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Electrochemical hydrogenation of 3-(methoxyphenyl)propenoic acids

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Electrosynthesis can successfully be used for double bond hydrogenation in 3-(methoxyphenyl)propenoic acids. The corresponding 3-(methoxyphenyl)propanoic acids were produced in a virtually quantitative yield under the conditions of both electrocatalytic hydrogenation at the Ni cathode modified by electrodeposited dispersed nickel in a DMF—H_2O mixture in the presence of AcOH and direct electroreduction using mercury and glassycarbon cathodes in DMF with Bu_4NClO_4 as the supporting electrolyte, although the mechanisms of these processes are different.

Key words: cinnamic acids, *trans*-3-(methoxyphenyl)propenoic acids, 3-(methoxyphenyl)propanoic acids, polarography, electrocatalytic hydrogenation, nickel cathode, direct electroreduction, mercury cathode, glassycarbon cathode.

3-(Methoxyphenyl)propanoic acids find use in the synthesis of cardiac pharmaceuticals[1] and antibiotics.[2] The known methods for their synthesis are based on reactions of the corresponding methoxybenzaldehydes with Meldrum´s acid[3] or malonic acid followed by hydrogenation of intermediate products over the catalyst Pd/C(10%).[2] The double bond of cinnamic acid derivatives is directly hydrogenated by the catalytic method[4] in an autoclave under hydrogen pressure (3 bar) in the presence of 10% Pd/C in ~80% yield.

In several cases, electrocatalytic hydrogenation (ECH) of unsaturated organic compounds at cathodes with a moderate hydrogen overvoltage competes successfully with heterogeneous catalytic hydrogenation, since ECH proceeds under mild conditions: at ambient temperature and atmospheric pressure and in non-aggressive media. Therefore, it seems topical to apply the ECH method to accessible *trans*-3-(methoxyphenyl)propenoic acids.

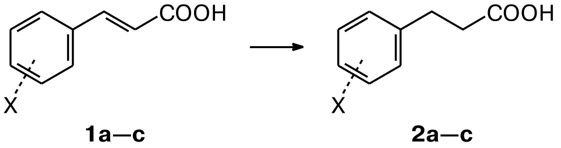
The ECH mechanism consists of the addition of electrochemically generated atomic hydrogen, which is adsorbed on the electrode surface,[5] to double bonds of an organic molecule. Unsaturated compounds can undergo hydrogenation either in the adsorbed state or in the near-electrode layer of the solution, depending on the material of the electrode, state of its surface, and composition of the medium.[6] For the successful ECH, it is essential that the potential of direct electroreduction (ER) of unsaturated compound would be substantially more negative than the potential of hydrogen evolution at the electrode used for hydrogenation. Note that ECH is not accompanied, as a rule, by the formation of dimeric products.

Earlier, in a detailed study of ECH of citral, we have proposed a method for preliminary modification of the Ni cathode surface by electrodeposited dispersed nickel (Ni_{disp}/Ni cathode),[7] which increased the catalytic activity of the cathode. A mixture of DMF—H_2O, KCl, and AcOH was an optimum medium[8,9] for the hydrogenation of the conjugated system of the C=C—C=O bonds. The products of complete hydrogenation of all double bonds, namely, 2-propylpiperidines,[10] were obtained under similar conditions by the ECH of *trans*-2-allyl-6-R-1,2,3,6-tetrahydropyridines (R = Me, All, Ph), *i.e.*, both terminal (allylic) and intracyclic nonconjugated double bonds are hydrogenated. Under these conditions, phenyl substituents and isolated sterically hindered double bonds are retained. The results obtained are generalized in the review.[11]

The purpose of this study is to extend the ECH method to compounds of another type: α,β-unsaturated carboxylic acids having the aromatic ring conjugated with the double bond. The second purpose is to compare the results of ECH and direct ER of these compounds at cathodes with high hydrogen overvoltage, such as mercury and glassy carbon (GC).

trans-3-(3-Methoxyphenyl)propenoic (**1a**), *trans*-3-(4-methoxyphenyl)propenoic (**1b**), and unsubstituted *trans*-3-phenylpropenoic (cinnamic, **1c**) acids were used as subjects of this study (Scheme 1).

