Review of Electrochemical Syntheses of Aroma Chemicals

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Electrochemical syntheses of organic chemicals become more and more important as simple and effective ways of preparing fragrance and flavour raw materials. The main advantages of these methods are:

—simplicity of technology
—reaction selectivity
—low pollution and wastes
—possible process-automation
—simple equipment and reaction conditions
—possible regeneration of materials
—unique chemistry of some of the reactions.

There are several literature references on practical industrial applications of electrochemical methods in the syntheses of some chemicals.[1,2] The examples given in Table I show syntheses of aroma chemical and intermediates. The range and variety of products manufactured by fragrance and flavour chemistry create interesting possibilities for introduction of electrochemical syntheses. In this review we collected data from available literature and our own experiments to show nearly unlimited possible applications of electrochemical methods in our industry.

The electrochemical processes can be separated into three groups.[3,4]

- Direct electrochemical processes where an organic molecule in electrolyte is donor or acceptor of electrons, i.e., is directly involved in the electrochemical reaction.
- Electrocatalytic processes where a substrate reacts with hydrogen atoms on the cathode surface or oxygen atoms on the anode surface whereby the atomic hydrogen and oxygen are formed in electrochemical reactions.
- Indirect electrochemical processes where products generated on electrodes undergo reactions with organic substrates. This group covers also reactions with transfering catalysts, i.e., amalgamate reductions, oxidation with metal ions.

In general, electrochemical processes are often divided into anodic and cathodic which are usually reduction and oxidation respectively.

Cathodic Syntheses

Electrochemical methods of reduction of triple bond. The reaction develops according to the scheme in figure 1. It was established that the best cathodes for electrochemical selective reduction of a triple bond to a double bond are copper, silver and copper-silver alloys.[5] By this method dimethylethynylcarbinol was reduced to give dimethylvinylcarbinol (an intermediate in the synthesis of terpenoids).[4]

Electrochemical reduction of double bonds. This type of reduction of isolated double bonds is not widely used as catalytic hydrogenation is easier and more effective. Electrochemical reduction of double bonds has limited applications in the reduction of so called activated double bonds, e.g., in alpha-, beta-unsaturated acids and their derivatives. (See Figure 2.)

The literature gives a very interesting example of the reduction of 4-methoxycoumarine to opti-

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$$-C\equiv C- \xrightarrow{2H^+, 2e} -CH=CH- \xrightarrow{2H^+, 2e} -CH_2-CH_2-$$

Figure 1

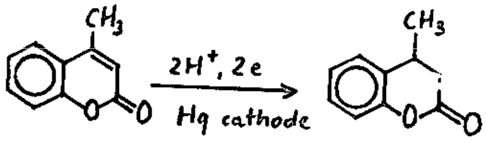
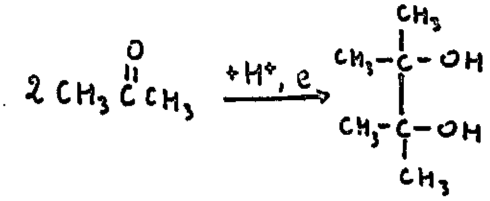


Figure 3

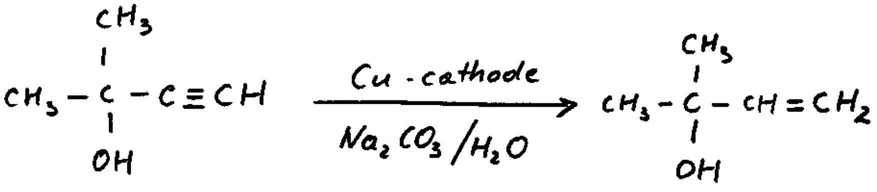


$$2\,CH_3COCH_3 \xrightarrow{+H^+, e} (CH_3)_2C(OH)-C(OH)(CH_3)_2$$

Figure 5

$$ArCOOH \xrightarrow[-H_2O]{+2H^+, 2e} ArCHO \xrightarrow{+2H^+, 2e} ArCH_2OH$$

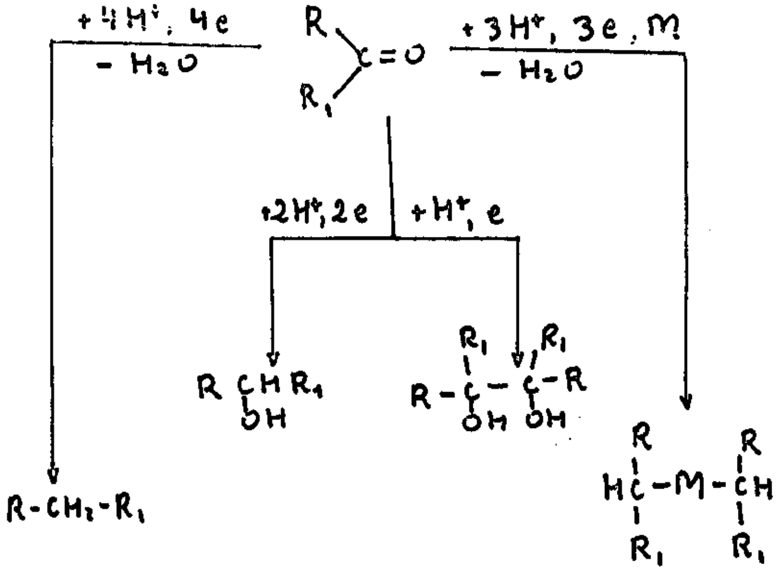
Figure 6



$$CH_3-C(CH_3)(OH)-C\equiv CH \xrightarrow[Na_2CO_3/H_2O]{Cu\text{-cathode}} CH_3-C(CH_3)(OH)-CH=CH_2$$

