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Mediator oxidation systems in organic electrosynthesis †

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Abstract. The data on the use of mediator oxidation systems activated by electric current (anodic or parallel anodic and cathodic) in organic electrosynthesis are considered and generalised. Electrochemical activation of these systems permits successful application of catalytic versions and easy scaling of mediator-promoted processes. Chemical and environmental advantages of electrochemical processes catalysed by mediator oxidation systems are demonstrated. Examples of the application of organic and inorganic mediators for the oxidation of various classes of organic compounds under conditions of electrolysis are given. The bibliography includes 297 references.

I. Introduction

Currently application of redox mediators (Latin, *mediator*, go-between; intermediatory) in organic chemistry has gained importance in view of development of new more efficient and nonpolluting synthetic methods as compared to traditional ones. Electrooxidation processes involving these reagents allow transformation of organic compounds at lower oxidation potentials than the standard respective potentials under mild conditions in the presence of catalytic amounts of a mediator, which is regenerated in the course of the process. They also increase the reaction efficiency and selectivity with simultaneous decrease in power consumption. The substrate oxidation occurs upon reaction with the oxidised form of the mediator generated on the electrode (so-called 'indirect' electrooxidation).

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This review summarises the literature data published in the last 15 years concerning the use of indirect electrochemical oxidation of organic compounds in organic synthesis. Earlier data on this topic are compiled in monographs [1–3] and reviews.[4–8] The material presented in a recently published monograph [9] and reviews [10–12] does not reflect all accumulated information in sufficient details, especially the achievements of Russian electroorganic chemists. The goal of the present review is to fill this gap and to demonstrate modern trends in the field of indirect electrooxidation of organic substrates catalysed by different mediators and mediator systems.

II. General regularities of action of redox mediators

For two recent decades, indirect electrooxidation of organic compounds has been the subject of intensive studies. The interest in this problem originates largely from the search for, and development of, methods of organic synthesis based on electrooxidation, which is promising for industrial use. In many cases, this process is characterised by much higher rate, selectivity and yields of the target products as compared to direct electrooxidation where direct electron transfer from a substrate to the electrode surface occurs.

Under conditions of the anodic oxidation, mediators (M) are either involved in the electron transfer from an organic substrate (RH) to the anode without formation of intermediates with components of the reaction medium (outer-sphere oxidation, redox catalysis) or transformed into oxidants in the course of the electron transfer (inner-sphere oxidation, chemical catalysis). In the latter case, the final products are formed, for instance, as a result of abstraction of hydrogen atoms from the substrate by electrogenerated radicals.

† The review is timed to the 75th anniversary of the N D Zelinsky Institute of Organic Chemistry of Russian Academy of Sciences.

The general mechanism of promotion of anodic oxidation of organic compounds by mediators includes the following stages:

1. Electrogeneration of the oxidised (active) form of a mediator (M_{ox}).

$$M \longrightarrow M_{ox}.$$

2. Outer-sphere one-electron substrate oxidation by the active form of the mediator with the regeneration of the parent form of the latter or inner-sphere one-electron substrate oxidation with the abstraction of the H atom.

$$M_{ox} + RH \rightleftharpoons M + RH^{+\bullet}$$

or

$$M_{ox} + RH \rightleftharpoons [M_{ox} \cdot RH] \longrightarrow MH^{+} + R^{\bullet}.$$

3. Deprotonation of the outer-sphere oxidation product (B is the base).

$$RH^{+\bullet} + B \longrightarrow R^{\bullet} + BH^{+}.$$

4. Regeneration of the mediator.

$$MH^{+} + B \longrightarrow M + HB^{+}.$$

5. Formation of the oxidation products.

$$R^{\bullet} \longrightarrow \text{oxidation products.}$$

Transition metal ions in higher oxidation states usually react with substrates (for example, with arenes and alkylarenes) as outer-sphere oxidants. Anions of hydrohalic, nitric and periodic acids, as well as organic compounds (for example, *N*-hydroxyphthalimide) and aminoxyl radicals [for example, 2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO)], are typical mediators, precursors of inner-sphere chemical oxidants.

Special place in a series of mediators of indirect electrooxidation is occupied by systems based on hydrogen peroxide generated from dioxygen and transition metal ions (for example, copper, vanadium ions, *etc*.), which play the role of genuine mediators. In this case, the oxidation involves cathodic current, which in most cases of direct and indirect anodic oxidation of organic compounds, is spent unpractically to the formation of dihydrogen due to proton reduction. Some researchers call electrooxidation using cathodic current 'cathodic oxidation'.‡ The indirect cathodic oxidation of organic substrates includes the following reactions:

1. Generation of hydrogen peroxide by cathodic reduction of dioxygen.

$$O_2 + 2H^{+} \longrightarrow H_2O_2.$$

2. Homolytic cleavage of electrogenerated H_2O_2 under the action of a mediator (metal ion in the lower valence state M^{n+}).

$$H_2O_2 + M^{n+} \longrightarrow HO^{\bullet} + HO^{-} + M^{(n+1)+}.$$

‡ See, for example, W Li, T Nonaka. *J. Electrochem. Soc.* **146** 529 (1999).

3. Oxidation of a substrate with the hydroxyl radicals formed (for example, as a result of either hydrogen atom abstraction from the substrate or addition to the substrate in the case of aromatic compounds).

$$RH + HO^{\bullet} \longrightarrow R^{\bullet} + H_2O$$

or

$$ArH + HO^{\bullet} \longrightarrow HO\dot{A}rH.$$

4. Transformation of radical intermediates under the action of oxidised form of the mediator [$M^{(n+1)+}$] into the products with the regeneration of the parent form of the mediator.

$$R^{\bullet}(\text{or } HO\dot{A}rH) + M^{(n+1)+} \longrightarrow \text{oxidation products} + M^{n+}.$$

Indirect electrooxidation of organic substrates and electrogeneration of mediators can occur under both homogeneous and heterogeneous conditions (upon immobilisation of the mediator on the surface of anode or solid supports). In both cases, the use of a mediator results in a decrease in overvoltage of the electrochemical process and an increase in its efficiency and selectivity. In essence, the mediator is an oxidant that can be regenerated electrochemically, which allows its use in catalytic rather than stoichiometric amount. Therefore, there is no need in disposal of waste reagents comprising a serious environmental problem.