Scheme 1



X = 3-MeO (**a**), 4-MeO (**b**), H (**c**)

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Results and Discussion

Bifunctionality is a specific feature of α,β-unsaturated carboxylic acids, *i.e.*, the following directions of the process are possible, in principle, during ER: hydrogenation of the double bond or formation of various dimeric products, hydrogen evolution from the carboxyl group and even its reduction to the carbonyl or hydroxymethyl group. The possibility of this or another direction depends mainly on the electrode material and composition of the medium. It should also be taken into account that α,β-unsaturated carboxylic acids themselves are proton donors.

Electrocatalytic hydrogenation

It has earlier been shown[7] that during ECH at the Ni_{disp}/Ni cathode in a medium DMF(40%)—H_2O and 0.1 *M* KCl in the presence of fourfold excess AcOH, the current of hydrogen evolution (I_w = 100 mA) is achieved at comparatively low cathodic potentials E_H ranging from −1.0 to −1.1 V (*vs* SCE). Since not only AcOH or H_2O but also 3-phenylpropenoic acids can be hydrogen sources in this case, we recorded the corresponding polarization curves (Fig. 1).

As follows from Fig. 1, upon the addition of 0.013 *M* acid **1c** to the supporting solution, the potential of hydrogen evolution decreases insignificantly compared to the supporting solution: I_w = 100 mA is achieved at E_H = = −1.29 V (curve *2*). At the same concentration of AcOH, E_H = −1.15 V (curve *3*), whereas in 0.052 *M* AcOH the same value of current is achieved at E_H = −0.85 V (curve *5*). This indicates that at the Ni_{disp}/Ni cathode AcOH exhibits its higher activity as a hydrogen source than acid **1c**.

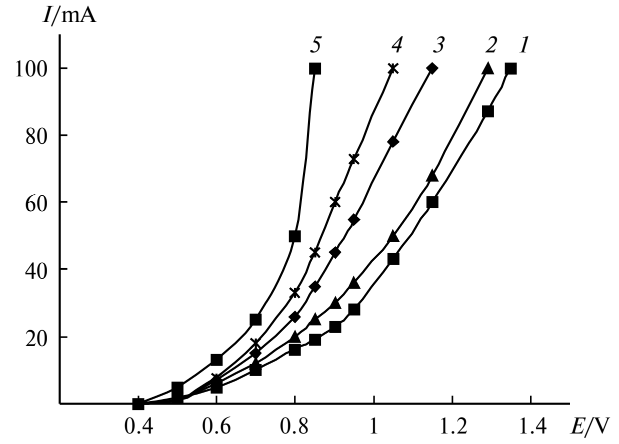


Fig. 1. Polarization curves of hydrogen evolution at the Ni_{disp}/Ni cathode (*E vs* SCE) for supporting electrolyte DMF(40%)—H_2O, 0.1 *M* KCl (*1*); with addition of 0.013 *M* 3-phenylpropenoic acid (**1c**) (*2*); with addition of 0.013 *M* AcOH (*3*); with addition of 0.026 *M* AcOH (*4*); with addition of 0.052 *M* AcOH (*5*).

Electrocatalytic hydrogenation of acids **1a—c** was carried out under the conditions proposed previously[11] as the optimal (DMF(40%)—H_2O, 0.1 *M* KCl) in the presence of fourfold molar excess of AcOH at the Ni_{disp}/Ni cathode. Unlike previous works, where ECH was carried out in the potentiostatic mode at E_{const} = −1.0 V ($I \approx$ 100 mA), in the present work we used the galvanostatic mode, I_{const} = = 100 mA ($E \approx -1.0$ V). The results of ECH of acids **1a—c** are presented in Table 1 (for GLC analysis, a mixture of acids was preliminarily esterified with diazomethane).

The quantity of electricity (*Q*) theoretically necessary for hydrogenation of one double bond is 2 F mol^{-1}, but a noticeable amount of starting acids **1a—c** along with target saturated acids **2a—c** was present in the mixtures even after an excess quantity of electricity (Q = 6 F mol^{-1}) was passed (entries *1—3*). Passing of a fourfold excess of electricity (Q = 8 F mol^{-1}) resulted in quite satisfactory result: hydrogenated acids were obtained in a yield of 97—98% (entries *4—6*).

Taking into account stoichiometry of the ethylene bond hydrogenation, we may assume that it is sufficient to use equimolar amount or a twofold excess of AcOH. Therefore, we carried out experiments on ECH of acid **1c** both in the absence of AcOH and at different contents of AcOH in solution. Samples were withdrawn during electrolysis.