95%

Figure 2



M - metal e.g. Hg

Figure 4

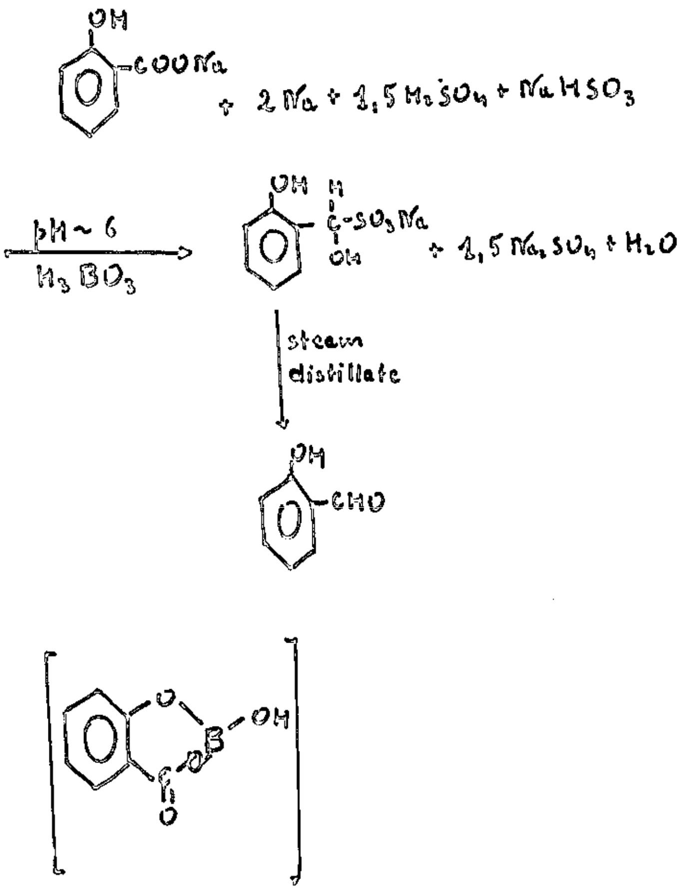


Figure 7

Table I. Some Reported Electroorganic Syntheses of Aroma Compounds (reference 1)

N°	Product	Raw material	Company /Country/	Scale /Status/	Type of processes
1.	Benzaldehyde	toluene	/India/	pilot plant	indirect oxidation /Mn III/
2.	Glyoxylic acid	oxalic acid	/Japan/	Commercial	reduction of functional group
3.	Maltol	furfuryl alcohol	Otsuka /Japan/	/pilot plant/	oxidation
4.	Pinacol	acetone	Japan BASF /FRG/	/ pilot plant/	reductive coupling
5.	Propylene oxide	propylene	BASF /FRG/ other in UK	/ pilot plant/	paired synthesis
6.	Salicylaldehyde	salicylic acid	/India/	/pilot plant/	reduction of functional group
7.	Sebacic acid esters	adipic acid half esters	BASF /FRG Japan USSR	/pilot plant/ -"- commercial	Brown - Walker
8.	Succinic acid	maleic acid	/India/	commercial	reduction
9.	Tetradecanedioic acid	monomethyl azelate	Soda Aromatic Co. Japan	commercial	Brown - Walker
10.	Pentadecanolide /2/	monoesters	USSR	commercial	Brown - Walker

Table II

Cathode	Temp. oK	Cathodic Current Density KA/m^2	Conc.of Oxalic Acid kg/m^3	Average Current Efficiency %	Product Yield %
Pb	288	1.5	50-55	60	85
Hg	288	3.0	80	75	95

$$\begin{matrix} COOH \\ | \\ COOH \end{matrix} \longrightarrow \begin{matrix} CHO \\ | \\ COOH \end{matrix}$$

Figure 8

cally active 3,4-dihydro-4-methylcoumarin on a mercury cathode in methanol with addition of optically active alkaloids.[6] (See Figure 3.)

Electrochemical reductions of carbonyl compounds. Cathodic reduction of aldehydes and ketones according to conditions can give hydrocarbons, alcohols, pinacones or metalorganic compounds. Figure 4 shows the possibilities.