There are two main versions of mediator-assisted electrolysis, *viz*., 'in-cell'- and 'ex-cell' processes. In the former case, substrate oxidation by the electrogenerated active form of the mediator is performed in one stage directly in the cell; in the latter case, it is carried out in two steps using a separate reactor. The versions for conducting indirect electrooxidation, general principles of action of different mediators and mediator systems, as well as many other aspects of application of these methods have been discussed.[1–12]

The efficient electrochemical oxidation can be achieved if mediators and mediator systems meet the following major requirements:

1) chemical stability of the oxidised form of the mediator under electrolysis conditions (upon transformation of even insignificant portion of M_{ox}, due to side reactions, into compounds that cannot be electroregenerated to M_{ox}, the mediator loses its catalytic activity very fast);

2) high rates and (whenever possible) irreversibility of electron transfer from the mediator to the electrode and of the reaction of the mediator active form with the substrate (otherwise, the use of electrodes with larger surface is required, which increases the probability of side reactions);

3) high solubility in the electrolyte in the case of electrolysis in a homogeneous system.

Inorganic mediators meet these requirements to a large extent (especially with regard to the first item). Activated forms of organic mediators, usually radicals or radical cations, often undergo irreversible side reactions. The most numerous group of inorganic mediators for electrooxidation of organic compounds consists of transition metal compounds and complexes containing ions Ce^{4+}, Mn^{3+}, Co^{3+}, Cr^{6+}, V^{5+}, Fe^{3+}, Pd^{2+}, Tl^{3+}, Ag^{2+}, Os^{8+}, Ru^{4+} and Ru^{8+}, which can be electrochemically regenerated. Among other inorganic mediators, halides and hypohalites are the most widely used. Among organic mediators, triarylamines, 2,2,6,6-tetramethylpiperidynyl-1-oxyl radicals and

benzoquinones, for example, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) proved to be the best.

Below are given particular examples of the use of different mediators in organic electrosynthesis.

III. Electrooxidation in the presence of mediators based on metal ions

1. Indirect electrooxidation of side chains of alkyl-substituted arenes and hetarenes

During two recent decades, more than six hundred papers have been published devoted to the methods for the synthesis of aromatic aldehydes, ketones and carboxylic acids by indirect anodic oxidation of alkyl-substituted (het)arenes involving metal ions as the redox mediators. The major theoretical and practical aspects of these processes have been comprehensively studied; large-scale manufacture of substituted benzaldehydes has been created on their base.[3,9] At the same time, the results obtained are only partially discussed in reviews[4–6,11] and monographs.[1–3,7,8]

Among redox mediators based on metal ions, the mediator pair Ce^{4+}/Ce^{3+} appeared to be the most efficient in indirect oxidation of alkylarenes.[13–34] In addition, pairs Mn^{3+}/Mn^{2+} (Refs 35–61), Co^{3+}/Co^{2+} (Refs 61–63), Cr^{6+}/Cr^{3+} (Refs 64–66) and other[67–72] are also used. The processes catalysed by the mediator pair Ce^{4+}/Ce^{3+} occur in aqueous solutions of sulfuric and methanesulfonic acids of moderate concentrations (1–2 mol litre^{-1}), for other pairs, more acidic solutions (>4 mol litre^{-1}) are used. Due to limited solubility of aromatic compounds in aqueous solutions of acids, the 'in-cell' indirect oxidation is conducted in a two-phase water–organic system. This occurs mainly at the interface and only to a small extent in the aqueous and organic phases. This reaction is activated using a phase-transfer catalyst (for example, hexadecyltrimethylammonium bromide[57] served as a catalyst for electrosynthesis of phenylacetaldehyde from ethylbenzene using a Mn mediator). Alternatively, sonication is applied. Thus, sonication in the oxidation of xylene catalysed by a Mn mediator increased the electrolysis rate and the yield of tolualdehydes.[58]

The solubility of arenes dissolved in the aqueous phase strongly influences the current efficiency of the mediator oxidised form, as well as selectivity of transformation of the starting substrates to the target products (chemical yield or substance yield), because oligomerisation and polymerisations of arenes on the anode surface result in its passivation. A number of techniques has been developed to suppress these side reactions, which are also typical of 'ex-cell' indirect oxidation of arenes. These allow a significant decrease in the arene content in the aqueous phase or their complete removal from the electrolyte. Organic solvents such as dichloromethane, dichloroethane (DCE), benzene and others are used in the one-stage process,[16,17,30,37] whereas in the two-stage process, either activated charcoal is added or arenes are extracted from the aqueous phase with hexane, dichloromethane or other solvents.[34,37] Thus extraction allowed an increase in the efficiency of electroregeneration of Mn^{3+} in the 'ex-cell'-process of the preparation of 4-chlorobenzaldehyde from 4-chlorotoluene from 45% to 93%–100%.[51]

The overall rate of electrochemical process is determined by the slowest stage, *viz*., oxidation of alkylarene with the electrogenerated active form of the mediator. Heating and more concentrated aqueous solutions of acids are used for acceleration of this stage (and the whole process). Among alkylarenes having only alkyl substituents, toluene is the most readily and selectively oxidised, among substituted alkylarenes, alkoxytoluenes are the most readily oxidised, then xylenes, alkyltoluenes with higher normal, secondary and tertiary alkyl groups; chloro- and nitro-substituted alkylarenes are the least reactive.[14,22] Oxidation of alkyltoluenes with higher normal and secondary alkyl groups occurs predominantly at the alkyl group to form aromatic ketones, for example, 4-isopropyltoluene transforms into 4-methylacetophenone.[15,29] In Table 1, examples are given of indirect electrooxidation of different alkyl-substituted arenes and methylpyridine involving redox mediators based on metal ions. These reactions provide possibility to obtain target products in good yields and selectivity.

