Peculiarities of electroreduction of *trans*-2-allyl-6-methyl(allyl,phenyl)-1,2,3,6-tetrahydropyridines

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Electrochemical reduction of *trans*-2-allyl-6-R-1,2,3,6-tetrahydropyridines (R = Me, All, and Ph) on the mercury cathode in anhydrous DMF (with 0.1 *M* Bu_4NClO_4 as the supporting electrolyte) resulted in catalytic hydrogen evolution, while in the case of anhydrous DMF the electrochemical activity of the endocyclic double bond was dictated by the nature of the R substituent at the carbon atom neighboring the double bond. The electrocatalytic hydrogenation of the piperideines under study on the Ni (Ni_{disp}/Ni) cathode in 40% aqueous DMF in the presence of a tenfold excess of AcOH yielded the corresponding *trans*-2-propyl-6-R^1-piperidines (R^1 = Me, Pr, and Ph). Using *trans*-2,6-diallyl-1,2,3,6-tetrahydropyridine as an example, the conditions (with annealed copper as the cathode) for selective hydrogenation of the double bonds in allyl substituents with preservation of the endocyclic double bond were found.

Key words: *trans*-2-allyl-6-methyl(allyl,phenyl)-1,2,3,6-tetrahydropyridine, *cis*- and *trans*-2-allyl-6-phenylpiperidine, *trans*-6-methyl(propyl,phenyl)-2-propyl-1,2,3,6-tetrahydropyridine, *trans*-6-propyl-2-methyl(propyl,phenyl)piperidine, electrocatalytic hydrogenation, electroreduction.

The electrosynthetic approach is often used to perform complicated multistage transformations of organic compounds. For example, the electrochemical properties of a number of natural nitrogen-containing heterocycles and their synthetic analogs and also examples of the electrosynthesis of a large number of pharmacologically active compounds have been reported.[1]

Electroreduction[1,2] (ER) or reductive coupling,[3] including intramolecular cyclization,[4] of aromatic N-heterocycles on the Hg cathode results in the formation of the corresponding unsaturated heterocyclic compounds. Electrocatalytic reduction[5] of pyridine on cathodes activated with Raney Ni or Co yields piperidine.

It is known that the isolated double bond in the linear chain is electrochemically inert on the Hg cathode and on other cathodes with high hydrogen overvoltage but is subjected to hydrogenation on metals with low hydrogen overvoltage (Pt, Pd).[2] At the same time, the presence of an electron-withdrawing substituent at one of the C=C atoms or lengthening the conjugation chain makes direct ER of the C=C bond possible.[6] The double bonds neighboring the heteroatom, *e.g.*, in dihydropyrroles, are also easily reduced.[2]

We report herein the results of a study of the ER of *trans*-2-allyl-6-R-1,2,3,6-tetrahydropyridines (R = Me (**1a**), All (**1b**), and Ph (**1c**)) on various cathodes and clarify the effect of proton donors (H_2O and AcOH) on this process. Piperideines **1a—c** are generated on reductive *trans*-2,6-dialkylation[7] of pyridine and are the precursors of a number of 2,6-disubstituted alkaloids and their analogs.[8] These compounds contain various double bonds, terminal and endocyclic, along with the NH group. Our aim was to find routes for selective hydrogenation of such bonds.

Results and Discussion

We assumed that the direct ER of piperideines **1a—c** on the Hg cathode (with the high hydrogen overvoltage) would result in the reduction of the endocyclic double bond, while the terminal double bond would retain intact.

Electroreduction on the mercury cathode. The polarization curves for piperideine **1a** in anhydrous DMF with 0.1 *M* Bu_4NClO_4 as the supporting electrolyte up to the discharge of the supporting electrolyte (with bottom Hg as the cathode) show no increase in the electric current. Electrolysis of compound **1a** at the potential of discharge of the supporting electrolyte (E = −2.9 to −3.0 V relative to the saturated calomel electrode) yields a significant amount of tributylamine, which is the result of decomposition of the supporting

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salt. No hydrogenation product was found though ~80% of the starting compound was consumed. It must not be ruled out that piperideine **1a** reacts with labile organomercuric intermediates like $Bu_4N...Hg$, which can be responsible for resinification. Piperideine **1a** is also not reduced on solid electrodes (Cu and Ni) in anhydrous DMF.

Electrolysis of piperideine **1b** on the Hg cathode under the same conditions is possible at lower negative potentials ($E = -2.8$ to -2.9 V) and results in the formation of dimeric and oligomeric products (tributylamine has not been detected). The allyl substituent in position 6 of heterocycle **1b** appears to slightly stabilize the radical—anion (RA) intermediate, though it activates the endocyclic double bond. This favors radical reactions resulting in oligomerization.

The electrolysis of phenyl-substituted tetrahydropyridine **1c** under the same conditions occurs already at $E = -2.74$ V ($Q \approx 2$ F mol^{-1}) and results in the formation of reduction products of the heterocyclic double bond, which is a mixture of *cis*- and *trans*-2-allyl-6-phenylpiperidine (**2**) in a 5 : 7 ratio (in almost quantitative yield)), the allyl bond being intact (Scheme 1). The proposed isomerization mechanism was discussed in our previous communication.[9] The isomerization itself points to the participation of the phenyl substituent at the carbon atom neighboring the reaction center in the stabilization of RA generated. The material of the cathode, mercury, appears to play an essential role in the stabilization of the intermediate particles. This can favor their subsequent selective conversions.[10] Mercury grinding during electrolysis points to the formation of surface-active, possibly organomercuric, intermediates. The results of the ER of piperideine **1c** on Cu and Ni cathodes under the same conditions are the indirect corroboration of the participation of the cathode material in the electrochemical process, as the yield of the isomeric piperidines **2** does not exceed 30% (the ratio of *cis*- and *trans*-isomers is 3 : 5), the essential amount of dimeric and oligomeric products being generated.