This reaction was introduced on industrial scale for hydrodimerisation of acetone to pinacone used in total synthesis of valuable violet odorants, such as irones. The reaction was carried out in an electrolyser with ion exchange diaphragm in aqueous solution of tetraethylammonium sulphate containing 80% acetone. Pinacone yield was 67%.[7] The same hydrodimerisation of acetone was carried out on a zinc cathode in alkaline solution with a 50-60% yield.[1] (See Figure 5.)

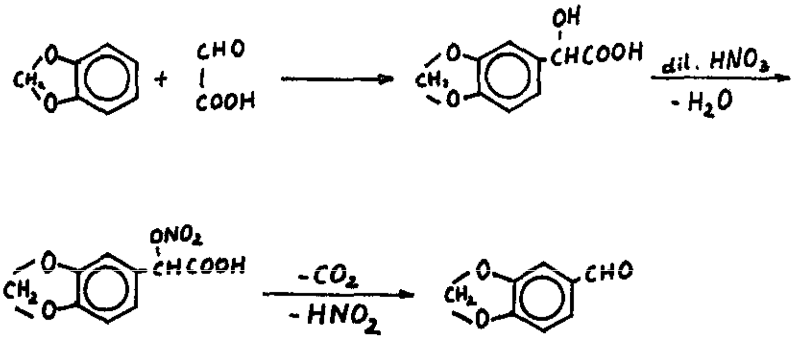


Figure 9

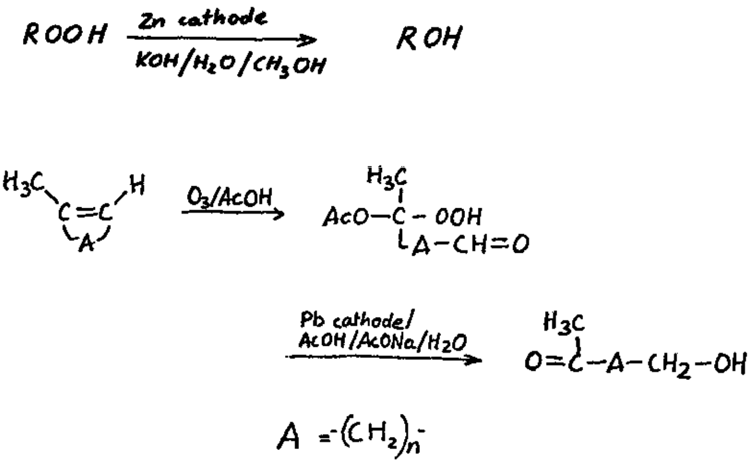


Figure 10

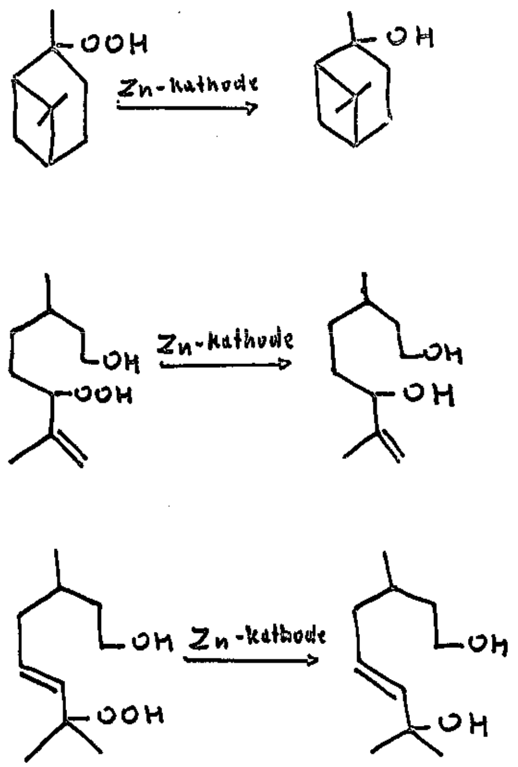


Figure 11

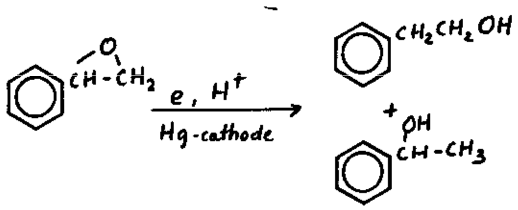


Figure 12

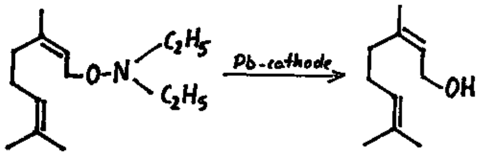


Figure 13

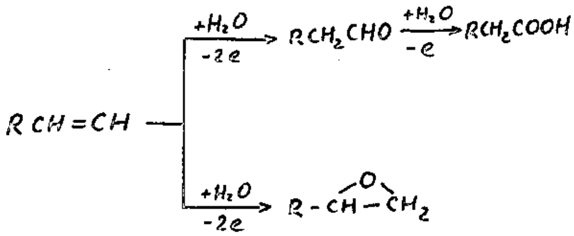


Figure 14

Cathodic reduction can be also applied in reduction of aromatic aldehydes to alcohols and alkylcycloalkanones to corresponding alcohols. Said reactions give good results (70-75% yield) on Ni, Cu, Pb and some other cathodes.[1,5]

Cathodic reduction of carboxylic acids. According to reaction conditions cathodic reduction of a carboxylic group can give aldehydes or alcohols or their mixtures. It should be emphasized that only these carboxylic groups are reduced which are bonded directly with an aromatic ring or some other strong electroacceptor group. (See Figure 6.)