2. Oxidation of aromatic rings

Indirect anodic and cathodic oxidation of the aromatic rings of arenes and hetarenes catalysed by metal ion-based mediators is most successfully used in the synthesis of quinones.[73–92] Silver salt demonstrated the best results among 3d-metal sulfates (manganese, cerium, silver, cobalt, iron and copper) used as mediators for the synthesis of 1,4-benzoquinone from benzene: current efficiency for benzoquinone was 67% (3 times as high as that with the use of other sulfates).[75] Even higher current efficiency for benzoquinone (83%–86%) was achieved when the reaction was catalysed by silver perchlorate in 2–4 M $HClO_4$ at the anode current density of 1.3 mA cm^{-2} (Table 2, entry 1). The efficiency of this process is determined also by the anodic potential, for which the optimum value is 1.18 V [versus the saturated calomel electrode (SCE)]. At higher anodic voltage, the current consumption for water electrolysis sharply increases, and the yield of the target product decreases.

The efficiency of the electrosynthesis of benzoquinone from benzene can be substantially enhanced[75] if cathodic current is involved. Cathodic current was successfully used for the synthesis of benzoquinone by copper ion-catalysed indirect cathodic oxidation of benzene involving dioxygen. In this electrochemical process, benzene is oxidised with hydroxyl radicals generated in the reactions of copper(I) ions with hydrogen peroxide formed upon protonation of O_2. Thus, the role of cathodic current is reduced to electroregeneration of Cu^+ ions and to generation of hydrogen peroxide (Scheme 1).

Scheme 1

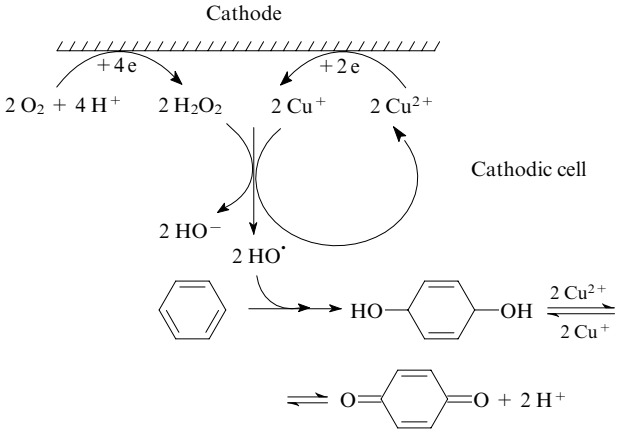
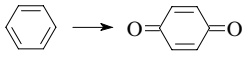
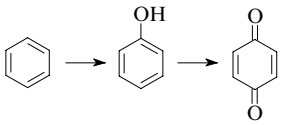
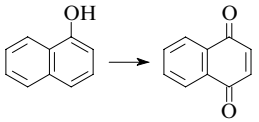
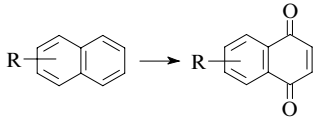
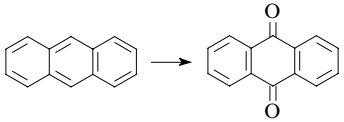


Table 1. Synthesis of aromatic aldehydes, ketones and carboxylic acids by indirect anodic oxidation of alkyl-substituted arenes and hetarenes mediated by metal ions.

Reaction	Entry	Yield (%)	Mediator	Reaction conditions			Ref.
				process	cell	electrolyte	
PhMe ⟶ PhCHO	1	91 (88)	Ce^{4+}/Ce^{3+}	B	DC	$MeSO_3H$, H_2O, CH_2Cl_2	14, 15
	2	59 – 90 (60 – 70)	Mn^{3+}/Mn^{2+}	B	UC	H_2SO_4, H_2O	53, 56, 59
	3	60 (60)	Co^{3+}/Co^{2+}	A	UC	AcOH, AcONa [a]	63
	4	71	V^{5+}/V^{4+}	A	UC	H_2SO_4, H_2O	69
PhMe ⟶ $PhCH_2OH$	5	78	MoO_4^{2-}/MoO_4^-	A	UC	MeOH, KOH	71
	6	78	Fe^{3+}/Fe^{2+}	B	DC	H_2SO_4, H_2O	72
PhEt ⟶ $PhCH_2CHO$	7	57	Mn^{3+}/Mn^{2+}	B	DC	H_2SO_4, H_2O, n-$C_{16}H_{33}NMe_3Br$	56
$PhCH_2R$ ⟶ PhC(O)R (R = Alk)	8	40 (38)	Ce^{4+}/Ce^{3+}	B	DC	$MeSO_3H$, H_2O, CH_2Cl_2	14, 15
$C_6H_4Me_2$ ⟶ MeC_6H_4CHO (Isomers: *ortho*, *meta*, *para*)	9	71 (88)	Ce^{4+} /Ce^{3+}	B	DC	$MeSO_3H$, H_2O, CH_2Cl_2	15
4-EtC_6H_4Me ⟶ 4-EtC_6H_4CHO + 4-AcC_6H_4Me	10	10 + 70	Ce^{4+}/Ce^{3+}	B	DC	$MeSO_3H$, H_2O	15
4-$Bu^tC_6H_4Me$ ⟶ 4-$Bu^tC_6H_4CHO$	11	88	Ce^{4+}/Ce^{3+}	B	DC	$MeSO_3H$, H_2O, CH_2Cl_2	14, 15
	12	84 (63)	Mn^{3+}/Mn^{2+}	B	DC	H_2SO_4, H_2O	40
4-$Pr^iC_6H_4Me$ ⟶ 4-$Pr^iC_6H_4CHO$ + 4-AcC_6H_4Me	13	19 + 53	Ce^{4+}/Ce^{3+}	B	UC	$MeSO_3H$, H_2O	15
4-$MeOC_6H_4Me$ ⟶ 4-$MeOC_6H_4CHO$	14	98 (94)	Ce^{4+}/Ce^{3+}	A	UC	H_2SO_4, H_2O	13
	15	71 (89)	Ce^{4+}/Ce^{3+}	B	DC	$MeSO_3H$, H_2O, CH_2Cl_2	14, 15
	16	89 (83)	Ce^{4+}/Ce^{3+}	B	DC	H_2SO_4, H_2O	33
	17	98 (92)	Mn^{3+}/Mn^{2+}	A	UC	H_2SO_4, H_2O	13
XC_6H_4Me ⟶ XC_6H_4CHO	18	86 (88)	Ce^{4+}/Ce^{3+}	B	DC	$MeSO_3H$, H_2O, CH_2Cl_2	14, 15
(X = 2-Cl, 4-Cl, 4-Br, 4-F)	19	78 (91)	Ce^{4+}/Ce^{3+}	B	DC	H_2SO_4, H_2O	30
	20	80 – 90 (60 – 84)	Mn^{3+}/Mn^{2+}	B	UC	H_2SO_4, H_2O	47, 50
4-BrC_6H_4Me ⟶ 4-$BrC_6H_4CO_2H$	21	81	Cr^{6+}/Cr^{3+}	B	UC	H_2SO_4, H_2O	66
4-$O_2NC_6H_4Me$ ⟶ 4-$O_2NC_6H_4CHO$	22	40 (> 90)	Ce^{4+}/Ce^{3+}	B	DC	$MeSO_3H$, H_2O, CH_2Cl_2	20
4-$O_2NC_6H_4Me$ ⟶ 4-$O_2NC_6H_4CO_2H$	23	81 (54)	Cr^{6+}/Cr^{3+}	B	DC	H_2SO_4, H_2O, $Bu^n_4NHSO_4$	64
4-MeC_5H_4N ⟶ 4-$(AcO)_2CHC_5H_4N$	24	45 – 68 (22 – 34)	Co^{3+}/Co^{2+}	A	UC	Ac_2O, AcOK	62
$RC_5H_4N(\rightarrow O)$ ⟶ $HO_2CC_5H_4N$ (R = 2-Me, 3-Me, 4-Me)	25	49 – 68	Ru^{4+}/Ru^{2+}	A	DC	H_2O, Bu^tOH	68