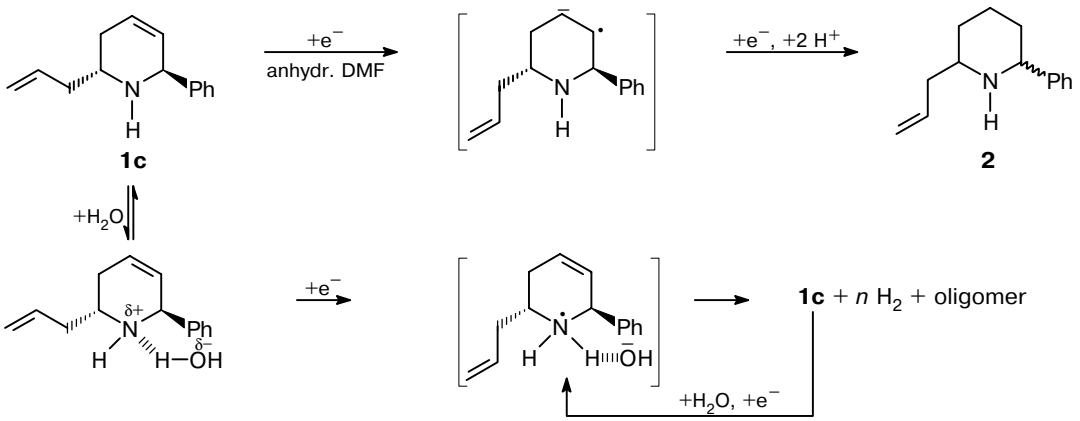
At the same time, the electrolysis of piperideine **1c** on the Hg cathode ($E = -2.75$ V) in the presence of even negligible (5%) amounts of water results in only traces of isomeric piperidines **2**. The same result was obtained for the ER of piperideine **1c** in 40% aqueous DMF with 0.1 M KCl as supporting electrolyte (under these conditions a significant electrolysis current occurs at a lower negative potential equal to -2.3 V).

Trying to clarify the reasons for such an unexpected effect of water additions on the ER, we studied the polarographic behavior of piperideines **1a—c** and their hydrogen chlorides in anhydrous and aqueous DMF. It should be noted that piperideines in an aprotic medium (anhydrous DMF) exist in the form of the base; however, they can form associates with water in its presence.

Compound **1a** is polarographically inert in anhydrous DMF (0.1 M Bu_4NClO_4 as the supporting electrolyte) up to the potentials of discharge of the supporting electrolyte ($E_{el} = -2.9$ V). Only a negligible shift of the discharge of the supporting electrolyte to the area of more positive values of the potential is observed in the solutions of **1b**. However, in the case of **1c** at its rather high concentration (>1 mmol L^{-1}), the beginning of the cathodic wave is observed at a potential *ca.* 30 mV more positive than E_{el}, and yet in this case the limiting current (i_{lim}) of the wave is overlapped by the discharge of the supporting electrolyte current. Nevertheless, we can conclude that electron transfer to molecules **1b** and **1c** probably proceeds owing to the activation of the endocyclic double bond by the substituent, to a greater extent occurring in the presence of the phenyl substituent in position 6 of heterocycle (**1c**).

It turns out that the wave at $E = -2.3$ V is observed for these compounds in aqueous DMF. Judging from the wave height dependence on the concentration of the depolarizer and the sharp increase of the wave height in solutions containing more than 40% H_2O, we can propose that this wave is analogous in nature to catalytic waves of hydrogen evolution that are observed in nonbuffer aqueous—alcohol solutions of pyridine and its homologs.[11]

Scheme 1



Hydrochlorides of piperideines **1a—c** in anhydrous DMF with Bu_4NClO_4 as the supporting electrolyte give distinct reduction waves with the following $E_{1/2}$ values: −2.1 (**1a · HCl**), −2.05 (**1b · HCl**), and −1.85 V (**1c · HCl**). The values of limiting current for these waves to some extent exceed the values corresponding to the one-electron diffusion process. It is important to underline that the addition of water to such solutions (up to 40—50%) practically does not affect (with regard to the change in viscosity) $E_{1/2}$ and i_{lim} of the waves for the compounds mentioned. However, in the case of electrolysis of **1b · HCl** on the Hg cathode (E_{start} = −2.05 V) in 40% aqueous DMF the hydrogen evolution does not stop after passage of an amount of electricity Q = 1 F mol^{-1}, whereas after passage of Q = 14 F mol^{-1} (E_{final} = −2.15 V) ~40% of **1b** is observed in the electrolysis solution. It is obvious that the electrochemical reduction of **1b · HCl** involves a one-electron transfer to the cation (protonated piperideine) to yield the corresponding radical, which either is decomposed to give hydrogen and free **1b**, or undergoes free radical conversions (including those with participation of the molecule of the starting unsaturated compound). Piperideine **1b** resulting from the corresponding hydrochloride in its turn catalyzes hydrogen evolution but at somewhat more negative potential.

It seems likely that the catalytic hydrogen evolution observed in the electrolysis of piperideine **1c** in aqueous DMF (see Scheme 1) occurs due to the reduction of the amine—water associate. In the case of 40% aqueous DMF (E = −2.3 V) the value of current does not fall even after passage of a marked amount of electricity (15 F mol^{-1}), and the free radical transformations therewith can result in practically complete resinification of **1c**.

Thus, the presence in the solution under study of H_2O molecules capable of changing the reactivity of both the starting molecule and RA due to the interaction with the free electron pair of the piperideine N atom reflects not only on the polarographic behavior (the formation of the hydrogen catalytic waves), but also on the results of the preparative electrolysis, which is more important.