High yields of aldehydes are obtained when acids having carboxylic groups activated by strong electroacceptor groups are reacted and the resulting aldehydes form hydrates which do not undergo further reduction or are blocked in situ to electrochemically inactive derivatives.[8] This method was used for reduction of salicylic acid to salicylic aldehyde—important raw material for synthesis of coumarin.[9]

As free salicylic acid does not undergo electrochemical reduction, its complex with boric acid is used in this reaction.

The process was carried out on a mercury cathode in the presence of boric acid and sodium sulphate. The real reducing agent is sodium amalgamate generated in situ on the cathode. The boric acid is required because it is not the salicylic acid itself which is reduced directly by the amalgamate, but rather boric acid-salicylic acid ester anhydride (shown in brackets in figure 7). This explains why p-hydroxybenzaldehyde can not be obtained from p-hydroxybenzoic acid in this process.

The optimal pH of the reduction is maintained by addition of sulphuric acid and the resulting salicylic aldehyde is converted into its bisulfite adduct to prevent further reduction. After decomposition of the adduct by steam distillation, 60% yield of aldehyde is obtained.[10] An industrial scale electrochemical process was established for reduction of oxalic acid to glyoxalic acid which can be used for synthesis of vanillin, ethylvanillin and heliotropin. (See Figure 8.)

The reaction is conducted on a mercury or lead cathode in a cell with diaphragms. A saturated solution of oxalic acid serves as electrolyte. Best results were obtained under the conditions outlined in Table II.[11]

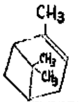
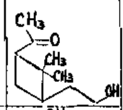
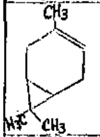
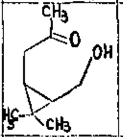
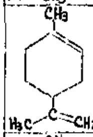
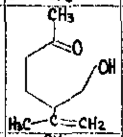
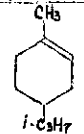
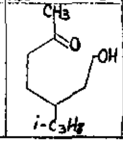
The processes can be run continuously with the starting material supplied as a saturated solution (Pb cathode) or solid (Hg cathode). In the latter case a solution containing 400 kg/m^3 of glyoxalic acid is obtained with current efficiency 85% and product yield of 88%.

According to Mölleken and Bauer[12] heliotropin can be economically produced by the reaction of methylenedioxybenzene with the inexpensive glyoxylic acid according to the scheme in figure 9.

As an overall yield is about 80% this procedure is competitive with heliotropin production from isosafrole. Reduction of acids to alcohols is much easier as no blockade is necessary as in aldehyde cases. Processes are carried out on Pb or Hg cathodes with 15-30% sulphuric acid in water or water-ethanol solution. By this method benzyl alcohol can be obtained from benzoic acid with a 85% yield.[12]

Electrochemical reduction of the hydroperoxide group. Alkyl hydroperoxides are important intermediates in industrial syntheses of some aroma chemicals, e.g., linalol from alpha-pinene via pinane hydroperoxide or rose oxide via citronellol hydroperoxide. For traditional reduction methods of hydroperoxides to alcohols, sodium sulphite, sodium sulphide, dialkyl sulphides, phosphines, etc., are used.[13] The main disadvantage of all these methods is the high quantity of inorganic salts as byproducts.

Table III. Odour Description of Some Monoterpene Ketoalcohols

starting material	ketoalcohol	% yield	B.P.		Odour description
			°C	mm Hg	
		64	114 116	1,5	moderate intensity pleasant, flowery, balsamic, stable
		65	93 95	0,7	moderate intensity balsamic,with fresh pinewood note, pleasant
		45	86 88	0,15	moderate intensity fresh, pleasant
		70	106 108	1,0	moderate intensity, flowery with cumin note, stable

In our experiments[14,15] we have found that cathodic electroreductions can be used for that purpose. The reaction is practically quantitative under very mild conditions and almost without byproducts. Both alkyl hydroperoxides and ozonides can be reduced.[14] Reactions are shown in figure 10.

Good results are obtained in a flow type electrolyser similar to a filtration press with ceramic diaphragm or ion-exchange membrane. As cathode a zinc plate is used and a steel plate as anode. By this method from pinane hydroperoxide we obtained cis/trans 2-pinanol and from a mixture of citronellol hydroperoxides a corresponding mixture of hydroxycitronellols.

Using the method in figure 11 for electrochemical reduction of products of ozonolysis of unsaturated mono and bicyclic terpene hydrocarbons: e.g., p-menth-1-ene, (+)-limonene, (+)-alpha-pinene, and (+)-car-3-ene, we obtained corresponding unknown ketoalcohols with interesting odour properties.[16,17] The data are colleted in Table III.