As follows from Fig. 2, in the absence of AcOH (curve *1*) the content of the target product in the mixture after ECH does not exceed 40% even upon passing Q = 8 F mol^{-1} (conversion is also 40%).

In the presence of an equimolar amount of AcOH with respect to the starting acid **1c** in the electrolyzed solution (see Fig. 2, curve *2*), after ECH the content of the target product **2c** in the mixture increased almost to 80%. The

Table 1. Results of electrocatalytic hydrogenation of acids **1a—c**[a]

Entry	Acid	Q/F mol^{-1}	Composition of mixture after ECH (%)[b]	
			1a—c	**2a—c**
1	**1a**	6	9	91
2	**1b**	6	7	93
3	**1c**	6	15	85
4	**1a**	8	3	97
5	**1b**	8	3	97
6	**1c**	8	2	98
7	**1c**[c]	4	9	91
		8	0	100

[a] Conditions of ECH: C_{1a-c} = 0.013 mol L^{-1}, Ni_{disp}/Ni cathode, galvanostatic mode. Composition of the medium: DMF(40%)—H_2O, 0.1 *M* KCl, AcOH (C = 0.052 mol L^{-1}).
[b] The composition of a mixture of acids after ECH and esterification with diazomethane was determined by GLC.
[c] C_{1c} = 0.027 mol L^{-1}, C_{AcOH} = 0.1 mol L^{-1}.

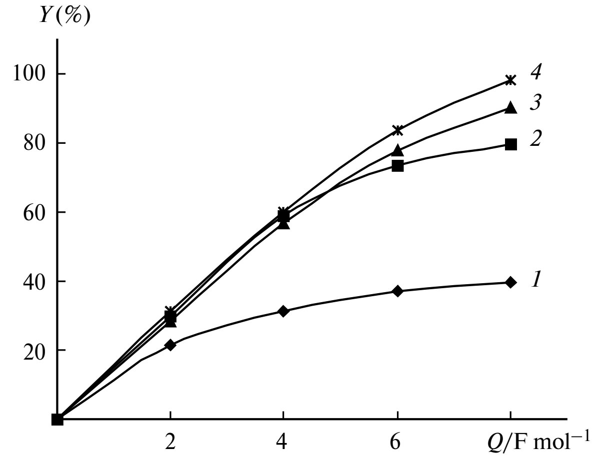


Fig. 2. Current yield (*Y*) of acid **2c** *vs* quantity of passed electricity (*Q*) at different compositions of the electrolyte at $C_{\mathbf{1c}}$ = = 0.013 mol L^{-1} in the absence of AcOH (*1*); at the equimolar amount, C_{AcOH} = 0.013 mol L^{-1} (*2*); and at twofold excess of AcOH, C_{AcOH} = 0.026 mol L^{-1} (*3*) and fourfold excess of AcOH, C_{AcOH} = 0.052 mol L^{-1} (*4*).

further increase in the AcOH concentration increases both the conversion and content of the target product **2c** in the mixture (curves *3* and *4*).

A comparison of the curves in Fig. 2 shows that the initial linear region of the curves extends with an increase in the AcOH concentration in the electrolyzate. In the presence of a fourfold molar excess of AcOH over acid **1c** in the electrolyzate, the linear character of this dependence is retained even upon passing $Q = 7$ F mol^{-1}. Thus, this excess of AcOH provides stability of the system for the ECH of acid **1c** even after the quantity of electricity considerably larger than the theoretically necessary value was passed.

The obtained results show (see Fig. 2) that for the ECH of acid **1c** the use of a fourfold excess of AcOH is sufficient, because the content of the target product in the mixture after ECH reaches 98% at ~98% conversion, which is very important for preparative electrolysis.

High solubility of acid **1c** in the DMF(40%)—H_2O system made it possible to perform ECH (see Table 1, entry *7*) also at a higher concentration in the solution ($C_{\mathbf{1c}}$ = 0.027 mol L^{-1}). It turned out that after passing $Q = 4$ F mol^{-1} the content of hydrogenated acid **2c** in the mixture upon electrolysis was 90.7% and that of the starting compound was only 9.3%.

Thus, taking into account high yield and good reproducibility of the results (at relatively simple renewal of the electrode surface before electrolysis), accessibility of the necessary equipment (galvanostatic mode), and low cost of the used reagents and cathodic material, the conditions proposed for ECH can be recommended for the hydrogenation of 3-arylpropenoic acids.