Note. Hereinafter, the following abbreviations are adopted: A is 'in-cell'-process, B is 'ex-cell'-process; UC is undivided cell, DC is divided cell; dash means that there is no data in the original paper or in the summary; in the column 'yield' chemical yield of the product is given, the value in parentheses is current efficiency. [a] In the presence of dioxygen.

Table 2. Indirect anodic oxidation of arenes mediated by metal ions.

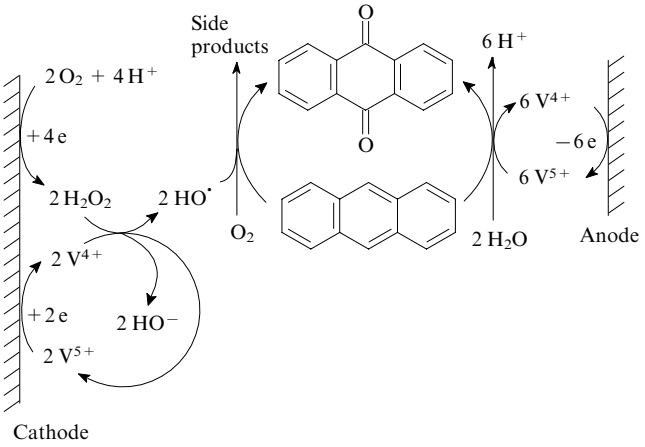
Reaction	Entry	Product yield (%)	Mediator	Reaction conditions			Ref.
				process	cell	electrolyte	
	1	> 90 (67–86)	Ag^{2+}/Ag^{+}	A	DC	H_2O, H_2SO_4 or $HClO_4$, PhH	75
	2	> 90 (~160)	Ag^{2+}/Ag^{+}, $Cu^{2+}/Cu^{+}/O_2$ (see [a])	A	UC	$HClO_4$, H_2O	75
	3	45	Ce^{4+}/Ce^{3+}	B	DC	$MeSO_3H$, H_2O, DCE	84
	4	–	$Cu^{2+}/Cu^{+}/O_2$	A	UC	$HClO_4$, H_2O	87
	5	–	$Cu^{2+}/Cu^{+}/O_2$ (see [b])	A	DC	H_2SO_4, H_2O	88
	6	–	Ce^{4+}/Ce^{3+}	B	DC	H_2SO_4, H_2O, CH_2Cl_2	79
 (R = H, 2-Me, 2-Bu^t, 1-NO_2)	7	84–98 (85–95)	Ce^{4+}/Ce^{3+}	B	DC	$MeSO_3H$, H_2O, DCE	14, 15
	8	93	Ce^{4+}/Ce^{3+}	B	UC	H_2SO_4, H_2O	84
	9	91 (88)	Mn^{3+}/Mn^{2+}	B	DC	$MeSO_3H$, H_2O	14, 15
	10	31	Ru^{4+}/Ru^{3+}	A	UC	MeCN, H_2O, $Bu^n_4NClO_4$	80
	11	69 (60–70)	$Cr^{3+}/Cr_2O_7^{2-}$	A	UC	$HClO_4$, MeCN	81
	12	98 (152)	V^{5+}/V^{4+}, H_2O_2/O_2 (see [c])	A	UC	$HClO_4$, H_2O	76
	13	97	Ce^{4+}/Ce^{3+}	B	UC	H_2SO_4, H_2O	84
	14	95 (89)	Ce^{4+}/Ce^{3+}	B	UC	$MeSO_3H$, H_2O	14, 15
	15	> 90 (61)	Mn^{3+}/Mn^{2+}	A	DC	$MeSO_3H$, H_2O, DCE, DBS	78
	16	(78)	Ru^{4+}/Ru^{3+}	A	UC	MeCN, H_2O, $Bu^n_4NClO_4$, KCl	89

[a] Electrosynthesis using parallel indirect anodic and cathodic oxidation and redox pairs Ag^{2+}/Ag^{+} and Cu^{2+}/Cu^{+} as anodic and cathodic mediators; [b] electrolysis using cathodic current; [c] electrosynthesis using parallel indirect anodic and cathodic oxidation and redox pairs V^{5+}/V^{4+} and H_2O_2/O_2 as anodic and cathodic mediators; DBS is dodecyl benzene sulfonate.