Electrolysis of epioxides to alcohols. Styrene oxide is a very interesting material for synthesis of beta-phenylethyl alcohol. An electrochemical method was published[18] for reduction of styrene oxide on a Hg cathode in DMF containing 0, 1m/dm^3 of tetrabutylammonium perchlorate. The reaction gives both alpha- and beta-phenylethyl alcohols with higher content of the beta isomer. (See Figure 12.)

Hydroxy compounds such as geraniol can be also prepared by electroreduction of corresponding substituted hydroxylamine. The process is carried out in a cell with a catholyte containing a solvent protonating agent and a substituted hydroxylamine separated by a membrane from anolyte which is usually an aqueous strong mineral acid.[19] This method may be used in synthesis of terpenoids based on dimerisation if isoprene resp. its aminoderivatives. Among others N-geranyloxydiethylamine on a Pb cathode gives geraniol with current yield of 90%. (See Figure 13.)

Anodic Syntheses

Oxidations on an anode create many possibilities such as functionalisation of alkenes and alkylaromatic hydrocarbons, and anodic C-C coupling.

Oxidation of Hydrocarbons. Alkanes are inactive in anodic processes and only under special conditions on a Pt anode can give some functional derivatives. According to reaction conditions anodic oxidation of alkenes leads to carbonyl compounds, epioxides or carboxylic acids. (See Figure 14.)

The reaction route depends on the anode type, potential of the reactants, type of electrolyte, pH of the solution and alkene concentration. Very selective is the oxidation of alkenes to ketones on a porous graphite anode in concentrated sulphuric acid solutions.[20] (See Figure 15.) By this method 1-undecene can give 2-undecanone, an important intermediate in industrial synthesis of MNA.

Oxidation of alkenes to epioxides is difficult and needs special conditions. Usually it is a porous anode containing catalytic amounts of Ag-Ag_2O in an electrolyser with diaphragm and anolyte containing alkaline metals, hydroxides or their salts with carboxylic acids.[4]

There are some patents on anodic epoxidation of lower alkenes[21] but low yields are recorded so far with higher molecular weight compounds.

Very interesting results were obtained in electrochemical epoxidation of a styrene to styrene oxide which is an intermediate in the synthesis of beta phenylethyl alcohol (see above). There is no direct reaction described but electrochemical epoxidation of styrene was successfully achieved via styrene halohydrine which is formed in the anodic cell as a result of addition to the subhalogenic acid generated from sodium chloride. Chlorohydrine created in this process is transferred into a cathodic cell where it is cyclised and sodium hydroxide is continuously generated in the cell. The processes are shown in figure 16.

According to patent data[22] electrosynthesis of styrene oxide should be carried out as a styrene emulsion in aqueous sodium chloride in an electrolyser with ion-exchange diaphragm, and platinum or graphite anode at 10°C with current density 10A/dm^2. Good results were also obtained in a CH_3CN-H_2O-NaBr system with Pt anode.

The important advantages of this process are the cyclic use of NaCl in a closed system and elimination of a relatively large volume of unwanted byproducts.

There is a good chance for industrial introduction of electrochemical oxidations of alkylaromatic hydrocarbons to aldehydes and ketones.[4,23,24] This is valid especially for indirect electrosynthesis with use of a transition metal ion—Ce (IV); Mn (IV); Co (III); Cr (VI) to transfer electrons from the organic substrate to the electrode.

The first part of the process is oxidation of the metal ion to a higher oxidation state. Second part is chemical reaction of the metal ion with the organic substrate. The process is carried out altogether in the electrolysis cell.[24,25] (See Figure 17.)

Electrochemical oxidation of toluene on Pt anode in 30% sulphuric acid results in benzaldehyde with current efficiency of 27-30%. An addition of 5-10% of MnSOy as ion transmitter increases yields up to 83-85%.[4] The same effect is obtained by addition of Co salts.[26]

Ethylbenzene and isopropylbenzene (cumene) are oxidised to a mixture of benzaldehyde and acetophenone. In the case of cumene the current efficiency for benzaldehyde is 70-80% and acetophenone 15-18%.[27]

Electrooxidation of substituted toluene in alcoholic solutions gives substituted benzaldehyde dialkylacetals. Another example is the electrolysis of p-methoxytoluene in methanol containg KF at 24-25°C using 4.7A/dm^2 and 4 Faraday/mole; p-methylanisole gives the dimethylacetal of anisaldehyde. This product yield is 57.7% and current efficiency 56.6%.[28]

Electrolysis in methanol containing collidine and tetraethylammonium-p-toluene-sulphonate as supporting electrolyte resulted in 67% of p-methoxybenzaldehyde dimethylacetal with current efficiency of 71%.[29]

There are several other patents on electrochemical oxidation of substituted toluene to corresponding aldehydes or dialkyl acetals.[30,35]

Car-3-ene was oxidised on stainless steel or carbon anode at 20, 40, and 60 V in aqueous CH_3COOH containing CH_3COO Li at 20°C to give a mixture of 1,1,4-trimethyl-4,6-cycloheptadien-3-ol (main product), p-menth-1-ene-8-ol, trans-carveol and p-cymene-8-ol.[36] (See Figure 18.)