The results presented are evidence of some activation of the endocyclic double bond of piperideines upon going from 2-allyl-6-methylpiperideine (**1a**) to 2-allyl-6-phenyl-substituted compound **1c**. However, the change in the state of the nitrogen-containing base molecule in the presence of the proton donor (or water) principally alters the direction of the process.

Electrocatalytic hydrogenation. Numerous examples of successful hydrogenation of various double bonds on metals with low hydrogen overvoltage (Pt, Pd) are reported. At the same time, the alteration in the direction of the process or in the depth of conversion, which means obtaining different products on the cathodes from various materials, is noted for pyridine[12] and oxoderivatives of piperidine.[13] There is a reason to believe that metals with moderate hydrogen overvoltage, which adsorb hydrogen more weakly (such as Cu and Ni) and which are more available and cheap, can be sufficiently effective in these processes.

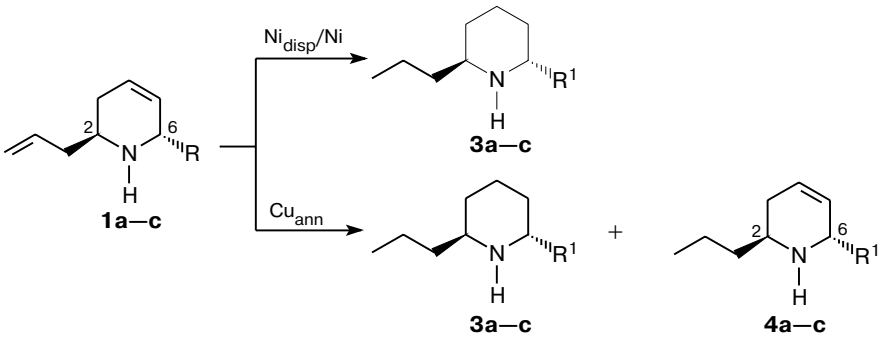
Previously[14,15] we have demonstrated the possibility of selective electrocatalytic hydrogenation (ECH) of double bonds on Cu and Ni cathodes using citral as a model compound. It was of interest to study the behavior of a series of piperideines **1a—c** under the same ECH conditions (aqueous DMF, 0.1 M KCl, in the presence of acetic acid). In should be noted that hydrogen evolution from AcOH on Cu and Ni cathodes occurs at much higher positive potentials than hydrogen evolution on the Hg cathode from hydrogen chlorides or associates of compounds **1a—c** with water (see above). For this purpose we used the procedure for the preliminary preparation of Cu and Ni electrode suggested previously (see Refs. 14 and 15, respectively) and the composition of the aqueous—organic solvent[14] that turned out to be optimum for the ECH of citral to citronellol.

Electrocatalytic hydrogenation of piperideines **1a—c** on the Ni electrode, which surface was covered with dispersed nickel (black), in an aqueous—organic solvent (40% aqueous DMF) in the presence of a tenfold molar excess of acetic acid relative to the starting bases **1a—c** (E = −1.0 V) appeared to result in the formation of *trans*-2-methyl-6-propylpiperidine (**3a**) (alkaloid (±)-epihydropinidine),[7,8] *trans*-2,6-dipropylpiperidine (**3b**), and *trans*-2-phenyl-6-propylpiperidine (**3c**) in almost quantitative yields (GLC data). Thus, under the experimental conditions both endocyclic and allyl double bonds in piperidines **3a—c** are hydrogenated to retain the *trans*-configuration of the substituents relative to the piperidine ring (Scheme 2).

The structure of piperidines **3a—c** was confirmed by the comparison of their ^{1}H and ^{13}C NMR spectra with those of the reference compounds **3a**,[7,8] **3b**,[16] and **3c**[9] obtained previously by catalytic hydrogenation on Raney Ni. It should be noted that in the case of ECH on the Ni_{disp}/Ni cathode the nature of the substituent in position 6 of the heterocycle has no effect on the yield of piperidines **3a—c** and the process is not accompanied by the generation of by-products.

In the case of the cathode from annealed copper the result is, however, not so unambiguous. Thus, a tenfold molar excess of AcOH relative to the starting piperideine **1a** results in the formation of a mixture of products with a double set of signals in the ^{13}C NMR spectrum. One set corresponds to the signals of piperidine **3a** (the product of total hydrogenation). In the second set, the characteristic signals of the allyl group (CH_2=CH) at 117 and 135 ppm are absent, but the signals of double-bonded C(4) and C(5) atoms in the ring at 124.17 and 131.4 ppm, respectively, are retained. This points to the fact that 6-methyl-2-propyl-1,2,3,6-tetrahydropyridine (**4a**) is the second component of the mixture. The presence of the multiplet at 5.6—5.8 ppm corresponding to the signals of the endocyclic double bond in the ^{1}H NMR spectrum also corroborates with this proposal.

Scheme 2



Similar results have also been obtained for piperideines **1b** and **1c**. It should be mentioned that ECH of amines **1a**—**c** on the Cu cathode as well as on the Ni cathode proceeds with retention the *trans*-configuration, as the ^{13}C NMR spectra of amines **4a**—**c** contain the signals of C(2) at 46—47 ppm and of C(6) at 47.47 (R = Me), 51.87 (R = Pr), or 55.56 ppm (R = Ph) that are close to the chemical shifts of C(2) and C(6) of structurally similar *trans*-2-allyl-6-R-1,2,3,6-tetrahydropyridines **1a**—**c** with an accuracy of ~0.5 ppm. It should be noted that the signals of C(2) and C(6) in *cis*-2-allyl-6-R-1,2,3,6-tetrahydropyridines are shifted downfield for 3—5 ppm:[8] the signals of C(2) are observed at 49—52 ppm and the signals of C(6) are registered at 51.16 (R = Me), 53.77 (R = All), or 60.21 (R = Ph) ppm.