The process presented in Scheme 1 is carried out with continuous extraction of benzoquinone from the catholyte with benzene and maintaining the medium acidity within the pH interval 3.5 to 4.6. The yield of benzoquinone in this process was 75%–89%. The combination of anodic and cathodic processes in one cell in the synthesis of benzoquinone called 'duet electrosynthesis' resulted in an almost double increase in the current efficiency for benzoquinone (to ~160%) (Table 2, entry 2).

Soon afterwards, electrosynthesis of anthraquinone was performed by parallel indirect oxidation of anthracene in an undivided cell. Redox pairs V^{5+}/V^{4+} and H_2O_2/O_2 were used as anodic and cathodic mediators (Scheme 2; Table 2, entry 12).[76]

Scheme 2

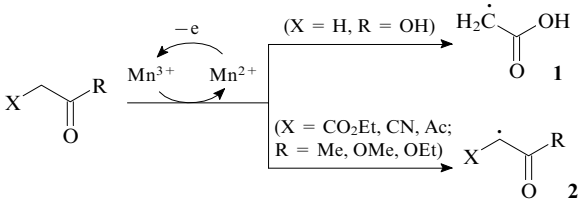


Alternative currently known methods for the electrosynthesis of quinones are based exclusively on indirect anodic oxidation of arenes catalysed by cerium, manganese and other mediators in divided and undivided cells in the 'ex-cell'- and 'in-cell'-versions (see Table 2).

3. Oxidative coupling of CH-acids with alkenes under the action of electrogenerated manganese and cerium ions

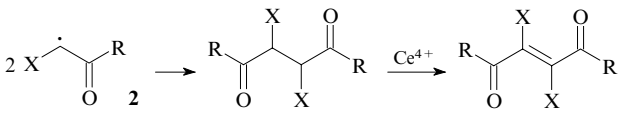
Electrogenerated *in situ* manganese triacetate is used for oxidative coupling of acetic acid, ethyl acetoacetate, diethyl malonate, ethyl cyanoacetate, 1,3-dicarbonyl compounds and α-nitroketones with alkenes, cycloalkenes, arylalkenes and dienes.[93–106] Examples of these reactions are presented in Table 3. The development of this method was caused by the necessity to replace the widely used traditional chemical synthesis that required the consumption of two and more equivalents of $Mn(OAc)_3$. This oxidant can easily be regenerated *in situ* by anodic oxidation of the $Mn(OAc)_2$ formed in acetic acid containing sodium or potassium acetate. The reaction occurs at the anodic voltage of ~1 V (*vs* SCE).

Under these conditions, the majority of organic compounds (except for phenols and anilines) are not oxidised directly on the anode. However, their indirect oxidation is possible in a homogeneous medium catalysed by a mediator pair Mn^{3+}/Mn^{2+}. For example, radicals **1** or **2** are generated from acetic acid or from active methylene compounds.



Subsequent reactions of these radicals with alkenes, cycloalkenes, arylalkenes and dienes give target products (Table 3). The prerequisite for the efficient process is that the rate of the chemical stage is close to that of electroregeneration of Mn^{3+}. It is achieved by performing the electrosynthesis with heating, usually at 60–110 °C. The fact that the process proceeds in both divided and undivided cells with approximately the same efficiencies indicates that practically no cathodic reduction of $Mn(OAc)_3$ occurs. The main results on the studies of these reactions are generalised [100] and surveyed.[11]

Note that in the absence of alkenes, radicals **2** recombine to give saturated dimers. The latter undergo oxidative dehydrogenation under the action of electrogenerated Ce^{4+} ions to form unsaturated dimers (Table 3, entry 20).[106]



In contrast to $Ce(NO_3)_4$, ammonium cerium nitrate $(NH_4)_2[Ce(NO_3)_6]$ dehydrogenates only dimeric derivatives of methyl cyanoacetate (X = CN, R = OMe).

4. Electrochemical conversion of alcohols, carbohydrates and alkenes into carbonyl compounds and carboxylic acids

The progress in electrochemical transformations of alcohols, glycols, carbohydrates and their derivatives, as well as alkenes into carbonyl compounds and carboxylic acids has been achieved due to efficient catalysis of the reactions by mediator redox systems based on ruthenium, manganese, cerium, chromium and copper ions. In addition, these processes were performed with involvement of nickel oxyhydroxide [$Ni^{III}(O)OH$] formed and regenerated on the surface of the Ni-anode in the course of electrolysis in an alkaline medium and acting as a fixed mediator. Examples of electrosynthesis of carbonyl compounds and carboxylic acids with the use of different mediators based on metal ions are given in Tables 4–6.[65, 107–133]

Indirect electrooxidation of alcohols, carbohydrates and their derivatives in an individed cell with a double mediatory system Ru^{VIII}/Ru^{IV}–$[Cl^+]/Cl^-$ in a two-phase system was studied.[107–112] The two-phase system consists of a solution of NaCl in a phosphate buffer (pH 4) and a nonmiscible organic solvent (for example, CCl_4) in a 2 : 1 ratio. These conditions allow conducting the stages of the process in different phases, to exclude the contact of the substrate and the products with electrodes thus preventing unde-

Table 3. Indirect electrooxidative coupling of CH-acids with alkenes mediated by the manganese and cerium ions.

