

Electrolysis for the benign conversion of renewable feedstocks^{*,**}

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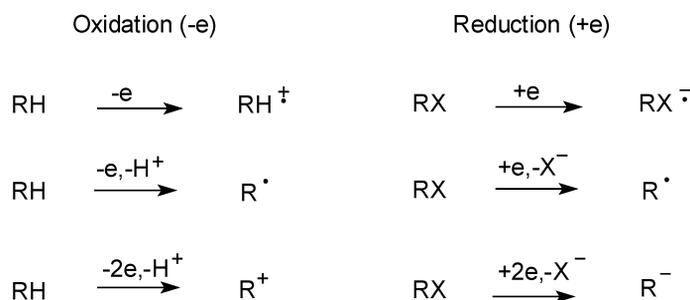
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Abstract: A large variety of C,C-bond forming reactions and functional group interconversions can be achieved by electron transfer. For the conversion of renewable feedstocks, electrolysis has been applied to coupling of radicals generated by anodic decarboxylation of fatty acids and carboxylic acids of carbohydrates. Furthermore, a derivative of L-gulonic acid is converted nearly quantitatively into L-xylonolacton. Trimethyl aconitate from trimethyl citronate is dimerized stereoselectively at the cathode in 72 % yield to a cyclic hexamethyl ester by an inter- and intramolecular Michael addition. Two acetoxy groups are added anodically to methyl conjugate (obtained from methyl linoleate) to form methyl (*E*)-9,12-diacetoxy-10-octenoate and methyl (*E*)-10,13-diacetoxy-11-octenoate in 85 % yield. The primary hydroxy groups in mono- and disaccharides can be oxidized to carboxylic acid groups in good yield and high selectivity by anodic oxidation with 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) as mediator. The results demonstrate that electrolysis is in good accordance with many of the 12 principles of green chemistry

Key words: green chemistry; electrosynthesis; oleochemistry; carbohydrates; trimethyl aconitate; selective oxidation.

INTRODUCTION

Essential conversions in organic synthesis, namely, C,C-bond forming reactions and functional group interconversions [1,2], can be achieved by electron transfer (Schemes 1 and 2) [3,4].

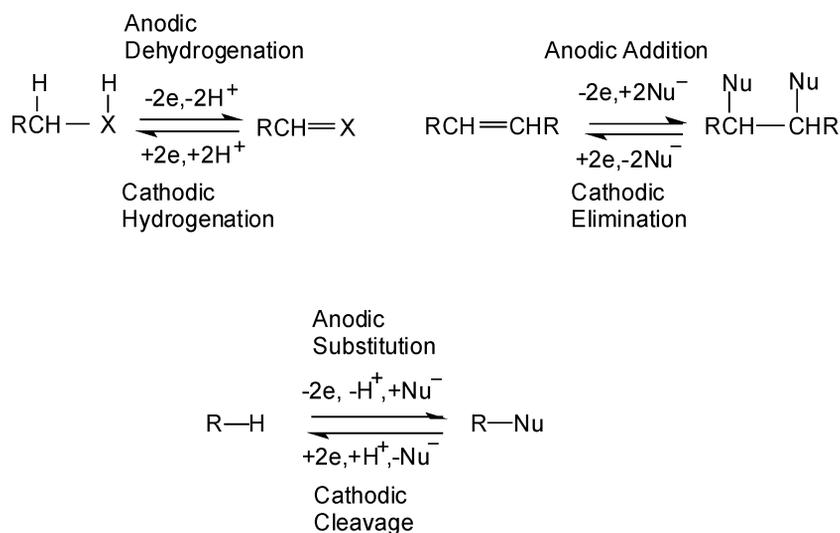


Scheme 1 Electrogenerated intermediates for C,C-bond formation.

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**This article is dedicated to R. Daniel Little, University of California, Santa Barbara, in celebration of his 60th birthday.

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Scheme 2 Electrochemical functional group interconversions.

At the anode, neutral compounds are oxidized to radical cations, these can be deprotonated to radicals, which can be further oxidized to carbocations. At the cathode, neutral compounds are reduced to radical anions, these can lose a leaving group to form a radical, which can be further reduced to a carbanion. The electrogenerated intermediates can react with carbon-nucleophiles, carbon-electrophiles, and radical scavengers or undergo radical coupling to afford new C,C-bonds.

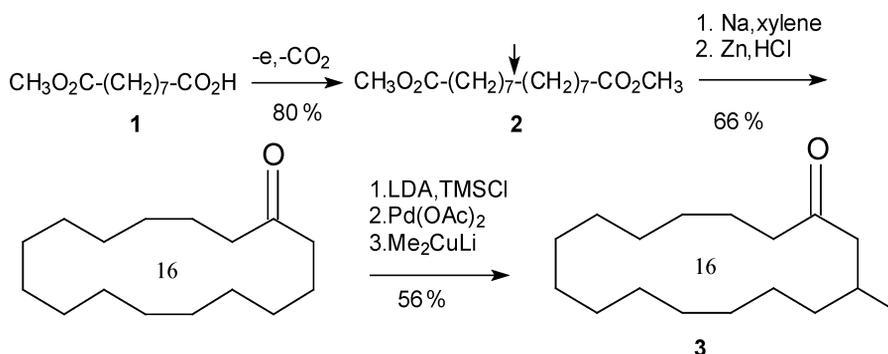
In functional group interconversions at the anode, the electron transfer is followed by deprotonation of the radical cation (anodic dehydrogenation), reaction with nucleophiles (anodic addition), or both (anodic substitution). In the reverse conversions at the cathode, the electron transfer is followed by protonation (cathodic hydrogenation), loss of leaving groups (cathodic elimination), or both (cathodic cleavage).