Direct electroreduction

The polarographic behavior of acids **1a—c** was studied in DMF with Bu_4NClO_4 as the supporting electrolyte at the mercury dropping electrode. It was shown that the ER of all three compounds proceeds in two stages (Table 2). The heights of the first and second waves are close to the one-electron level, which follows from the calculation by the Ilkovic equation.[12] Therefore, we may conclude that the corresponding radical anions (RA), whose subsequent reduction occurs at the second wave potentials, are formed at the first wave potential. Table 2 also contains the literature data[13] obtained in a an aqueous-ethanolic buffer medium.

As can be seen from Table 2, the half-wave potentials of acids **1a—c** differ insignificantly. Upon the addition of water to DMF or using of a proton-donating medium EtOH(50%)—H_2O, the first wave potentials somewhat decrease.

As known,[14] dimerization is a characteristic reaction of RA of activated olefins in media with low proton-donating activity. It is also asserted[15—18] that the ER of cinnamic acids at the mercury cathode in acidic and buffer media mainly affords dimers. Nevertheless, it is known[19] that acid **1c** is reduced with sodium amalgam to acid **2c** in 80—90% yield.

Under the conditions of direct ER, we carried out the preparative electrolysis of acid **1c** in DMF with 0.1 *M* Bu_4NClO_4 as the supporting electrolyte at the Hg cathode at the first wave potential ($E = -1.7$ V). During electrolysis, the current decreased rapidly to the background level after approximately $Q = 1$ F mol^{-1} was passed. The results of GLC analysis of the reaction mixture after standard treatment and esterification with diazomethane showed that the mixture contains ~50% starting acid **1c** and ~50% hydrogenated product **2c**. An attempt to continue electrolysis by increasing *E* to approximately −2.0 V demonstrated a noticeable increase in the current and then its gradual decrease to the background level. In this case, the

Table 2. First ($E^{I}_{1/2}$) and second ($E^{II}_{1/2}$) reduction waves of 3-phenylpropenoic acids at the mercury dropping electrode at different compositions of the supporting electrolyte. The values of $E_{1/2}$ were determined *vs* SCE

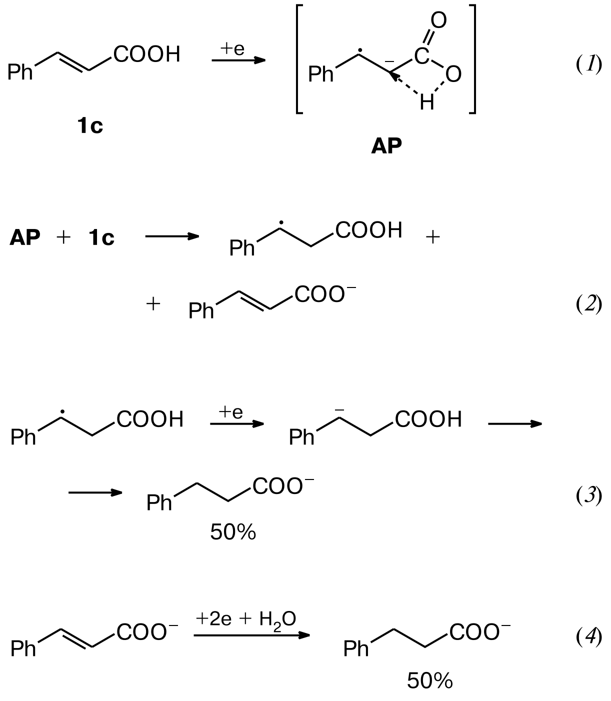
Compound	DMF, 0.1 *M* Bu_4NClO_4		H_2O(16%)—DMF, 0.1 *M* Bu_4NClO_4	EtOH(50%)—H_2O*
	$-E^{I}_{1/2}$/V	$-E^{II}_{1/2}$/V	$-E^{I}_{1/2}$/V	
1a	1.69	2.49	1.59	1.61
1b	1.75	2.48	1.71	1.67
1c	1.66	2.48	1.57	1.62

* Data of Ref. 13; conditions: acetate buffer, pH 6.7.

total amount of passed quantity is Q = ~2 F mol^{-1}. The single product of this stepwise ER is the corresponding hydrogenated acid **2c** (conversion 98—99%).