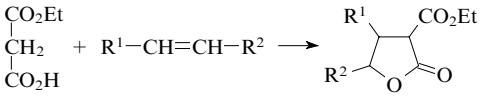
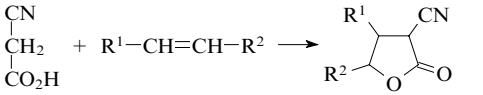
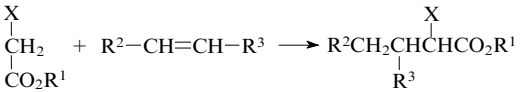
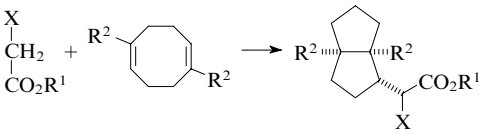
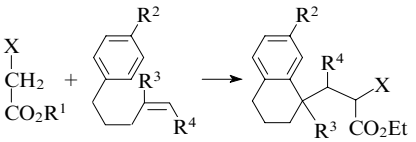
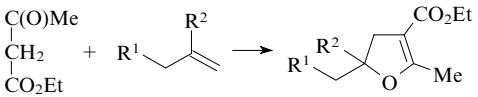
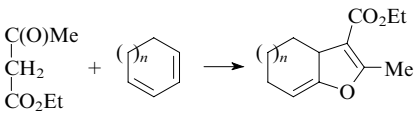
Reaction	Entry	Yield (%)	Conditions [a]			Ref.
			cell	electrolyte	T/°C	
$Mn(OAc)_3$ as a catalyst						
	1	65 – 66 (29 – 72)	UC	AcOH, AcONa	25	101
[R^1 = Ph: R^2 = H, Ph; $R^1 - R^2 = (CH_2)_4$]						
	2	60 (60)	UC	AcOH, AcOK	60	99
[R^1 = H, Alk; R^2 = H, Ph; $R^1 - R^2 = (CH_2)_n$ (n = 3 – 10)]						
	3	50 – 60 (50 – 60)	DC	AcOH, Ac_2O, AcONa	95 – 97	93, 95, 99
[X = CN, CO_2R^1; R^1 = Me, Et; R^2 = Alk, R^3 = H; $R^2 - R^3 = (CH_2)_n$ (n = 3 – 10)]						
	4	76 – 78 (50 – 51)	DC	AcOH, AcOEt, AcONa	25 – 60	94, 98, 99
(X = CN, CO_2R^1; R^1 = Me, Et; R^2 = H, Me)						
	5	37 – 79 (24 – 52)	DC	AcOH, AcOEt, AcONa	50	94, 96
(X = CN, CO_2R^1; R^1 = Me, Et; R^2 = H, Me, F; R^3, R^4 = H, Me)						
	6	(80 – 86)	DC	AcOH, AcOEt, AcONa	40	94
(R^1 = Alk; R^2 = H, Me)						
	7	41 – 43 (27 – 28)	DC	AcOH, AcOEt, AcONa	40	94
(n = 1, 3)						

Table 3 (continued).

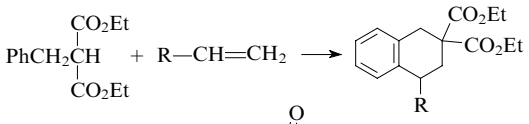
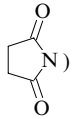
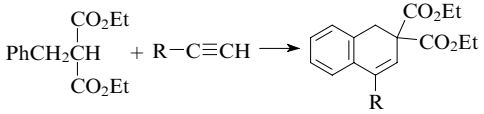
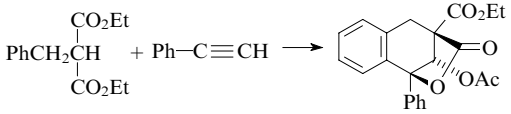
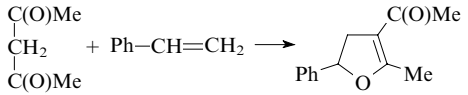
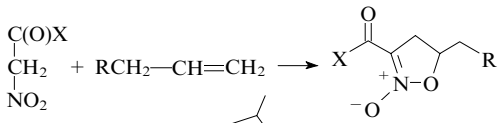
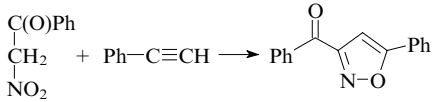
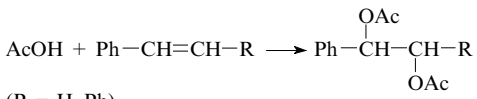
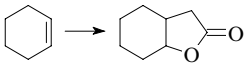
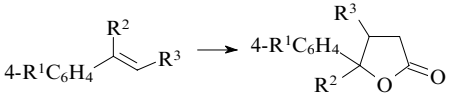
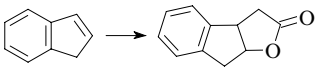
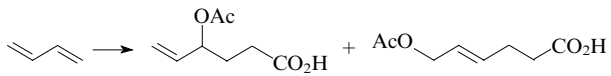
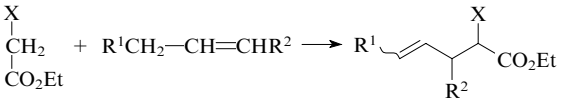
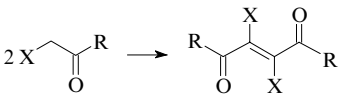
Reaction	Entry	Yield (%)	Conditions [a]			Ref.
			cell	electrolyte	T/°C	
$Mn(OAc)_3$ as a catalyst						
 (R = Alk, Ph, CO_2Et, OAc, )	8	64 – 68	DC	AcOH, AcOK	70	98
 (R = Alk, Me_3Si)	9	70	DC	AcOH, AcOK	70	98
	10	77	DC	AcOH, AcOK	70	98
	11	40	UC	AcOH, AcOK	60	99
 (R = Pr^n, OAc; X = Ph, )	12	37 – 59 (32 – 59)	DC	AcOH, $Bu^n_4NBF_4$	60	100
	13	49 (49)	DC	AcOH, $Bu^n_4NBF_4$	60	100
 (R = H, Ph)	14	49 – 60 (26 – 54)	UC	AcOH, AcONa	70	101

Table 3 (continued).