The combination of ^{13}C and ^{1}H NMR spectroscopy and GLC data permits us to estimate the ratio of products in the mixtures and to argue that in all cases mixtures of the products of complete hydrogenation (**3a**—**c**) and of the products of hydrogenation of the allyl substituent with the double bond in the heterocycle preserved (**4a**—**c**) (Table 1) have been obtained, the latter product being noticeably dominant.

Obviously, the ECH mechanism involves the addition of nascent hydrogen, which is generated electrochemically at $E = -1.0$ V and is adsorbed on the cathode surface, to the multiple bonds of the unsaturated organic compound that is also adsorbed on the electrode surface. Table 1 shows that the alteration of the nature of the substituent in position 6 of the piperideine ring markedly affects the yield and the ratio of the products of ECH on the Cu cathode. With a tenfold molar excess of AcOH, the total yield of hydrogenation products decreases in the row of piperideines **1a**, **1b**, and **1c**.

Based on the ECH mechanism, this fact can be explained by the influence of both steric and electronic factors on the adsorption of piperideines **1a**—**c** on the electrode. In particular, the presence of the Ph substituent in position 6 of the piperideine ring hinders the effective interaction of the π-electrons of the All group in position 2 with the cathode surface.

We have previously shown the essential influence of the concentration of the acidic component (AcOH) on the effectiveness of ECH using citral as an example.[17] We have also found that ECH of citral on the annealed copper cathode occurs even in the absence of AcOH. Upon ECH of piperideine **1a** in the absence of AcOH and upon passage of 10 $F\cdot$ mol^{-1} of electricity, only half of the starting compound reacted to give **4a**, which is the product with the endocyclic double bond. The ^{13}C NMR spectrum of the mixture of electrolysis products contains a double set of signals. One of these sets corresponds to the starting piperideine **1a**. Another set has no characteristic signal of the C atoms of the allyl group at 117 and 136 ppm. A similar result was also obtained upon the ECH of Ph-substituted piperideine **1c**. It should be noted that in the absence of AcOH the products of complete hydrogenation **3a**—**c** are not produced and the process is not accompanied by resinification.

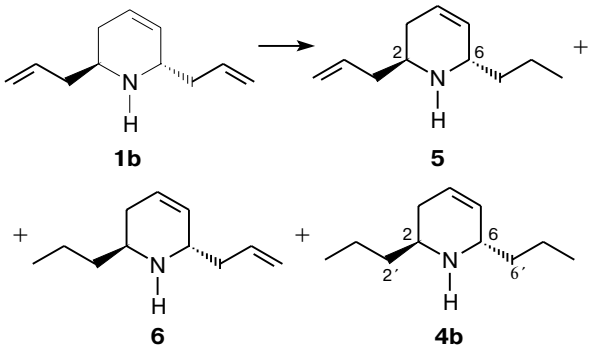
The ECH of diallylpiperideine **1b** in the absence of the acid besides the starting **1b** (22%) and dipropylpiperideine **4b** (44%) resulted in the formation of a mixture containing isomers **5** and **6** (33%), which are the products of hydrogenation of only one of the two allyl groups (the peak of the isomer mixture in the GL-chromatogram is situated between the peaks of dipropylpiperideine **4b** and the starting **1b**) (see Scheme 3).

Table 1. The total yield and the ratio of the products of the ECH of *trans*-2-allyl-6-R-1,2,3,6-tetrahydropyridines (**1a**—**c**) on the Cu cathode in the presence and in the absence of AcOH (40% aqueous DMF, 0.1 *M* KCl)

C_{AcOH}/C_{start} (мол.)	Piperideine	Residual **1** (%)	Yield* **3**+**4** (%)	Ratio** **3** : **4**
10 : 1	**1a**	—	90—95	2 : 3
	1b	—	60—65	3 : 7
	1c	—	45—50	1 : 3
0 : 1	**1a**	50	50	0 : 1
	1c	50	50	0 : 1

* According to GLC data.
** According to ^{13}C and ^{1}H NMR spectroscopy and GLC data.

Scheme 3



From a comparison of the results given in Table 1 it follows that the ratio of concentrations of AcOH and substrate **1a—c** in the catholyte is the primary factor that affects the selectivity of hydrogenation of the allyl double bonds in piperideines **1a—c** with the endocyclic double bond kept intact. Thus, we have performed a series of experiments to study the ECH of piperideine **1b** at various C_{AcOH}/C_{start} ratios. The results are given in Fig. 1. It should be noted that in the case of diallylpiperideine **1b** the GLC analysis of the ethereal catholyte extracts after ECH permits one to determine the ratio of all products. A change in AcOH content in the electrolysis solution significantly affects the composition of the ECH products. Thus, at an equimolar ratio of AcOH and the starting piperideine **1b**, the mixture was found to contain isomers **5** and **6** and piperideine **4b** in approximately equal amounts at ~60% conversion of the starting compound, whereas in the presence of a twofold excess of AcOH compound **4b** is the dominant component of the mixture after ECH. A threefold excess of AcOH gives piperideine **4b** in close to quantitative yield. A further increase in AcOH content in the catholyte results in a decrease of the yield of piperideine **4b** and in the appearance of the product of complete hydrogenation **3b** (see Fig. 1, curve *4*). It should be mentioned that at $C_{AcOH} : C_{\mathbf{1b}} > 4$ the ratio of **3b** and **4b** changes insignificantly, but their total yield falls.