As equipment for electrolysis in the laboratory scale, an undivided beaker-type cell with platinum, graphite, glassy carbon, or steel electrodes, and a d.c. power supply are mostly sufficient. Sometimes a divided cell and a potentiostat combined with a reference electrode can be useful. The practice of organic electrochemistry in laboratory and industrial scale is well described in the literature [5].

ANODIC C,C-BOND FORMATION VIA THE CARBOXYL GROUP

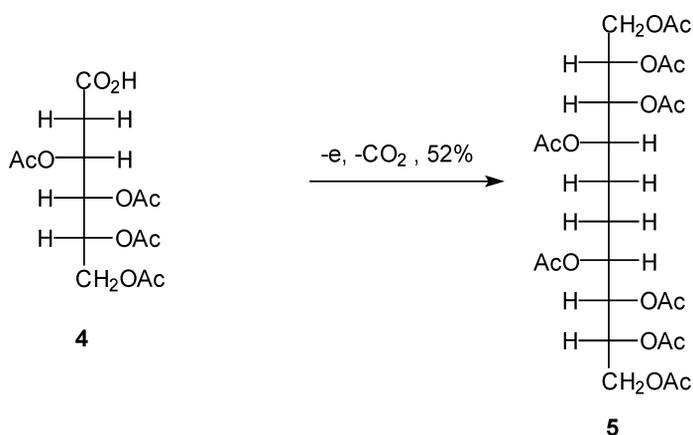
The carboxyl group is a frequent functional group in renewable feedstocks. Anodic decarboxylation can be used to generate radicals for C,C-bond formation by radical coupling or addition [6]. The radical pathway is supported by platinum or glassy carbon as anode material, a high current density, and hydrogen or electron-withdrawing groups in α -position.

Methyl nonanedioate (**1**) that is obtained by ozonolysis of methyl oleate can be converted by anodic decarboxylation to dimethyl hexadecanedioate (**2**), which can be further transformed into a muscone homolog **3** (Scheme 3) [7]. Isostearic acid, which has a methyl branching in the alkyl chain and is obtained as a side product in the production of dimer fatty acid from tallow or plant oil, can be coupled to a C₃₄ hydrocarbon that has cosmetic properties close to those of squalane [7].



Scheme 3 Synthesis of the muscone homolog **3** from methyl nonanedioate (**1**).

2-Desoxy-gluconic acid **4**, which is prepared from glucose, can be dimerized to 5,6-dideoxy-decitol octaacetate **5**, which is a C-disaccharide and a potential glycosidase inhibitor (Scheme 4).

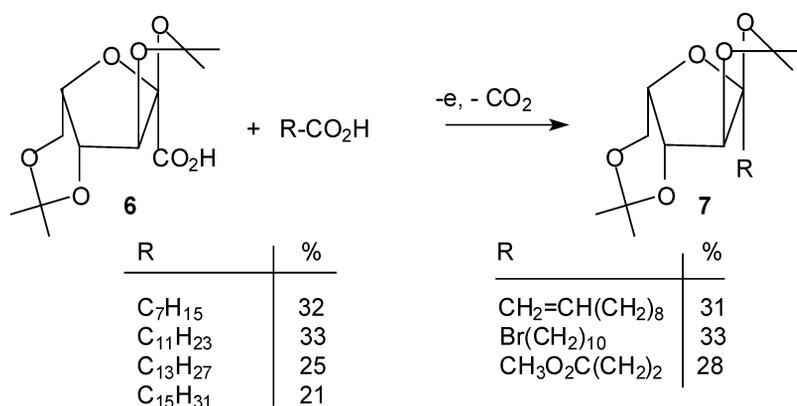


Scheme 4 Anodic coupling of 2-desoxy-gluconic acid **4** to 5,6-dideoxydecitol octaacetate **5**.

Further examples describing the homocoupling (coupling of two identical carboxylic acids) by anodic decarboxylation of organic acids are reviewed in ref. [6].

Coelectrolysis of two different carboxylic acids (heterocoupling) affords a mixture of two homodimers and one heterodimer. To favor the incorporation of the more costly acid into the heterodimer, the cheaper acid is mostly used in excess.