Reaction	Entry	Yield (%)	Conditions [a]			Ref.
			cell	electrolyte	T/°C	
$Mn(OAc)_3$ as a catalyst						
AcOH + 	15	50 (22)	UC	AcOH, AcONa	70	101
$Mn(OAc)_3 - Cu(OAc)_2$ as a catalyst						
AcOH + 	16	> 90 (58 – 80)	DC	AcOH, Ac_2O, AcONa	95 – 97	93
(R^1 = H, Cl, Me; R^2 = H, Me; R^3 = H, Ph, CO_2Et, CH_2OH)						
AcOH + 	17	> 90 (58 – 80)	DC	AcOH, Ac_2O, AcONa	95 – 97	93
AcOH + 	18	(84) [b]	DC	AcOH, Ac_2O, AcOK	100	95
	19	~ 50 (44 – 48)	DC	AcOH, AcOEt, AcONa	40 – 60	93
[X = CN, CO_2Et; R^1 = Alk, R^2 = H; $R^1 - R^2$ = $(CH_2)_n$ (n = 2 – 9)]						
Mediator pair $Ce(NO_3)_4/Ce(NO_3)_3$						
	20	49 – 84 (48 – 76)	DC	MeCN, HNO_3	–	106
(X = Ac, CO_2Me, CN; R = Me, OMe)						

[a] In all cases, 2.0 – 2.2 F of electricity per mole of unsaturated compound or CH-acid was passed (entry 20) (F is the Faraday number having a dimension of 96500 C mol^{-1}); [b] the product ratio is 3 : 2.

Table 4. Synthesis of aldehydes, ketones and carboxylic acids by indirect anodic oxidation of alcohols and allyl ethers in the presence of ruthenium-containing redox systems.

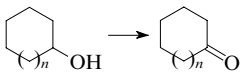
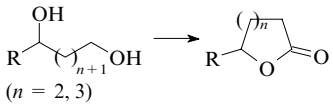
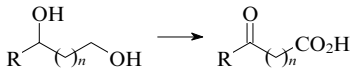
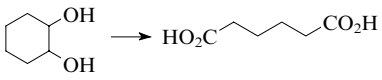
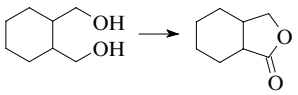
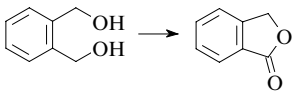
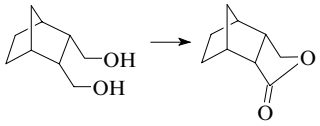
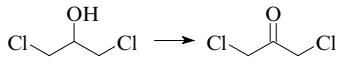
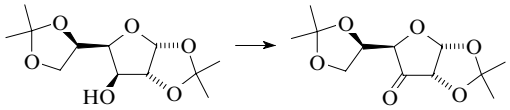
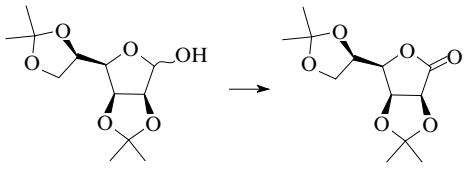
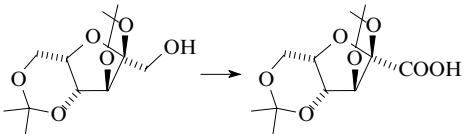
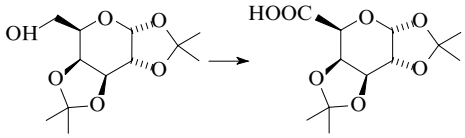
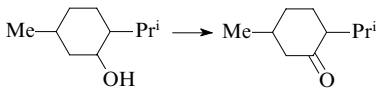
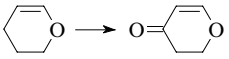
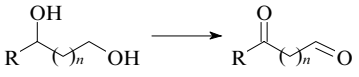
Reaction	Entry	Yield (%)	Conditions		Ref.
			cell	electrolyte	
Double mediatory system RuO_2 – NaCl [a]					
$RCH_2OH \longrightarrow RCO_2H + RCO_2CH_2R$ (R = Alk)	1	60 – 70 (34 – 46) + + 13 – 16 (7 – 10)	UC	H_2O, CCl_4	107
$PhCH_2OH \longrightarrow PhCO_2H$	2	90 (90)	UC	H_2O, CCl_4	107, 108
$PhCH_2OH \longrightarrow PhCHO$	3	80 (70)	UC	H_2O, CCl_4	107, 108
$R^1R^2CHOH \longrightarrow R^1R^2C{=}O$ (R^1, R^2 = Alk; Alk, Ph)	4	83 – 95 (69 – 79)	UC	H_2O, CCl_4	107
 (n = 1, 3, 7)	5	93 – 100 (77 – 83)	UC	H_2O, CCl_4	109
 (n = 2, 3)	6	74 – 79 (41 – 63)	UC	H_2O, CCl_4	107
 (n > 4)	7	65 – 80 (30 – 56)	UC	H_2O, CCl_4	107
	8	75 (51 – 67)	UC	H_2O, CCl_4	107
	9	79 (54)	UC	H_2O, CCl_4	107
	10	60 (34)	UC	H_2O, CCl_4	107
	11	83 (41)	UC	H_2O, CCl_4	107
	12	98 (98)	DC	H_2O, EtOAc	110
	13	94 (62)	UC	H_2O, EtOAc	110
$RCH(OH)CH_2Hal \longrightarrow RC(O)CH_2Hal$ (R = Me, Ph; Hal = Cl, Br)	14	83 – 98 (83 – 98)	DC	H_2O, EtOAc	111
	15	65 – 77 (65 – 77)	UC	H_2O, EtOAc	111
	16	90 (28)	UC	H_2O, CCl_4, Bu^tOH	107, 112
	17	92 (57.5)	UC	H_2O, Me_2CO	107, 112

Table 4 (continued).