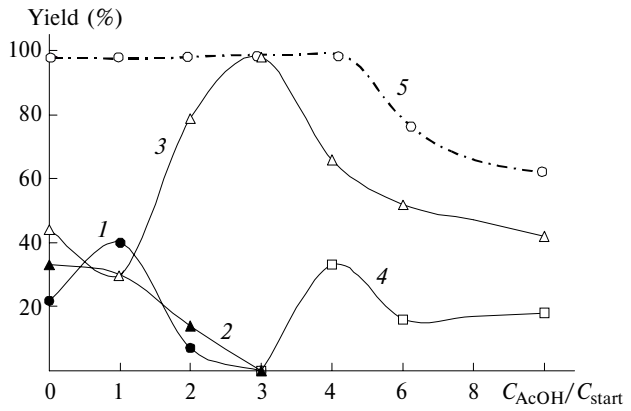


Fig. 1. The composition of the mixture after the ECH of *trans*-2,6-diallyl-1,2,3,6-tetrahydropyridine (**1b**) on the Cu cathode at various C_{AcOH}/C_{start} ratios in the electrolysis solution (0.1 *M* KCl as the supporting electrolyte, 40% aqueous DMF, C_{start} = 0.015 mol L^{-1}): (*1*) piperideine **1b**; (*2*) isomers **5** + **6**; (*3*) dipropylpiperideine **4b**; (*4*) piperidine **3b**; and (*5*) the total content of components **1b, 3b, 4b, 5,** and **6** in the mixture.

The results given in Fig. 1 point to the ambiguous role of AcOH in the ECH process. On the one hand, it is a source of hydrogen for hydrogenation; on the other hand, its interaction with the free electron pair of the N atom of the substrate results in the formation of an associate capable of being adsorbed on the electrode surface compared to the free amine. This is probably the cause of the sharp change in the ratio of the hydrogenation products upon the addition of an equimolar amount of AcOH (relative to **1b**) in the catholyte. A threefold molar excess of AcOH is the optimum for the formation of **4b**. It results in a decrease of the total yield of the hydrogenation products, which can be explained by the competitive adsorption of the acid itself on the cathode and by the exclusion of the organic substrate from its surface.

Electrolysis of piperideine **1b** with a fivefold load as compared to the previous experiments was performed at a $C_{AcOH} : C_{start} = 3$ ratio. The starting compound was completely spent after passage of $Q = 6.6\ F\ mol^{-1}$. As expected, piperideine **4b** appeared to be the main product (the yield was ~80% according to GLC data). The resulting mixture was found to contain 13% of isomeric allylpropylpiperideines **5** and **6** (the total current efficiency was 57% of theoretical). Piperideine **4b** was isolated by column chromatography on Al_2O_3 (eluent diethyl ether—hexane, 2 : 1). Its structure was confirmed by the ^{13}C and ^{1}H spectroscopy data. Treating **4b** with an ethereal HCl solution gave the corresponding hydrochloride. Its spectra also confirmed the structure of **4b**.

GLC analysis of specimens sampled in the process of electrolysis points to the subsequent hydrogenation of double bonds: at first only the isomeric allylpropylpiperideines **5** and **6** are generated and then product **4b** is formed. The further increase of the amount of product **4b** occurs in parallel with the decrease of the content of isomers **5** and **6**.

It was of interest to clarify whether ECH changes its direction when the starting piperideine **1b** is used in the form of hydrochloride **1b · HCl**. Taking into account the presence of the acid in the molecule of hydrochloride **1b · HCl**, the ECH was performed at $C_{AcOH} : C_{\mathbf{1b \cdot HCl}} = 2$, resulting in a mixture of dipropylpiperideine **4b** (48%) and isomers **5** and **6** (42%). Obviously, the conditions reported are also suitable for ECH of piperideine hydrochlorides after preliminary optimization of the AcOH concentration in the catholyte. The resulting data also point to the specific role of AcOH in the ECH process, as not only the amount of the proton donor necessary for hydrogenation, but also the nature of the acid, is important.

We propose that there is an optimum C_{AcOH}/C_{start} ratio for the selective hydrogenation of the allyl group in piperideines **1a** and **1c** containing one allyl substituent. The ECH of phenylpiperideine **1c** at $C_{AcOH}/C_{start} = 2$ resulted in the formation of the corresponding propylphenylpiperideine **4c** in 80% yield (with 80% conversion).

Thus, from the data obtained it follows that the electroreduction of *trans*-2-allyl-6-R-1,2,3,6-tetrahydropyridines **1a** (R = Me), **1b** (R = All), and **1c** (R = Ph) principally changes its direction with alteration of the electrolysis conditions (cathode material, medium composition, etc.). The nature of the substituent in position 6 of piperideine is especially important in the case of direct ER on the Hg cathode in DMF, as the quantitative reduction of the endocyclic double bond is observed only for the phenyl-substituted compound. Catalytic evolution of hydrogen occurs in aqueous—DMF solutions of piperideines **1a—c**.

The total hydrogenation of all the C=C bonds of the compounds under study occurs at ECH on the Ni_{disp}/Ni cathode with a tenfold excess of AcOH, the nature of the substituent in position 6 of the heterocycle exerting no marked effect on the effectiveness of the process. The selective hydrogenation of the allyl double bonds in piperideines with retention of the endocyclic double bond can be performed on the Cu cathode precisely following the predetermined optimum ratio of concentrations of AcOH and the starting piperideine. In this case the selectivity is probably connected with the steric factor, as the terminal double bonds are more accessible for hydrogenation than the endocyclic double bond. The ECH on the Cu cathode is more sensitive to both structural modifications of the molecule and alterations in the composition of the medium. The Cu cathode appears to offer more promise for working out the approaches for selective hydrogenation of the double bonds in the polyunsaturated compounds.

Experimental

^1H and ^{13}C NMR spectra were registered on a Bruker AC-200P spectrometer in $CDCl_3$. IR spectra were recorded on a UR-20 spectrophotometer. Mass spectra (EI, 70 eV) were taken on a Kratos MS-30 spectrometer. GLC was performed on an LKhM-80 instrument using 3 m × 3 mm columns with 5% XE-60 or OV-17 on Chromaton N-AW-DMCS. TLC was carried out on precoated Al_2O_3 (Alufol) plates in diethyl ether—hexane, 1 : 1.