Probably, RA is formed at the first stage of electrolysis at $E = -1.7$ V (Scheme 2, reaction *1*) and is protonated by another molecule of acid **1c**, which is not only a depolarizer but also a proton donor (reaction *2*). As a result, the anion of the starting acid **1c** and the free radical species, which can be reduced at the first stage potential ($E^{\mathrm{I}} = -1.7$ V), are formed (reaction *3*). The anion of the starting acid should be electroreduced at a more negative potential (reaction *4*). It is known,[15] for example, that the anions are reduced, as a rule, at the potential 0.2—0.4 V more negative than that for the ER of non-dissociated molecules of the same acids. The possibility of formation of the electroactive anionic form of the acids in aqueous non-buffer media has been considered earlier.[13]

Scheme 2



At the same time, it should be taken into account that DMF initially contains 0.2—0.3% water (~0.16 mol L^{-1}), which is more than an order of magnitude higher than the substrate concentration. Although water molecules are bound by hydrogen bonds with DMF molecule, at this molar excess water still can be a proton donor (although weak) for anionic species formed upon electrolysis. Therefore, a complex of the anion of the starting acid with water can be formed or it can slowly be protonated during electrolysis. This explains the increase in the current with the stepped increase in the potential to -2.0 V during electrolysis. As a consequence, the starting unsaturated acid **1c** is completely consumed to form saturated product **2c**.

The ER of acids **1a** and **1b** at the Hg cathode in DMF with Bu_4NClO_4 as the supporting electrolyte affords the corresponding hydrogenated acids **2a** and **2b** as the single products of "stepwise" reduction, which does not contradict the proposed scheme. Similar results were obtained by the electrolysis of acids **1a—c** at the GC cathode.

Thus, we showed that, under these only formally "aprotic" conditions, the ER of acids **1a—c** affords no dimeric and oligomeric products, but only the electrochemical hydrogenation of the C=C bonds occurs. Note that the results of preparative electrolysis could not be predicted on the basis of polarographic studies.

Taking into account that the protonation of primary RA is the key stage of direct ER, we performed a series of electrolyses at the GC cathode at different compositions of the electrolyte (Table 3).

It turned out that the corresponding hydrogenated acids are also the major products in aqueous-organic (DMF—H_2O) or proton-donating (EtOH) media. Experiment *1* was performed at $E = -1.7$ V and stopped after the current dropped to the background level. It was found that in the presence of 16% H_2O about 2/3 of starting acid **1c** is reduced to form product **2c** at this potential. Experiments *2—4* were carried out at the specified initial $E = -1.7$ V and its subsequent stepwise increase to $E = -2.0$ V. As can be seen from a comparison of the results of entries *1* and *2*, an increase in the potential during electrolysis in the presence of H_2O also does not result in the complete consumption of the starting compound. Moreover, with an increase in the amount of H_2O in the electrolyzate (see Table 3, entries *2* and *3*) the conversion even decreases after the theoretically necessary quantity of electricity (Q = 2 F mol^{-1}) was passed, while hydrogen evolution is observed at $E = -2.0$ V.

The addition of a lithium salt to the electrolyzed solution of acid **1a** (see Table 3, entry *4*) results in the situation that the ER occurs only at $E_{.} = -1.7$ V, whereas with an increase in the potential to $E = -2.0$ V deposition of lithium begins on the electrode, and the conversion does not exceed 50% in this case.

For the ER of acid **1c** in the proton-donating solvent EtOH (entry *5*) (galvanostatic mode), a large amount of the starting acid remains in the electrolyzate in spite of the knowingly excessive amount of passed electricity. The process is apparently accompanied by hydrogen evolution from acid **1c** (entry *5*), while in entry *6* hydrogen is additionally evolved from AcOH, which strongly decreases conversion. Note that the measured value of $E_{.}$ does not exceed -1.55 V under these conditions (entries *5* and *6*).

