Electrochemical Oxidation of Primary Alcohols to Aldehydes at the Nickel Hydroxide Electrode[1]

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Primary alcohols were oxidized to aldehydes at the nickel hydroxide electrode in an emulsion of water and a nonpolar organic solvent. Benzylic and allylic primary alcohols afforded good yields, whereas the oxidation of saturated primary alcohols was less satisfactory.

Aldehydes are valuable intermediates in organic synthesis. They can be prepared from primary alcohols with oxidizing agents such as dimethyl sulfoxide,[2] dipyridine-chromium(VI) oxide,[3] pyridinium chromate,[4] silver carbonate[5] and lead tetraacetate.[6] These reagents, however, have disadvantages: they are expensive or partially toxic and in the case of transition metal oxidants large scale conversions create waste disposal problems.

We found an electrochemical route to oxidize primary alcohols to aldehydes at the nickel hydroxide electrode. Primary alcohols are easily converted in alkaline aqueous solutions to carboxylic acids in high yields at the nickel hydroxide electrode.[7] Under these conditions no aldehyde is found. Benzylic type aldehydes can be obtained from the corresponding alcohols in a mixture of water *tert*-butanol; 33:66.[8]

In order to achieve the selective oxidation of primary alcohols to aldehydes we investigated biphase systems of water and nonpolar organic solvents. Direct extraction of the aldehyde into the organic phase during the reaction should prevent its further oxidation to the carboxylic acid. For the oxidation of the alcohols **1a–k** (Table) the reaction conditions have been optimized with regard to the kind of nonpolar solvent, pH value of the electrolyte and current density.

The results demonstrate that benzylic and allylic alcohols can be oxidized in high selectivity to the aldehydes. According to a control experiment the low yield of the aldehyde in the case of **1e** is probably due to a competing retro-aldol cleavage. Saturated alcohols are oxidized in lower yields and poorer selectivity to the aldehydes. This indicates that the aldehydes are presumably futher oxidized in their hydrate form. The different selectivities reflect the higher reactivity of saturated aliphatic aldehydes towards hydration.

The advantages of the nickel hydroxide electrode are simple reaction conditions (low cell voltage, undivided cell, constant current electrolysis with an inexpensive dc-power supply), low

Table.

$$\underset{\mathbf{1}}{\mathrm{R{-}CH_2OH}} \xrightarrow[-e^-]{\text{Ni-anode/OH}^-\ \text{biphasic system}} \underset{\mathbf{2}}{\mathrm{R{-}CHO}} + \underset{\mathbf{3}}{\mathrm{R{-}CO_2H}}$$

Alcohol 1	R	Reaction Conditions[a]	Current Consumption F/mol	Yield (%)[b]		mp (°C)[c]	
				2	3	found	reported[9]
a	Ph	A	3.4	66 (86)	4	137	137
b	$MeOC_6H_4$	A	3.8	(83)	6	249	250
c	2-furanyl	A	4.2	(78)	11	209	212
d	$C_6H_4CH{=}CH$	A	2.5	54 (75)[d]	4[e]	168	168[f]
e	$CH_3CH{=}CH$	B	3.0	(36)	(<1)	189	190
f	$(CH_3)_2C{=}CH$	A	2.8	(86)	4[g]	181	182
g	$(CH_3)_2C{=}CH(CH_2)_2(CH_3)C{=}CH$	C	3.3	83 (86)	(2)	116	116
h	$(CH_3)_2C{=}CH[(CH_2)_2(CH_3)C{=}CH]_2$	C	6.5	63 (70)	(<1)	105	106[11]
i	$CH_3(CH_2)_6$	D	3.5	15 (30)	(6)	80	80[h]
j	$CH_3(CH_2)_4$	D	4.4	(46)	(20)	104	104
k	$CH_3(CH_2)_3$	A	3.7	(32)	(39)	107	107

[a] Constant current electrolysis of 4.2 to 10 mmol at r.t. with intensive pumping in a circulation cell to form relatively stable emulsions. The nickel anode was activated prior to each electrolysis. For details of the activation see Ref. 10.

A. Beaker type circulation cell: 400 cm^2 nickel anode, 400 cm^2 steel cathode, 450 mL electrolyte volume, current: 0.2 A, 0.4 M aq. K_2CO_3/petroleum ether; (1 : 1);

B. Beaker type circulation cell, 0.2 A, 0.4 M aq. K_2CO_3/Et_2O : petroleum ether; (3 : 2 : 1);

C. "Swiss-roll" cell[12]: 1500 cm^2 nickel anode, 1500 cm^2 steel cathode, 500 mL electrolyte volume, current: 0.4 A, 0.4 M aq. K_2CO_3/petroleum ether (1 : 1), 0.1 g dodecanoic acid.