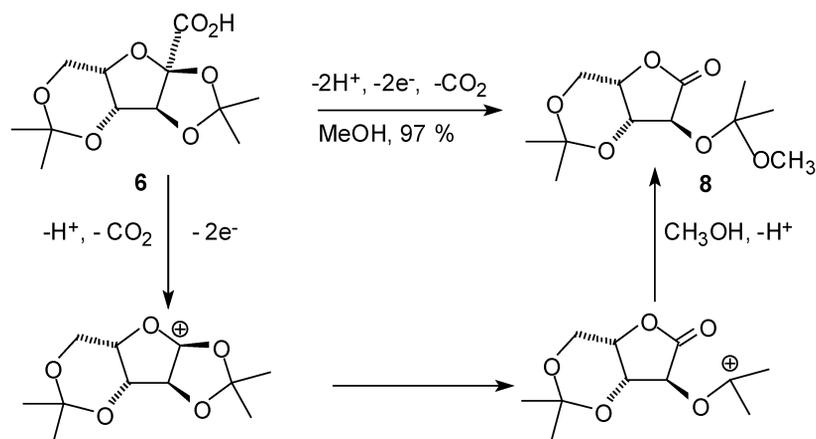
This way, methyl 18-bromo-octadecanoate has been obtained in 79 % yield by coelectrolysis of methyl nonanedioate (from oleic acid) with 11-bromo-undecanoic acid (from ricinoleic acid) [8]. Alkylated ketopentoses **7** have been synthesized by coelectrolysis of 2,3:4,6-diisopropylidene-2-oxo- α -L-gulonic acid (**6**) with different coacids (Scheme 5) [9]. The acid **6** is an intermediate in the technical vitamin C synthesis that starts from D-glucose. The products **7** could be useful as synthetic building blocks in medicinal chemistry and as neutral tensides. For further examples of heterocoupling, see ref. [6].



Scheme 5 Heterocoupling of 2,3:4,6-diisopropylidene-2-oxo- α -L-gulonic acid **6** with different coacids.

ANODIC FUNCTIONAL GROUP INTERCONVERSION VIA THE CARBOXYL GROUP

If 2,3:4,6-diisopropylidene-2-oxo- α -L-gulonic acid (**6**) is electrolyzed without coacid, no dimer but exclusively the product of the cationic pathway in anodic decarboxylation [6] is obtained (Scheme 6). This change is due to the electron-donating oxygens in the α -position of acid **6**, which favors the further oxidation of the radical to a carbocation. This undergoes a fragmentation to form the energetically stable carbonyl group of the lactone, and the exocyclic cation reacts with methanol to the ketal. In the coelectrolysis of **6** (Scheme 5), the more oxidation-resistant alkyl coradicals can trap by coupling a significant part of the radicals derived from **6** before these are further oxidized. The reaction makes the otherwise difficult to prepare L-xylonolactone **8** readily accessible. For further examples of cation-derived products from carboxylic acids bearing electron-donating α -substituents, e.g., amino acids, see ref. [6].



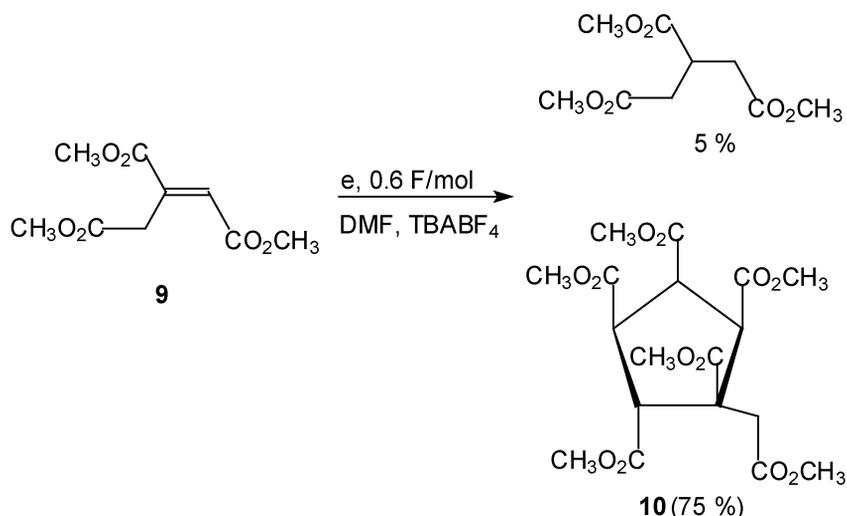
Scheme 6 Anodic decarboxylation of acid **6** to L-xylonolactone.