Electrochemical Oxidation of Alcohols and Aldehydes. Electrochemical oxidation of alcohols and aldehydes according to reaction conditions gives carbonyl compounds, carboxylic acids or their esters.[41] Practical application was found in preparing ketones from secondary alcohols. For example, according to a Japanese patent[37] the ketone was obtained by catalytic electrooxidation of the secondary alcohol in presence of iodine or iodides. Easily available lower aliphatic alcohols can be oxidised to carboxylic acids used in the preparation of esters for flavouring materials (e.g., isobutyric acid from isobutyric alcohol).

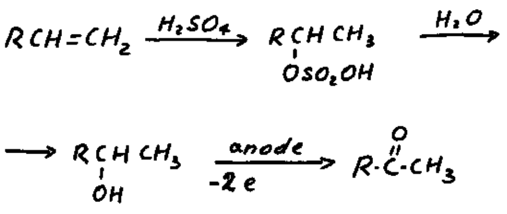


Figure 15

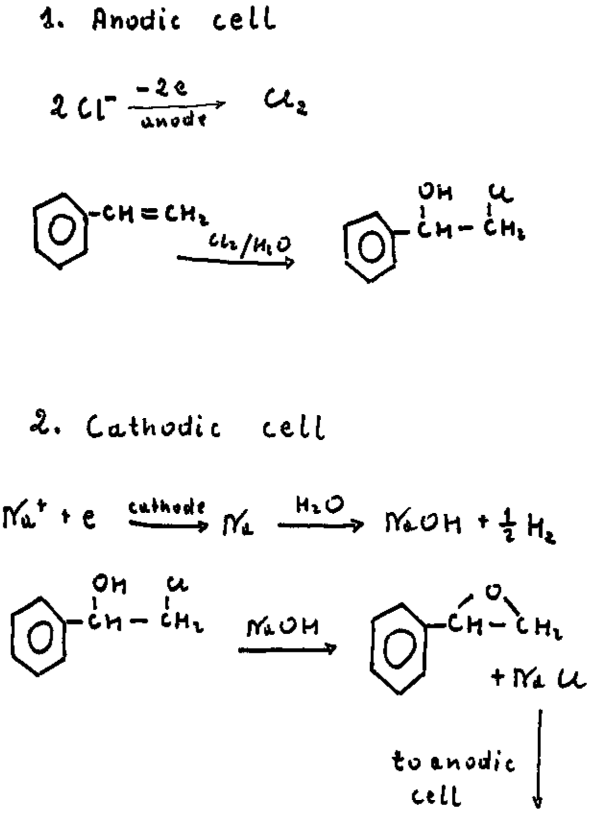


Figure 16

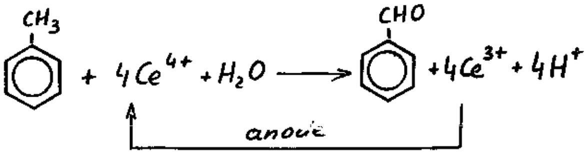


Figure 17

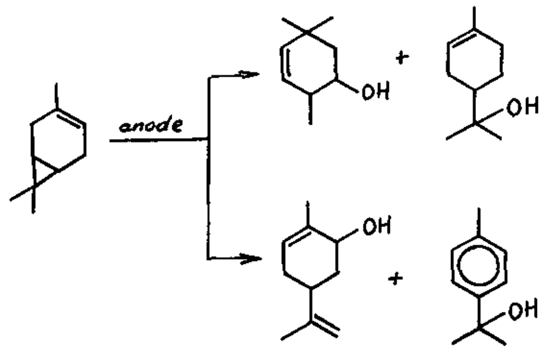


Figure 18

$$RCH_2OH + 4NiOOH + H_2O \longrightarrow$$
$$\longrightarrow RCOOH + 4Ni(OH)_2$$

Figure 19

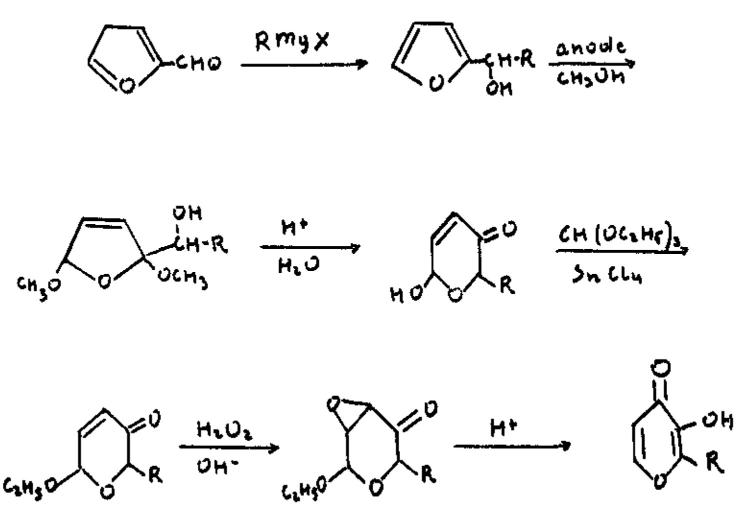
The reaction should be carried out in alkaline solution on a graphite anode activated with nickel salts[38] or Ni-oxide anode.[39] Most probably the reduction occurs via peroxide NiOOH (generated on anode) which oxidize alcohol molecules according to the scheme in figure 19.