Polarographic measurements were performed on PU-1 and PA-2 instruments using the tree-electrode technique of cell connection including the mercury dropping electrode ($m = 1.94$ and 1.12 mg s^{-1}; $t = 0.3$ and 0.78 s, respectively), bottom mercury as the anode, and the saturated calomel electrode as the reference electrode.

Preparative electrolysis at the controlled potential was performed using a P-5848 potentiostat in the cells ($V = 15$ and 50 mL) with a porous glass diaphragm under argon. Nickel and copper plates in the form of a cylinder ($S_{work} \approx 0.9$ dm^2) and bottom mercury ($S_{work} \approx 0.45$ dm^2) were used as the cathode. A platinum net was used as the anode. The saturated calomel electrode was used as the reference electrode. After electrolysis was over, the solution was diluted with water, alkalized to pH = 12, and extracted with diethyl ether. The extract was washed with water, dried over K_2CO_3, and analyzed by GLC and TLC.

Before distillation DMF was kept over K_2CO_3 and dried with molecular sieves 4 Å (dry DMF after distillation contained 0.2—0.3% of H_2O determined according to Fischer).

The starting *trans*-2-allyl-6-methyl-1,2,3,6-tetrahydropyridine (**1a**), *trans*-2,6-diallyl-1,2,3,6-tetrahydropyridine (**1b**), and *trans*-2-allyl-6-phenyl-1,2,3,6-tetrahydropyridine (**1c**) were synthesized by the procedure reported previously.[8,16] The hydrochlorides were obtained by treating amines **1a—c** with an ethereal solution of HCl, their characteristics matching those reported for **1a · HCl** [8], **1b · HCl** [16], and **1c · HCl**.[8]

Electroreduction of piperideines 1a—c on the mercury cathode. Electrolysis of 0.015 *M* solutions of amines **1a—c** was performed using 0.1 *M* Bu_4NClO_4 as the supporting electrolyte in anhydrous DMF (the catholyte volume was 15 mL) at $E = -2.8$ to -3.0 V for 2 h and treated according to the standard procedure. **Electroreduction of *trans*-2-allyl-6-phenyl-1,2,3,6-tetrahydropyridine (1c)** was performed at $E = -2.8$ V for 1 h ($Q = 2$ F mol^{-1}). After the standard treatment, the highly volatile compounds were evaporated *in vacuo* to give a mixture of *cis*- and *trans*-2-allyl-6-phenylpiperideine **2** in a 5 : 7 ratio (according to GLC and ^{13}C NMR spectroscopy data). The spectral characteristics were reported earlier.[9]

Electroreduction of *trans*-2,6-diallyl-1,2,3,6-tetrahydropyridine hydrochloride (1b · HCl) on the mercury cathode was performed in 40% aqueous DMF at $E = -2.05$ to -2.15 V ($Q = 14$ F mol^{-1}) for 2.5 h. After the standard treatment, the ethereal extract was found to contain ~40% of amine **1b** (from the starting **1b · HCl** according to GLC data).

Electrocatalytic hydrogenation of piperideines 1a—c on the nickel cathode. Before electrolysis, the nickel cathode was activated by electroprecipitation of dispersed nickel (nickel black) from 0.5 *M* $NiCl_2 \cdot 6H_2O$ solution on the conditioned surface for 1 h at a cathode current density of 0.1 A dm^{-2} and then washed with water. Electrolysis of 0.015 *M* solutions of piperideines **1a—c** was performed (the catholyte volume was 50 mL) in the presence of 0.15 *M* AcOH with 0.1 *M* KCl as the supporting salt (40% aqueous DMF) at $E = -1.0$ V ($I = 80$—100 mA, $Q \approx 10$ F mol^{-1}). The resulting mixture was treated according to the standard procedure.

Piperideines **1a—c** were converted to products with NMR spectra matching those described earlier for *trans*-2-methyl-6-propylpiperidine[7,8] **3a** ((±)–epidihydropinidine), *trans*-2,6-dipropylpiperidine[16] **3b**, and *trans*-2-propyl-6-phenylpiperidine[9] **3c**, respectively.

Electrocatalytic hydrogenation on the copper cathode. *Electrocatalytic hydrogenation of piperideines 1a—c on the copper cathode in the presence of a tenfold molar excess of AcOH.* Before electrolysis, the copper cathode was kept in the flame of the glass-blowing burner for 4 min and then washed with diluted HNO_3 (1 : 10) and water. Electrolysis of 0.015 *M* solutions of **1a—c** was performed with 0.1 *M* KCl as the supporting electrolyte (40% aqueous DMF) in the presence of AcOH (0.15 mol L^{-1}) (the catholyte volume was 50 mL) at $E = -0.9$ to -1.0 V ($I = 80$—100 mA, $Q \approx 10$ F mol^{-1}). The resulting mixture was treated according to the standard procedure. After evaporation of diethyl ether, the residue was analyzed by ^1H and ^{13}C NMR spectroscopy. Piperideine **1a** gave a mixture of amines **3a** + **4a**; **1b** yielded a mixture of amines **3b** + **4b**; and **1c** resulted in a mixture of **3c** + **4c**.