CATHODIC C,C-BOND FORMATION OF ACTIVATED OLEFINS

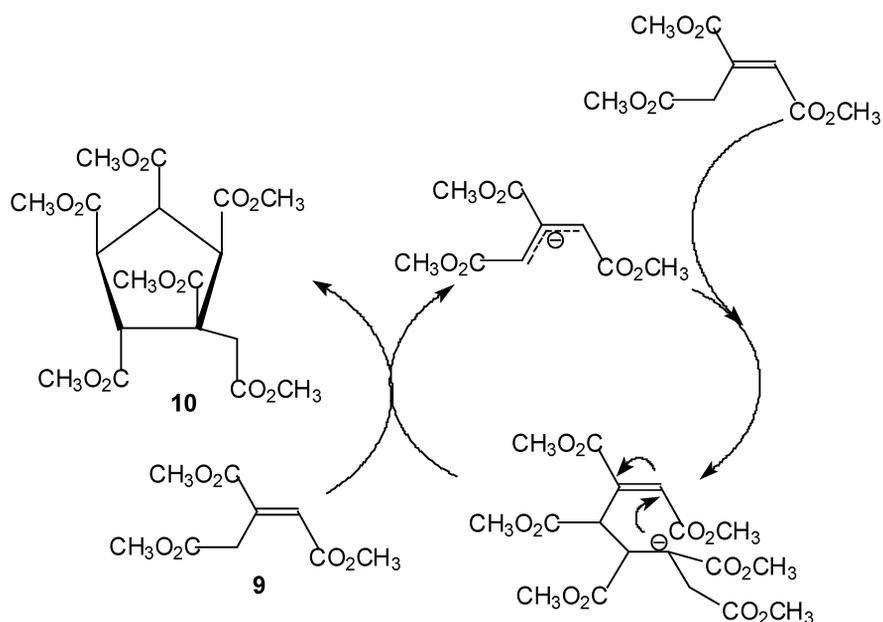
Activated olefins can be coupled in large variety to hydrodimers at the cathode [3,4,10]. The reaction is applied in technical scale to produce up to 300 000 t/year adipodinitrile from acrylonitrile [5c]. Furthermore, at the cathode, bases can be formed via radical anions. These electrogenerated bases can

induce alkylations of CH-acidic compounds, generation of ylids, additions to carbonyl compounds, or Michael reactions [10].

Trimethyl aconitate (**9**), which is available by dehydration of trimethyl citrate, affords at the cathode in a catalytic process in 75 % yield the hexamethyl ester **10** (Scheme 7, the presented structure is the major (75 %) diastereomer) [11]. The acid of **10** could be a potential complexing agent or water adsorbent. The hexaester is probably formed by deprotonation of **9** with an electrogenerated base to a 1,2,3-trimethoxycarbonyl-allyl anion that undergoes a Michael addition with trimethyl aconitate followed by the cyclization of the adduct to **10** (Scheme 8).



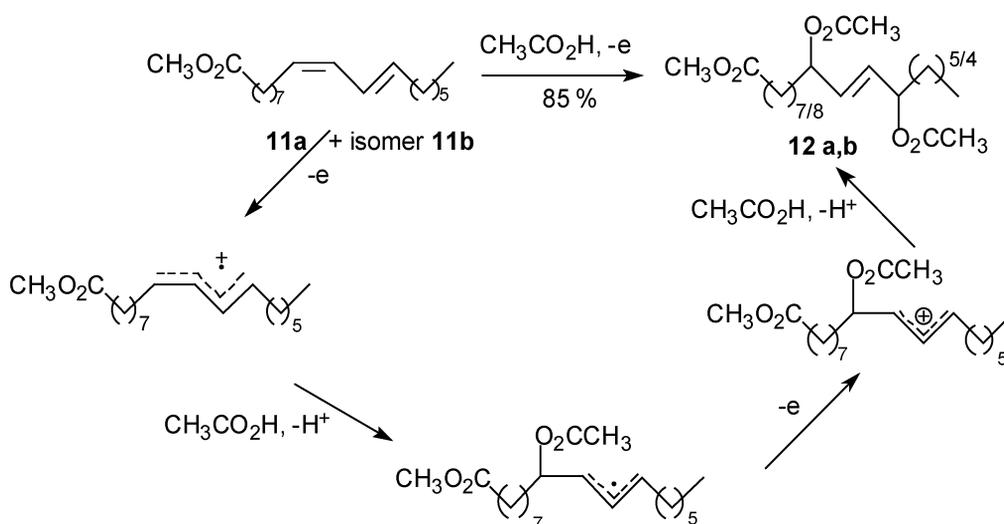
Scheme 7 Condensation of trimethyl aconitate **9** at the cathode to the hexaester **10**.



Scheme 8 Possible mechanism for the cyclodimerization of triester **9** to hexaester **10**.

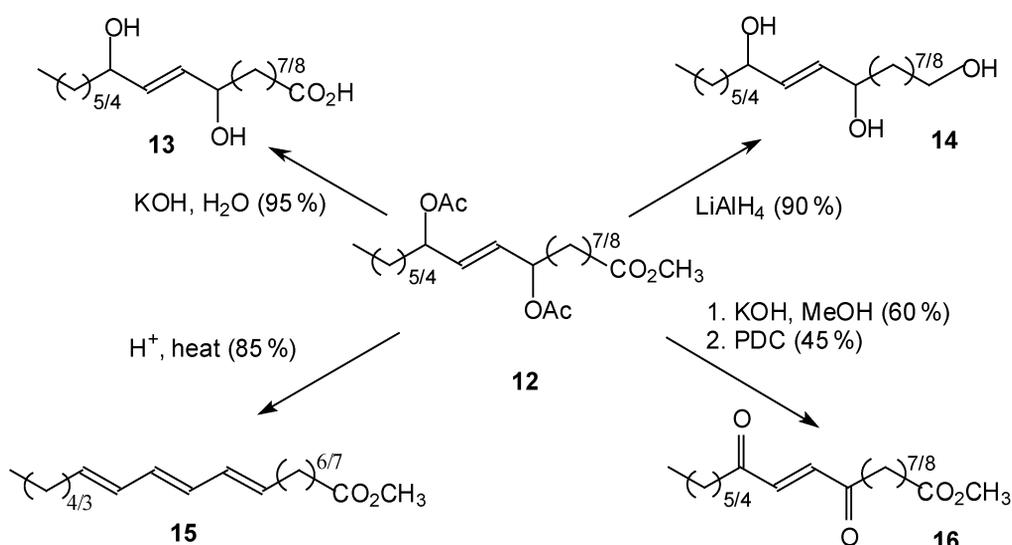
FUNCTIONAL GROUP INTERCONVERSION BY ANODIC ADDITION OF TWO NUCLEOPHILES TO A DIENE