The $Ni(OH)_2$ created in the process is again oxidised on anode to NiOOH. Total yield is 90-92% and current efficiency 60%. This method is claimed[38,39] to be more effective than same oxidations on a PbO_2 anode in sulphuric acid.[40]

Anodic Alkoxylations. Anodic methoxylation was successfully applied in the synthesis of maltol and ethylmaltol from furfural[41] according to the scheme in figure 20.

Total yield of the reaction is 73-74% and most probably industrial production is already achieved.[42] We used this reaction for synthesis of methoxyderivatives of unsaturated terpene alcohols.[43] (See Figure 21.)

The process was carried out in a typical electrodyser on a Pt anode with excess methanol in the presence of sodium-p-toluenesulfonate as supporting electrolyte. Methoxylation of alcohols with terminal double or triple bonds gave an

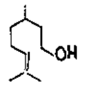
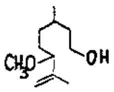
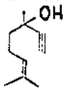
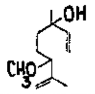
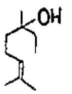
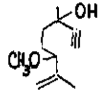
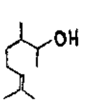
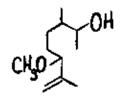
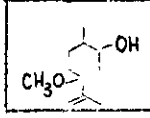
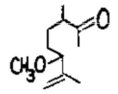


Maltol : $R = CH_3$

Ethylmaltol: $R = C_2H_5$

Figure 20

Table IV. Some Characteristics and Odour Description of Monoterpene Methoxyalcohols and Methoxyketones

Starting alcohol	Methoxy derivative	% yield	Boiling point °C	mm Hg	n_D^{22}	Odour description
		51	135	18	1,4520	Intensive, fresh, floral with hagberry note
		22	110	16	1,4582	Intensive, fresh, floral, with coumarine note, very pleasant
		13	112,5	18	1,4613	Intensive, pleasant, floral, with gardenia note, fresh
		42	120	18	1.4515	Medium Intensity, spicy-floral with lovage note, interesting, fresh
		85	114	20	1,4422	Intensive, diffusing, cumon note, very stable

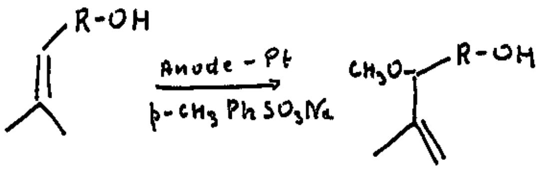


Figure 21

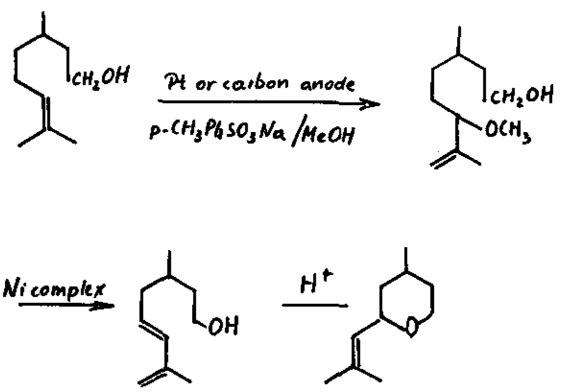


Figure 22

unidentified mixture from which some monomethoxyalcohols were separated by distillation with a yield of 13-22%. (The alcohols are shown in Table IV).

Good yield was obtained with methoxylation of citronellal and elgenol. All products presented in Table IV have pleasant, stable flowery odours, different from starting alcohols. It is also interesting that 3, 7-dimethyl-6-methoxy-7-octen-2-ol with spicy odour and lovage notes is totally different from its near analogue 3, 7-dimethyl-7-methoxyocten-2-ol (osyrol).[43]

Electrochemical Syntheses of Rose Oxide. Rose oxide (4-methyl-2/2-methyl-1-propenyl)-tetrahydropiran is a very important fragrance component and can be prepared from citronellol by a variety of synthetic routes.

There are few syntheses from citronellol,[44] and total synthesis from glucose[45] and isoprene[46] known. In industrially applied multistep methods total yields do not exceed 50%.[44] Therefore the method of one step electrochemical anodic cyclisation of citronellol to rose oxide published by Shono et al.[47] is very interesting.