Mixture of *trans*-2-methyl-6-propylpiperidine (3a) and *trans*-6-methyl-2-propyl-1,2,3,6-tetrahydropyridine (4a). The ratio of amines **3a** : **4a** in the mixture was 2 : 3; the total yield was ~90%. ^{13}C NMR ($CDCl_3$, δ): 13.98 (**4a**, **3a**: CH_3 in Pr); 18.98 (**4a**: CH_3—$\underline{C}H_2$); 19.20 and 19.32 (**3a**: CH_3—$\underline{C}H_2$, NCH$\underline{C}H_3$); 20.65 (**3a**: C(4)); 21.36 (**4a**: NCH$\underline{C}H_3$); 30.19 (**3a**: C(3)); 31.31 (**4a**: Et—$\underline{C}H_2$); 32.46 (**3a**: C(5)); 35.80 (**3a**: Et—$\underline{C}H_2$); 37.97 (**4a**: C(3)); 45.75 (**3a**: C(2)); 46.77 and 47.47 (**4a**: C(2), C(6)); 50.34 (**3a**: C(6)); 124.17 (**4a**: C(4)); and 131.40 (**4a**: C(5)).

Mixture of *trans*-2,6-dipropylpiperidine (3b) and *trans*-2,6-dipropyl-1,2,3,6-tetrahydropyridine (4b). The ratio of amines **3b** : **4b** in the mixture was 2 : 3; the total yield was ~60 %. ^{13}C NMR ($CDCl_3$, δ): 14.08 (**4b**, **3b**: CH_3); 19.14 and 19.57 (**4b**: CH_3—$\underline{C}H_2$); 19.3 (**3b**: C(4), CH_3—$\underline{C}H_2$); 30.40 (**3b**: Et—$\underline{C}H_2$); 31.38 (**4b**: C(2′)); 35.99 (**3b**: C(3), C(5)); 37.34 and 37.75 (**4b**: C(3), C(6′)); 47.32 (**4b**: C(2)); 50.35 (**3b**: C(2), C(6)); 51.87 (**4b**: C(6)); 124.62 (**4b**: C(4)); and 129.81 (**4b**: C(5)).

Mixture of *trans*-2-propyl-6-phenylpiperidine (3c) and *trans*-2-propyl-6-phenyl-1,2,3,6-tetrahydropyridine (4c). The ratio of amines **3c** : **4c** in the mixture was 1 : 3; the total yield was ~45%. ^{13}C NMR ($CDCl_3$, δ): 13.88 (**4c**: CH_3); 13.99 (**3c**: CH_3); 18.67 (**4c**: CH_3—$\underline{C}H_2$); 19.49 (**3c**: C(3)); 20.02 (**3c**: CH_3—$\underline{C}H_2$); 29.45 (**3c**: C(4)); 31.55 (**4c**: Et—$\underline{C}H_2$); 33.35 (**3c**: Et—$\underline{C}H_2$); 34.46 (**3c**: C(5)); 38.21 (**4c**: C(3)); 46.42 (**4c**: C(2)); 51.62 (**3c**: C(2)); 54.02 (**3c**: C(6)); 56.22 (**4c**: C(6)); 126.42 (**4c**: C_p); 126.73 (**4c**: C(4)); 127.49 and 128.08 (**4c**: $C_{o,m}$); 126.53 and 128.18 (**3c**: $C_{o,m,p}$); 127.63 (**4c**: C(5)); 143.60 (**4c**: C_i); and 144.89 (**3c**: C_i).

ECH of piperideines 1a and 1c on the copper cathode in the absence of AcOH was performed as described for ECH in the presence of AcOH but at $E = -1.4$ to -1.5 V. After the standard treatment, the extracts were analyzed by GLC and TLC. The residue after evaporation of diethyl ether was analyzed by ^{1}H and ^{13}C spectroscopy. Piperideine **1a** gave a mixture of amines **4a**+**1a**; **1c** yielded a mixture of amines **4c**+**1c**.

Mixture of *trans*-2-allyl-6-methyl-1,2,3,6-tetrahydropyridine (1a) and *trans*-6-methyl-2-propyl-1,2,3,6-tetrahydropyridine (4a). The ratio of amines **1a** and **4a** in the mixture was 1 : 1; the total yield was ~100%. ^{13}C NMR ($CDCl_3$, δ): 13.96 (**4a**: CH_3 in Pr); 18.95 (**4a**: CH_3—$\underline{C}H_2$); 21.39 (**1a**, **4a**: CH_3); 31.05 (**4a**: C(3)); 31.36 (**1a**: C(3)); 38.01 (**4a**: Et—$\underline{C}H_2$); 40.03 (**1a**: =CH—$\underline{C}H_2$); 46.48 (**1a**: C(2)); 46.73 and 47.38 (**4a**: C(2), C(6)); 47.47 (**1a**: C(6)); 116.96 (**1a**: CH_2=); 123.85 (**1a**: C(4)); 124.13 (**4a**: C(4)); 131.23 (**1a**: C(5)); 131.44 (**4a**: C(5)); and 135.37 (**1a**: CH_2=$\underline{C}$H).

Mixture of *trans*-2-allyl-6-phenyl-1,2,3,6-tetrahydropyridine (1c) and *trans*-2-propyl-6-phenyl-1,2,3,6-tetrahydropyridine (4c). The ratio of amines **1c** : **4c** in the mixture was 1 : 1; the total yield was ~100%. ^{13}C NMR ($CDCl_3$, δ): 13.87 (**4c**: CH_3); 18.66 (**4c**: CH_3—$\underline{C}H_2$); 31.23 (**1c**: C(3)); 31.53 (**4c**: C(3)); 38.20 (**1c**: Et—$\underline{C}H_2$); 40.17 (**1c**: =CH—$\underline{C}H_2$); 45.89 (**1c**: C(2)); 46.40 (**4c**: C(2)); 56.21 (**1c**, **4c**: C(6)), 117.01 (**1c**: CH_2); 126.11 (**1c**: C(4)); 126.42 (**4c**: C(4)); 126.72 (**4c**: C_p); 126.78 (**1c**: C_p); 127.49, 127.60, and 128.06 (**1c**, **4c**: $C_{o,m}$, C(5)); 134.9 (**1c**: CH_2=$\underline{C}$H—); 143.4 (**1c**: C_i); and 143.6 (**4c**: C_i).

