5)-methyl-5(3)-carboxylic acid.** 3(5)-Methyl-5(3)-carboxylic (0.64 g, 0.005 mol) acid and 1 *M* aq. solution of NaOH (100 mL) were placed into a cell and the electrolysis was carried out as indicated above (see entry *1*), passing 6 *F* (mol of the starting compound)$^{-1}$ (2895 C) of electricity. After the electrolysis was stopped, the reaction mixture was stirred for 30 min, then cooled to ~20 °C, acidified with conc. HCl (to pH 1), and water was evaporated at reduced pressure. The residue was extracted with Me_2CO (2×25 mL) and EtOH (2×25 mL), the solvent was evaporated to obtain a white powder (0.76 g), which, according to the ^{1}H NMR spectroscopic data, was a mixture of 3(5)-methyl-5(3)-carboxylic acid and pyrazole-3,5-dicarboxylic acid. Their molar ratio, 5.4 : 1.0, was determined based on the integral intensities of the signals for 3(5)-methyl-5(3)-carboxylic acid at δ 6.45 (s, 1 H, H(4)) and pyrazole-3,5-dicarboxylic acid at δ 7.05 (s, 1 H, H(4)). Based on these data, the yield of pyrazole-3,5-dicarboxylic acid was 16%, the conversion of 3(5)-methyl-5(3)-carboxylic acid was 17%.

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