The process was performed at room temperature with carbon electrodes under constant agitation. Tetraethylammonium-p-toluene-sulphonate was used as supporting electrolyte. The electrooxidation of citronellol in acetonitrile was carried out at current density of 40mA/cm² and working anode potential 1.8V. Yield was 26%. In acetic acid and propylene carbonate solutions, the yields were 10.0% and 18.8% respectively.

In our experiments we tested many variations of this method[48] aiming to find optimal conditions and possibilities of scale expansion. Best results were obtained with RuO_2/TiO_2 anode.

Regression equation in full form was given to show dependence of rose oxide yield on following parameters:

- —supporting electrolyte concentration $(E + N)_4 ClO_4$ (0.2-0.7 mol/dm³)
- —citronellol concentration (0.2-0.8 mol/dm³)
- —electrode potential vs. Ag/Ag^+ (1.7-1.9V)
- —current density (0.46-2.31 A/dm²)
- —temperature (283-313°)
- —F/mole (1.0-3.0)
- —solution flow rate (6.0-10.5 dm³/h)

Under optimum conditions a 35% yield of rose oxide (cis/trans) was obtained.

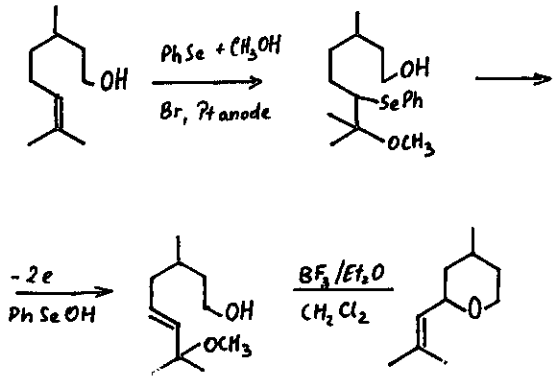


Figure 23

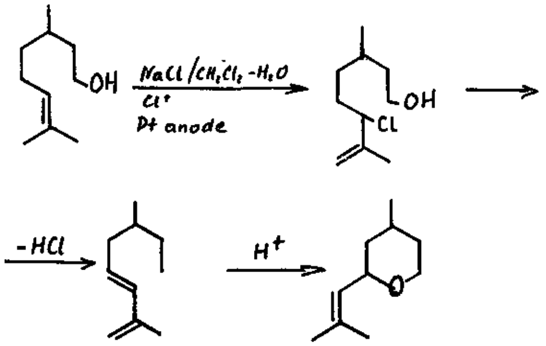


Figure 24

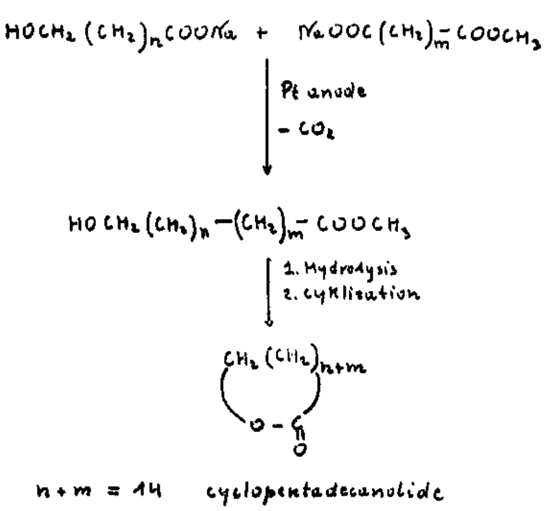


Figure 25

Other electrochemical methods should be mentioned here. A European Patent Application[49] provides a three step route:

1. Anodic alkylation of citronellol with use of alkali metal aromatic sulphonate as supporting electrolyte.
2. Dealkoxylation of resulting 2,6-dimethyl-3-alkoxyoct-1-en-8-ol in the presence of palladium or nickel complex.
3. Cyclisation of resulting dehydrocitronellol in the presence of an acid.

The above method gives rose oxide without high temperatures or difficult to handle materials. (See Figure 22.)

Another interesting method which gave an 84% yield of rose oxide (cis/trans 4.4:1) was published in 1980.[50] (See Figure 23.) The same group published another method in 1981.[51] (See Figure 24.)

Allyl chlorination of citronellol gave 78% yield. Further steps are routine procedure.

Electrochemical Syntheses of Macrocyclic Compounds. One of the oldest electrochemical methods, so called anodic dimerisation (Kolbe synthesis 1948), was applied in USSR for production of pentadecanolide (Tybetolide) according to the scheme in figure 25.[2]

Anodic dimerisation of the potassium salt of adipic acid monoester with potassium salt of 11-acetoxyundecanic acid is carried out on Pt anode in a water/alcohol solution. Disadvantages of the method are platinum loss and byproducts. Some improvements may be expected with use of titanium anodes covered with a thin layer of platinum oxide or other noble metal oxides.[52]

Conclusion

The above review lead to the optimistic expectation that electrochemical methods in the near future will be applied for full scale production of a number of aroma chemicals.

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