The double bonds in methyl linoleate are conjugated with catalytic amounts of sodium hydride in dimethylsulfoxide (DMSO)/tetrahydrofuran (THF) to afford in 90 % yield a 1:1 mixture of methyl (*Z,E*)-9,11-octadienoate and methyl (*E,Z*)-10,12-octadienoate **11a,b** [12]. In cyclic voltammetry, the two isomers **11a,b** exhibit in methanol a peak potential of 1.38 V vs. Ag/AgCl at a graphite anode. Potential controlled preparative-scale electrolysis at 1.4 V in 1 M sodium acetate in acetic acid affords in an undivided cell at graphite electrodes 85 % of a mixture of methyl (*E*)-9,12-diacetoxy-10-octenoate **12a** and methyl (*E*)-10,13-diacetoxy-11-octenoate **12b** and their diastereomers (Scheme 9).



Scheme 9 Anodic addition of two acetoxy-groups to methyl conjugate **11** (isomers omitted in the intermediates).

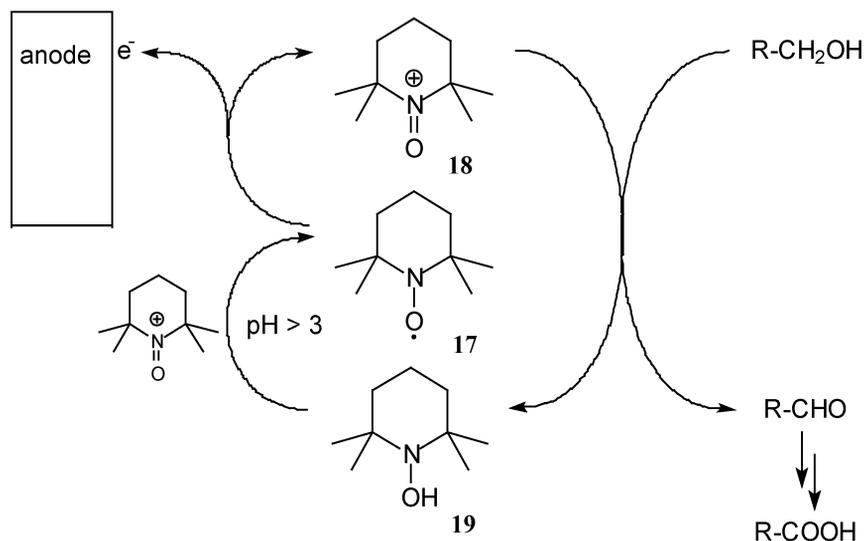
The reaction proceeds by anodic oxidation of the diene to the radical cation, which undergoes acetolysis to an allyl radical. After oxidation to an allyl cation, a further acetolysis affords the product. This is an example of redox-“umpolung”. Thereby, the diene reacts with two acetate anions by anodic “umpolung” of the nucleophilic diene to an electrophilic radical cation. The diacetate **12**, which has the properties of a plasticizer, can be further converted by hydrolysis into the dihydroxycarboxylic acid **13** (Scheme 10), which is a potential polyester component. By reduction, the triol **14** is obtained, which is a potential component for polyurethanes. By acid-catalyzed HOAc-elimination in refluxing toluene, two (*E,E,E*)-trienes **15** are formed. These are isomers of α -eleostearic acid, which occurs in Chinese tung oil and is used as component for a water-resistant varnish [13]. By hydrolysis and oxidation, an enedione **16** is formed that is a potential dienophile or Michael acceptor (Scheme 10).



Scheme 10 Conversion of the diacetate **12** into the oleochemicals **13–16**.