ECH of trans-2,6-diallyl-1,2,3,6-tetrahydropyridine (1b) on the copper cathode in the presence of a threefold molar excess of AcOH. Electrolysis of 0.56 g (0.069 mol) of piperideine **1b** was performed as described above in the presence of 0.21 *M* AcOH at $E = -0.9$ to -1.0 V for 8 h (I = 80—100 mA, Q = 6.6 F mol^{-1}). The specimens sampled during electrolysis were treated according to the standard procedure and analyzed by GLC and TLC. After the electrolysis was over, a mixture of *trans*-2,6-dipropyl-1,2,3,6-tetrahydropyridine **4b** (80% yield) and isomeric amines **5** and **6** (13%) was obtained. The admixture of monoallylated tetrahydropyridines **5** and **6** was separated on a column with Al_2O_3 (eluent diethyl ether—hexane, 2 : 1).

***trans*-2,6-Dipropyl-1,2,3,6-tetrahydropyridine (4b).** ^{1}H NMR (200 MHz, $CDCl_3$, δ): 0.8—1.1 (m, 6 H, CH_3); 1.2—1.6 (m, 10 H, —CH_2—); 1.65—1.85 (m, 1 H); 1.95—2.20 (m, 1 H); 2.75—2.95 (m, 1 H, H(2)); 3.25—3.35 (m, 1 H, H(6)); and 5.6—5.8 (m, 2 H, —CH=). ^{13}C NMR ($CDCl_3$, δ): 13.99 (CH_3); 19.09 and 19.56 (CH_3—$\underline{C}H_2$); 31.83 (C(2′)); 37.57, 38.19 (C(3), C(6′)); 47.07 (C(2)); 51.92 (C(6)); 124.5 (C(4)); and 130.46 (C(5)).

Mixture of *trans*-6-allyl-2-propyl-1,2,3,6-tetrahydropyridine (5) and *trans*-2-allyl-6-propyl-1,2,3,6-tetrahydropyridine (6). ^{13}C NMR ($CDCl_3$, δ): 14.0 (CH_3); 19.09 and 19.46 (CH_3—$\underline{C}H_2$); 31.55, 31.83, 37.57, and 38.19 (C(3), Et—$\underline{C}H_2$); 39.55 and 40.18 (=CH—CH_2 in All); 46.71 (C(2)); 51.78 (C(6)); 117.05 and 117.32 (CH_2=); 124.06 and 125.06 (C(4)); 129.17 and 130.0 (C(5)); and 135.21 and 135.73 (CH_2=CH—).

***trans*-2,6-Dipropyl-1,2,3,6-tetrahydropyridine hydrochloride (4b · HCl)** was obtained from amine **4b** and an ethereal solution of HCl, m.p. 156—158 °C (from diethyl ether—MeOH). MS, m/z (I_{rel} (%)): 167 $[M - HCl]^+$ (4), 160 $[M - C_3H_7]^+$ (2), 125 $[M - (HCl + C_3H_6)]^+$ (14), 124 $[M - (HCl + C_3H_7)]^+$ (100), 94 $[M - (HCl + C_3H_7 + NH_2CH_2)]^+$ (13), and 81 $[M - (HCl + 2\ C_3H_7\ )]^+$ (24). ^{1}H NMR (200 MHz, $CDCl_3$, δ): 0.9—1.1 (m, 6 H, CH_3); 1.35—1.9 (m, 7 H); 2.0—2.4 (m, 2 H); 2.4—2.65 (m, 1 H); 3.3—3.5 (m, 1 H, H(2)); 3.7—3.9 (m, 1 H, H(6)); 5.7—6.0 (m, 2 H, —CH=); 9.45 (br.s, 1 H, NH); and 9.9 (br.s, 1 H, NH). ^{13}C NMR ($CDCl_3$, δ): 13.67 (CH_3); 18.75 (CH_3—$\underline{C}H_2$); 26.81 (C(3)); 33.26 and 34.66 (Et—$\underline{C}H_2$); 49.34 (C(2)); 50.93 (C(6)); 123.77 (C(4)); and 124.67 (C(5)).

ECH of trans-2,6-diallyl-1,2,3,6-tetrahydropyridine hydrochloride (1b · HCl) on the copper cathode in the presence of a twofold molar excess of AcOH. Electrolysis of 0.012 *M* solution of **1b · HCl** was performed with 0.1 *M* KCl as the supporting electrolyte (40% aqueous DMF) in the presence of AcOH (0.025 mol L^{-1}) (the catholyte volume was 50 mL) at $E = -0.9$ to -1.0 V (I = 80—100 mA, $Q \approx 12\ F$ mol^{-1}). The standard treatment gave a mixture of *trans*-2,6-dipropyl-1,2,3,6-tetrahydropyridine **4b** (45%) and isomeric amines **5** and **6** (40%) (according to GLC and ^{13}C NMR data).

ECH of trans-2-allyl-6-phenyl-1,2,3,6-tetrahydropyridine (1c) on the copper cathode in the presence of a twofold molar excess of AcOH. Electrolysis of 0.012 *M* solution of **1c** was performed with 0.1 *M* KCl as the supporting electrolyte (40% aqueous DMF) in the presence of AcOH (0.024 mol L^{-1}) (the catholyte volume was 50 mL) at $E = -1.05$ to -1.55 V (I = 80—100 mA, $Q \approx 12\ F$ mol^{-1}). The standard treatment gave a mixture of *trans*-2-propyl-6-phenyl-1,2,3,6-tetrahydropyridine (**4c**) (80%) and the starting **1c** (20%) (according to GLC and ^{13}C NMR data).

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