D. see A, additionally 0.1 g dodecanoic acid.

[b] Yield of isolated product after purification. Yields determined by GLC are given in parentheses.

[c] 2,4-Dinitrophenylhydrazone derivative.

[d] Additionally 14% dihydrocinnamic aldehyde was found.

[e] Cinnamic acid/dihydrocinnamic acid, 1 : 3.

[f] Phenylhydrazone derivate.

[g] 3-Methylcrotonic acid/3-methylbutanoic acid, 7 : 1.

[h] 4-Nitrophenylhydrazone derivate.

cost, easy scale-up and almost no waste problems. For the preparation of aromatic and α,β-unsaturated aldehydes the nickel hydroxide electrode can be considered as a good alternative to the reagents mentioned above.

In general for the oxidation of primary alcohols to aldehydes the following reaction conditions should be applied: The pH value of the electrolyte should be between 10 and 14. At lower pH values the activity of the nickel hydroxide electrode is insufficient for alcohol oxidation. A current density between 0.26 and 0.5 mA/cm^2 is favorable. Higher current densities lower the current yield due to a competitive discharge of hydroxyl ions to oxygen. Lower current densities increase the electrolysis time, which may lead to an unwanted aldol condensation of the aldehyde. The reaction conditions are optimal, when the alcohol is in the aqueous phase and the aldehyde in the organic phase. For example, using a petroleum ether/water emulsion, an 86% yield of benzaldehyde was found after a passage of 3.5 F/mol. In a diethyl ether/water emulsion, where most of the alcohol is dissolved in the organic phase, only a 50% yield of benzaldehyde resulted. If the alcohol is too lipophilic, the addition of surfactants allows a better conversion. Thus the addition of 0.1 g dodecanoic acid raised in the oxidation of **1g** the yield of citral from 43% to 86% under otherwise identical reaction conditions. The type of the electrolysis cell can also influence the yield. Geraniol was oxidized in the presence of dodecanoic acid to give a 31% yield of citral after 5.6 F/mol in the beaker type cell, whereas in the "swiss roll" cell[12] an 86% yield of citral was found after 3.3 F/mol.

Citral (2g); Typical procedure:

Geraniol (**1g**, 1.54 g, 10 mmol), petroleum ether (250 mL) and a 0.4 M aq. K_2CO_3 solution containing dodecanoic acid (0.1 g, 0.05 mmol) are placed in the "swiss roll" cell.[12] The mixture is electrolized at r.t. at a constant current of 0.4 A and a cell voltage of 1.7 to 1.8 V. After a consumption of 3.3 F/mol the organic phase is separated from the aqueous phase. The aqueous phase is saturated with NaCl, extracted with Et_2O (2 × 200 mL) and the combined organic phase is dried ($MgSO_4$). GLC-analysis (column: carbowax; temperature program: 100–200 °C with 8 °C/min; standard: octanol) indicates a yield of 86% citral and 5% unreacted geraniol. The solvent is evaporated under reduced pressure and the crude product is separated by flash chromatography on silica gel [eluent: petroleum ether/Et_2O; (15:1)] to give **2g**; yield: 1.3 g (83%). The alkaline solution is acidified with hydrochloric acid to pH = 1 and extracted with Et_2O (3 × 200 mL). The combined organic phase is dried ($MgSO_4$). Evaporation of the solvent leads to a mixture (0.13 g) of dodecanoic and geranoic acid. GLC analysis of the methyl ester reveals a ratio of dodecanoic acid to geranoic acid of 2:1, which corresponds to a 2% yield of geranoic acid. Geranoic acid was identified as its methyl ester by GLC-MS.

*Citral (**2g**):*

2,4-dinitrophenylhydrazone m.p. 116 °C (Lit.[9] mp: 116 °C).

^{1}H-NMR ($CDCl_3$): $\delta = 1.59–1.76$ (2s, 6H, 2 CH_3); 2.12–2.32 (m, 7H, CH_2CH_2, CH_3); 5.05 (m, 1H); 5.85 (dd, 1H, $J = 1.04$ Hz, 8.06 Hz); 9.97 (d, 1H, CHO, $J = 8.06$ Hz).[13]

*Geranoic acid Methyl Ester (**3g**):*

MS (70 eV): $m/z = 182$ (3%, M^+); 151 (7%, $M^+ - OCH_3$); 123 (18%, $M^+ - OCH_3 - CO$); 114 (30%, $M^+ - C_5H_8$); 83 (18%; $M^+ - C_5H_8OCH_3$); 69 (100%, $C_5H_9^+$); 41 (58%, $C_3H_5^+$).[14]

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