FUNCTIONAL GROUP INTERCONVERSION BY SELECTIVE ANODIC OXIDATION OF PRIMARY ALCOHOLS

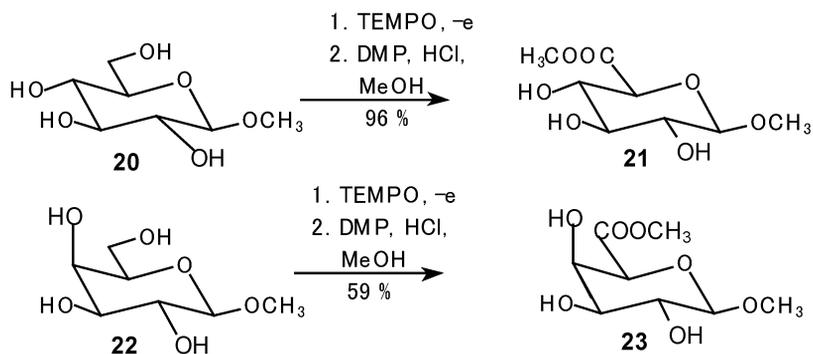
The stable radical TEMPO **17** (2,2,6,6-tetramethylpiperidine-*N*-oxyl) can be converted with a number of oxidants into the oxonium cation: TEMPO⁺ **18**, which is a selective oxidant for primary alcohols [14]. The oxidation of TEMPO to TEMPO⁺ is also possible at the anode [15,16]. In the alcohol oxidation, TEMPO⁺ is reduced to the hydroxylamine **19**, which can symproportionate with TEMPO⁺ to form TEMPO. TEMPO can be reoxidized at the anode to TEMPO⁺, which opens the possibility to oxidize primary alcohols selectively in an indirect anode process with TEMPO as mediator (Scheme 11).



Scheme 11 Indirect anodic oxidation of primary alcohols with TEMPO **17** as mediator.

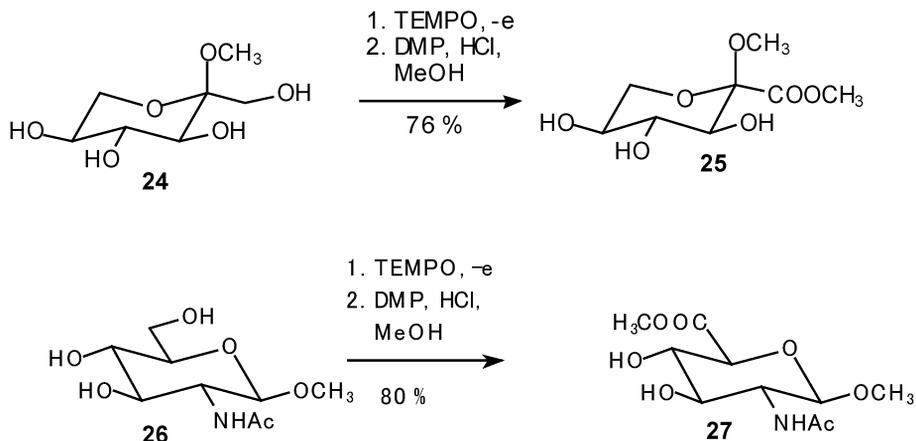
This way, with 0.2 equiv of TEMPO in 0.4 M aqueous sodium carbonate and 0.3 M sodium hydrogen carbonate acting both as supporting electrolyte and base, the primary hydroxy group in carbohydrates is selectively oxidized to a carboxylic acid. The carbohydrates are oxidized as glycosides to protect the hydroxy group at the anomeric center, which is most easily oxidized. For work-up, the sodium cation is removed by stirring the electrolyte with a cation exchanger, and after rotaevaporation of water, the product is obtained in high yield and good purity [16,17].

Methyl- β -D-glucopyranoside (**20**) is converted nearly quantitatively into the corresponding uronic acid **21**, which is isolated as methyl ester, in somewhat lower yield due to the higher sensibility of the axial 4-OH-group against oxidation methyl α -D-galactopyranoside (**22**) is oxidized to the ester **23** (Scheme 12) [16].



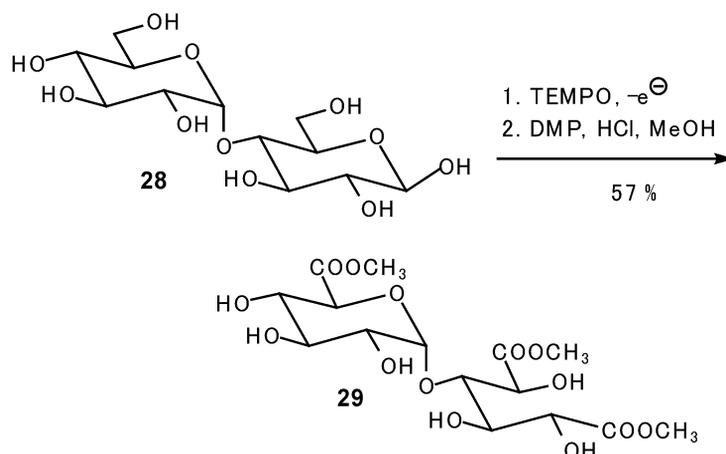
Scheme 12 Selective oxidation of the primary hydroxyl group in the glycosides **20** and **22**.

Furthermore, the ketohexose: methyl-L-sorbopyranoside (**24**) and the *N*-acylated monomer of chitin: methyl-2-acetamido-2-desoxy- β -D-glucopyranoside (**26**) were oxidized to the corresponding uronates and isolated as methyl esters **25** and **27** (Scheme 13) [17].