As follows from the obtained experimental data, the direct ER of acids **1a—c** at the Hg and GC cathodes with high hydrogen overvoltage makes it possible to obtain target 3-phenylpropanoic acids **2a—c** in a virtually quantita-

Table 3. Results of direct electroreduction of acids **1a** and **1c** at the GC cathode at different compositions of the medium (supporting salt 0.1 *M* Bu_4NClO_4)

Entry	Acid	C/mol L^{-1}	Mode	Medium	Q/F mol^{-1}	Composition of mixture after ER (%)	
						Starting **1a** or **1c**	Products **2a** or **2c**
1	**1c**	0.013	$E_{const} = -1.7$ V	H_2O(16%)—DMF	1.5	26	74
2	**1a**	0.013	$E = -1.7 \to 2.0$ V	H_2O(16%)—DMF	2	16	84
3	**1a**	0.013	$E = -1.7 \to 2.0$ V	H_2O(30%)—DMF	2	22	78
4	**1a**	0.013	$E = -1.7 \to 2.0$ V	H_2O(10%)—DMF + + 0.1 *M* $LiClO_4$	2	49	51
5	**1c**	0.027	I_{const} = 70 mA	EtOH	3	61	39
6	**1c**	0.027	I_{const} = 70 mA	EtOH + 0.05 *M* AcOH	3	45	55

tive yield in DMF with Bu_4NClO_4 as the background electrolyte. It is important to emphasize that no dimerization and resinification occur under these conditions. The electrocatalytic hydrogenation of acids **1a—c** at the catalytically active cathode with the moderate hydrogen overvoltage (Ni_{disp}/Ni) in a medium of DMF(40%)—H_2O, 0.1 *M* KCl in the presence of fourfold excess of AcOH makes it possible to obtain the corresponding saturated acids **2a—c** in high yield.

Thus, we showed that the electrochemical method can quite successfully be used for the hydrogenation of the double bond of 3-(methoxyphenyl)propenoic acids, and the position of the MeO substituent in the aromatic ring exerts almost no effect on the results of both ECH and direct ER. The yield in the ECH and direct ER under the described conditions is close to the quantitative one, although the mechanisms of these processes are principally different. Evidently, the mechanism of direct ER of 3-phenylpropenoic acids requires detailed investigation using other electroanalytical methods.

Experimental

^1H NMR spectra were recorded on a Bruker AM 300 spectrometer with the working frequency 300 MHz in $CDCl_3$ using Me_4Si as an internal standard. GLC was carried out on an LKhM-80 instrument, column 2 m × 3 mm with 3% OV-17, stationary phase Inerton AW-DMCS. TLC was carried out on plates with the fixed layer of SiO_2 (Silufol UV-254) using a hexane—ether (3 : 2) mixture as an eluent. The melting point was determined on a Boetius heating stage.

Polarographic measurements were carried out on a PU-1 polarograph according to the three-electrode scheme of switching-on the cell: mercury dropping electrode (m = 1.05 mg s^{-1}, t = 0.8 s) and bottom mercury as an auxiliary electrode. A saturated calomel electrode (SCE) connected with the studied solution through a salt bridge filled with a solution of 0.1 *M* Bu_4NClO_4 in DMF was used as a reference electrode. Oxygen from the cell was removed by blowing with argon. Measurements were carried out at 25 °C.

Preparative electrochemical hydrogenation was carried out under argon atmosphere using a B5-50 current source or a P-5848 potentiostat. All electrolyzers were equipped with a porous glass membrane. Cathodes were as follows: a cylindrical nickel plate (visible surface ~0.9 dm^2, V_{cell} = 50 mL), bottom mercury with the working surface $S_w \approx 0.16$ dm^2 (V_{cell} = 15 mL), or a beaker of glass carbon (SU-2000), which served as an electrolyzer with $S_w \approx 0.20$ dm^2 (V_{cell} = 30 mL). A Pt net was used as an anode, and a saturated calomel electrode was a reference electrode. Prior to each electrolysis, the nickel cathode was activated by the electrodeposition of dispersed nickel from a solution of 0.5 *M* $NiCl_2 \cdot 6H_2O$ (analytically pure grade) on the surface cleaned, washed with water, and degreased with ether for 1 h at a cathodic current density of 0.1 A dm^{-2}, $E = -(0.60—0.70)$ V; then the electrode was washed with water. The surface of the nickel electrode was covered with a smooth black precipitate.

Commercial 3-(3-methoxyphenyl)propenoic (**1a**), 3-(4-methoxyphenyl)propenoic (**1b**), and 3-phenylpropenoic (**1c**) acids and Bu_4NClO_4 (Acros Organics) were used. Prior to distillation DMF was stored above K_2CO_3 and dried with molecular sieves 4 Å (after distillation anhydrous DMF contained 0.2—0.3% H_2O determined by the Fischer method). Commercial EtOH contained about 4% H_2O and was not additionally purified. Argon used for blowing was not additionally dried.