Scheme 13 Selective oxidation of the primary hydroxyl group in the glycosides **24** and **26**.

D-Maltose (**28**) was oxidized unprotected at the anomeric center in a 67.5 mmol (24.3 g) scale and afforded in reasonable yield the triacid, isolated as triester **29** without significant oxidation of five secondary hydroxyl groups (Scheme 14) [18].



Scheme 14 Selective anodic oxidation of D-maltose (**28**) at the primary hydroxyl groups and the anomeric center to the triacid isolated as triester **29**.

SUMMARY

Oleochemicals, carbohydrates, and trimethyl aconitate as examples of renewable feedstocks have been converted to higher-value compounds by electrochemical C,C-bond formation and functional group interconversion.

The results demonstrate that electrolysis is in good accordance with many of the 12 principles of green chemistry [19]:

- Rule 1: Reduction of waste is achieved by using the immaterial reagent: electron.
- Rule 3: Hazards are decreased due to the replacement of frequently toxic oxidants or reductants by electricity.
- Rule 5: In many cases, safe solvents are applied; in technical processes, water and methanol are used in flow reactors that run continuously for months or even years [5c].
- Rule 6: The processes are energy-efficient as the reactions are conducted mostly at normal pressure and temperature and cheap electricity is used as redox-reagent.
- Rule 7: Electrochemical conversions can be applied to all substrates that either bear electroactive groups (electrophores) or can react with electrogenerated intermediates. This also holds for renewable feedstocks such as carbohydrates, fatty acids, amino acids, or hydroxy acids.
- Rule 8: Activation through derivatives becomes unnecessary because the substrate is selectively activated by electron transfer. The possibility of changing the polarity of a substrate, e.g., from an electrophile to a nucleophile, by redox-“umpolung” saves reaction steps. Electrochemistry allows one to conduct radical reactions easily and in large scale. As polar groups are mostly tolerated in radical conversions, protecting groups become less necessary.
- Rule 9: The electrode can regenerate valuable catalysts in oxidation or reduction reactions.

EXPERIMENTAL

The following section describes hitherto unpublished experimental procedures.

Preparation of 5,6-didesoxydecitol octaacetate 5: 2-Desoxy-gluconic acid **4** (347 mg, 1.0 mmol) [20] is dissolved in dry methanol (2 ml), neutralized with 1 N KOH in methanol to 10 % and electrolyzed at a current density of 200 mA cm⁻² at -5 °C in an undivided beaker-type cell (4 ml) at platinum electrodes (1.7 cm²) until 1.4 F mol⁻¹ had been consumed. The product that precipitated during electrolysis was filtered off. After the electrolysis, the solvent was rotaevaporated, the residue dissolved

in water (5 ml) and dichloromethane (5 ml) and acidified with 2 N HCl to pH 3. The phases are separated and the aqueous phase extracted with dichloromethane (3×5 ml). For the separation of unconverted **4**, the organic phase was extracted with saturated sodium hydrogen carbonate solution (3×5 ml). After drying (MgSO_4), the solvent was removed and the product **5** (157 mg, 0.26 mmol, 52 %) recrystallized from ether. Additionally, the two disproportionation products (0.2 mmol, 20 %) of the intermediate radical from **4** were found [20].

5,6-Didesoxy-1,2,3,4,7,8,9,10-octa-O-acetyl-D-arabino-D-gulo-decitol (5): R_f -value: 0.37 (diethyl ether:petroleum ether, 3:1); m.p. 196 °C (from diethyl ether); $[\alpha] = +28.9$ ($c = 1.7$ in chloroform); IR(KBr): $\nu = 1740$ (cm^{-1} (s), 1377 (m), 1245 (s), 1028 (m)); $^1\text{H NMR}(\text{CDCl}_3)$: δ (ppm) = 1.48 (m, 4H), 2.04 (2s, 6H), 2.05 (2s, 6H), 2.06 (2s, 6H), 2.11 (2s, 6H), 4.08 (2dd, $J_{\text{gem}} = 12.43$ Hz, $J_{1a,2} = J_{9,10a} = 5.27$ Hz, 2H), 4.20 (2dd, $J_{\text{gem}} = 12.43$ Hz, $J_{1b,2} = J_{9,10b} = 2.64$ Hz, 2H), 5.11 (m, 4H), 5.18 (2dd, $J = 2.64$ Hz, $J = 8.66$ Hz, 2H); $^{13}\text{C NMR}(\text{CDCl}_3)$: δ (ppm) = 20.59, 20.69 (8q), 25.95 (2t), 61.90 (2t), 68.31 (2d), 69.79, 69.96 (4d), 169.80 (2s), 169.87 (2s), 170.38 (2s), 170.51 (2s); MS (GC/MS, 70 eV): $m/z = 533$ (3), 461 (2), 431 (7), 389 (1), 371 (1), 359 (7), 341 (4), 329 (8), 287 (60), 264 (3), 227 (12), 217 (7), 185 (6), 145 (7), 125 (13), 115 (14), 103 (11), 43 (100); $\text{C}_{26}\text{H}_{38}\text{O}_{16}$ (606.58): calc. C 51.47; H 6.32; found C 51.43; H 6.15.