Electrocatalytic hydrogenation in the galvanostatic mode (general procedure). Electrolysis of 0.013 *M* solutions of acids **1a—c** was carried out at the Ni_{disp}/Ni cathode with 0.1 *M* KCl as the supporting electrolyte in 40% aqueous DMF (catholyte volume 50 mL) in the presence of 0.052 *M* AcOH at I = 100 mA (current density 0.11 A dm^{-2}, measured $E = -(0.9—1.1)$ V). Electrolysis was stopped after passing Q = 6 F mol^{-1} (0.12 A h) or 8 F mol^{-1} (0.16 A h). After the end of electrolysis, the solution was concentrated *in vacuo*, water was added, and the solution was acidified with 10% aqueous HCl to pH 2 and extracted with ether. The extract was washed with water and dried with $MgSO_4$. Then the solvent was distilled off *in vacuo*, and the residue was weighed. The weight of the extracted residue was ~90% of the weight of the starting acid. The residue was analyzed by TLC and ^1H NMR. A sample from the residue was methylated with diazomethane according to the known procedure.[20] A mixture of methyl esters of the starting acid and hydrogenated product was analyzed by TLC and GLC.

The ECH of a 0.013 *M* solution of acid **1a** in the presence of 0.026, 0.052, and 0.078 *M* AcOH was performed similarly with sampling during electrolysis. After passing Q = 2, 4, 6, and 8 F mol^{-1}, samples (2 mL each) of the electrolysis solution were taken without interruption of electrolysis. Electrolysis was ceased after passing Q = 8 F mol^{-1}. Each sample was treated as described above and analyzed by GLC.

Electroreduction at the mercury and glasscarbon cathodes at the controlled potential (general procedure). Electrolysis of 0.013 M solutions of acids **1a—c** was carried out with 0.1 M Bu_4NClO_4 as the supporting electrolyte in anhydrous DMF at E = –1.7 V for 20 min, and then the potential was increased to E = –2.0 V (as a whole, approximately Q = 2 F mol^{-1} was passed). After the end of electrolysis, the solution was worked up and analyzed according to the procedure described above.

Electroreduction at the glassycarbon cathode in the galvanostatic mode (catholyte volume 30 mL). Electrolysis of 0.027 M solutions of acid **1c** was carried out with 0.1 M Bu_4NClO_4 as the supporting electrolyte in EtOH and with an additive of 0.05 M AcOH, I = 70 mA (current density 0.35 A dm^{-2}, measured E = –(1.5—1.55) V) for 1 h. After passing Q = 3.0 F mol^{-1}, electrolysis was stopped, and the reaction mixture was worked up as described above.

3-(3-Methoxyphenyl)propanoic acid (2a), m.p. 42—44 °C (from hexane) (*cf.* Ref. 21: m.p. 43—45 °C). ^{1}H NMR ($CDCl_3$), δ: 2.70 (t, 2 H, $ArCH_2\underline{CH_2}$, J = 7.7 Hz); 2.95 (t, 2 H, $Ar\underline{CH_2}CH_2$, J = 7.7 Hz); 3.80 (s, 3 H, OMe); 6.73—6.85 (m, 3 H, H_{Ar}); 7.20—7.30 (m, 1 H, H_{Ar}).

3-(4-Methoxyphenyl)propanoic acid (2b), m.p. 94—96 °C (from hexane) (*cf.* Ref. 21: m.p. 98—100 °C). ^{1}H NMR ($CDCl_3$), δ: 2.65 (t, 2 H, $ArCH_2\underline{CH_2}$, J = 7.7 Hz); 2.92 (t, 2 H, $Ar\underline{CH_2}CH_2$, J = 7.7 Hz); 3.80 (s, 3 H, OMe); 6.85 (d, 2 H, $H_{Ar}(3)$, $H_{Ar}(5)$, J = 8.6 Hz); 7.13 (d, 2 H, $H_{Ar}(2)$, $H_{Ar}(6)$, J = 8.5 Hz).

3-Phenylpropanoic acid (2c), m.p. 44—46 °C (from hexane) (*cf.* Ref. 21: m.p. 47—49 °C). ^{1}H NMR ($CDCl_3$), δ: 2.70 (t, 2 H, $ArCH_2\underline{CH_2}$, J = 7.7 Hz); 3.0 (t, 2 H, $Ar\underline{CH_2}CH_2$, J = 7.8 Hz); 7.19—7.25 (m, 5 H, Ph).

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