Electrolysis of 2,3:4,6-diisopropylidene-2-oxo- α -L-gulonic acid (6): **6** (2.92 g, 10.0 mmol) is dissolved in methanol (40 ml), neutralized to 40 % with 1 N potassium hydroxide in methanol and electrolyzed with a current density of 20 mA cm^{-2} at 0 °C in an undivided beaker-type cell at platinum electrodes until 3F mol^{-1} had been consumed. The electrolyte was then rotaevaporated to nearly dryness and the residue dissolved in water (50 ml) and diethyl ether (50 ml). After drying (MgSO_4) of the ethereal solution, the solvent was rotaevaporated and the crystalline product dried in high vacuum to afford 2.52 g (9.7 mmol, 97 %) **8** as colorless crystalline product. The electrolysis could be scaled up to 30 g **6** (94 % **8**) and 50 g **6** (88 % **8**) in a flow-through cell.

3,5-O-isopropylidene-2-O-(2-methoxyisopropyl)-L-xylonolactone (8): R_f -value: 0.28 (petroleum ether:diethyl ether 1:1); $[\alpha] = -27^\circ$ ($c = 1.00$ in acetone); m.p. 104–108 °C; IR (film): $\nu = 2970$ (cm^{-1} (m), 2920 (m), 1780 (s), 1370 (s), 1180 (s), 1070 (m), 1040 (s), 925 (m), 810 (m)); $^1\text{H NMR}([\text{D}_6]\text{-acetone})$: δ (ppm) = 1.27 (s, 3H), 1.34 (s, 3H), 1.35 (s, 3H), 1.49 (s, 3H), 3.23 (s, 3H), 4.00 (dm, 1H, $J_{\text{gem}} = 13.9$ Hz), 4.08 (s, 1H), 4.24 (dd, $J_{\text{gem}} = 13.8$ Hz, $J_{5,4} = 2.3$ Hz, 1H), 4.48–4.51 (m, 2H); $^{13}\text{C NMR}(\text{CDCl}_3)$: δ (ppm) = 19.57 (q), 24.66 (q), 24.93 (q), 27.97 (q), 49.28 (q), 59.47 (t), 71.32 (d), 72.16 (d), 73.09 (d), 98.06 (s), 102.51 (s), 174.12; MS(GC/MS, 70 eV): m/z (%): 245 (4), 229 (8), 173 (25), 171 (18), 159 (2), 130 (20), 114 (18), 73 (100), 59 (36), 43 (68); $\text{C}_{12}\text{H}_{20}\text{O}_6$ (260.5): calc.: C 55.37; H 7.75; found: C 55.18; H 7.68. The structure is furthermore supported by an X-ray structure [21].

Anodic oxidation of a 1:1 mixture of methyl (Z,E)-9,11-octadienoate and methyl (E,Z)-10,12-octadienoate (11a,b): **11a,b** (0.918 g, 3.12 mmol) [12] were dissolved in 1 M sodium acetate in acetic acid (20 ml) and electrolyzed in a beaker-type cell at a potential of 1.4 V vs. Ag/AgCl at graphite electrodes and room temperature until 2.5 F mol^{-1} were consumed. After electrolysis acetic acid was rotaevaporated, the residue extracted with petroleum ether, the solution dried and the solvent evaporated. Column chromatography (silica gel, Merck, petroleum ether:diethyl ether = 5:2) afforded **12** (1.10 g, 2.66 mmol, 85 %).

Methyl (E)-9,12-diacetoxy-10-octenoate (12a) and methyl (E)-10,13-diacetoxy-11-octenoate (12b) and their diastereomers: R_f value: 0.44 (petroleum ether:diethyl ether = 5:2); IR (film): $\nu = 2929$ (cm^{-1} (s), 2857 (s), 1738 (s), 1460 (m), 1436 (m), 1371 (m), 1238 (m), 1173 (m), 1021 (m), 969 (m)); $^1\text{H NMR}(\text{CDCl}_3)$: δ (ppm) = 0.85 (t, 3H), 1.15–1.62 (m, 22H), 2.01 (s, 6H), 2.26 (t, 2H), 3.63 (s, 3H), 5.15–5.25 (m, 2H), 5.50–5.65 (m, with $^3J = 15$ Hz, 2H); $^{13}\text{C NMR}(\text{CDCl}_3)$: δ (ppm) = 13.9, 14.0 (each q), 21.2 (q), 22.3, 24.7, 24.9, 25.0, 29.0, 29.1, 29.2, 31.5, 31.7, 34.0, 34.3 (all t), 51.4 (q), 73.8 (d), 130.9, 131.0, 131.1 (each d), 170.1 (s), 174.1 (s); MS (GC/MS, CI): m/z (%) = 430 (100, M +

NH₄⁺), 353 (30), 319 (70), 312 (72), 293 (42); C₂₃H₄₀O₆ (412.573) calc. C 66.96, H 9.77; found: C 67.23, H 10.07.

The conversion of **12a,b** into **13–16** is described in [22].

ACKNOWLEDGMENTS

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