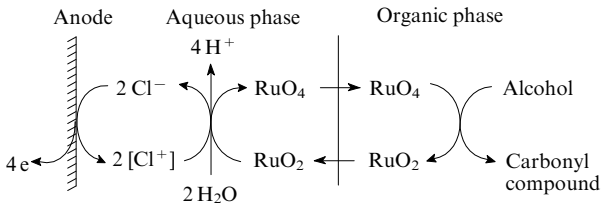
Reaction	Entry	Yield (%)	Conditions		Ref.
			cell	electrolyte	
Double mediatory system RuO_2 – NaCl [a]					
	18	83 (47)	UC	H_2O, CCl_4	107
	19	86 (50)	UC	H_2O, CCl_4	107
$RCHO \longrightarrow RCO_2H$ (R = Alk)	20	80 – 86 (40 – 43)	UC	H_2O, CCl_4	107
Mediatory system RuO_2 – Bu^n_4NOH – Bu^n_4NBr [b]					
$RCH_2OH \longrightarrow RCHO$ (R = Alk)	21	87 – 92 (35 – 37)	UC	MeCN, H_2O	113, 114
$R^1R^2CHOH \longrightarrow R^1R^2C{=}O$ (R^1, R^2 = Alk; Alk, Ph)	22	85 – 94	UC	MeCN, H_2O	113, 114
	23	94	UC	MeCN, H_2O	113
Mediatory system $[(bipy)(trpy)Ru(O)]^{2+}$/$[(bipy)(trpy)Ru(OH_2)]^{2+}$ – poly$(RuL_3)^{2+}$ (see [c])					
$RCH{=}CHCH_2OBu^n \longrightarrow RCH{=}CHCO_2Bu^n$ (R = H, Me)	24	40 (20 – 27)	DC	H_2O, Bu^tOH	115
	25	71 (36 – 47)	DC	H_2O, Bu^tOH	115
PhOH or $RCH{=}CHCH_2OPh \longrightarrow$ 	26	41 – 47	DC	H_2O, Bu^tOH	115
	27 28	47 (n = 0) 41 (n = 1)	DC DC	H_2O H_2O	116 116

[a] The amount of RuO_2 used was 0.5 mol % – 3 mol %, pH 4 – 7; [b] 5 mol % RuO_2, pH 10; [c] 5 mol % – 6 mol % mediator, pH 8, $[(bipy)(trpy)Ru(O)]^{2+}$ and $[(bipy)(trpy)Ru(OH_2)]^{2+}$ are oxo and aqua complexes of Ru^{IV} and Ru^{II}, respectively, with bipyridine (bipy) and terpyridine (trpy) ligands, poly$(RuL_3)^{2+}$ is a modified anode obtained by polymerisation of Ru^{II} *N*-(bipyridylbutyl)pyrrole complex on its surface; experiments with these complexes were conducted at a potential control, others at a current control.

sirable side reactions. These conditions ensure high yield of the target product (83% – 94%), if 0.5 mol % – 3 mol % of a mediator with respect to the substrate is used. An example of the catalytic cycle for the transformation of alcohols into carbonyl compounds using the double mediatory system RuO_4/RuO_2 – $[Cl^+]/Cl^-$ in two-phase water – organic medium is given in Scheme 3.

Other ruthenium mediators, $RuCl_3 \cdot (H_2O)_x$, $Ru_3(CO)_{12}$, $RuCl_2(Ph_3P)_3$ and $[Ru_3O(OAc)_6(H_2O)_3]OAc$ catalyse indirect electrooxidation of alcohols in a similar way and with comparable efficiency.[107]

Scheme 3



It is of note that under the conditions of oxidation of alkan-2-ols and secondary benzylic alcohols in CCl_4, methyl

Table 5. Synthesis of aldehydes, ketones and carboxylic acids by indirect oxidation of alcohols, lactones and aldehydes at the hydroxide nickel anode.

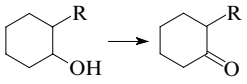
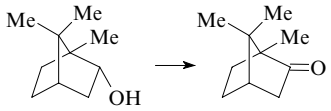
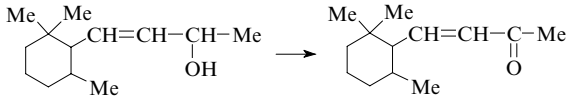
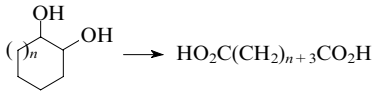
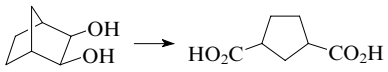
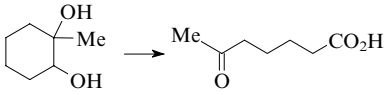
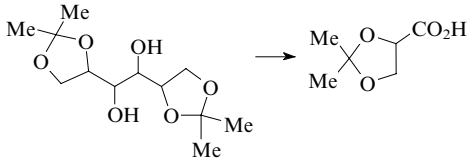
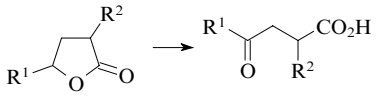
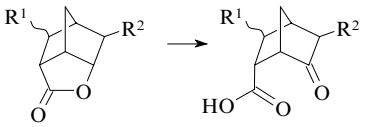
Reaction	Entry	Yield (%)	Ref.
One-phase system [a]			
$RCH_2OH \longrightarrow RCO_2H$ (R = Alk)	1	67 – 92 (7 – 37)	117, 118
$RCH_2OH \longrightarrow RCO_2H$ (R = Ar, furyl)	2	79 – 86 (30 – 46)	117, 118
$R^1CH(OH)R^2 \longrightarrow R^1C(O)R^2$ (R^1, R^2 = Alk)	3	73 – 76 (5 – 9)	117, 118
$ArCH(OH)R \longrightarrow ArCO_2H$	4	90 (48)	117, 118
 (R = H, Et)	5	72 – 80 (6 – 53)	117, 118
	6	72 – 81 (11 – 12)	117, 118
$RCH{=}CHCH_2OH \longrightarrow RCH{=}CHC_2H$ (R = Alk, Ph)	7	90 – 96	119
$RCH{=}CH(CH_2)_nCH_2OH \longrightarrow RCH{=}CH(CH_2)_nCO_2H$ [n = 0, R = Alk; n = 1, R = $HO(CH_2)_3$]	8	68 – 82 (7 – 16.5)	117, 118
$RC{\equiv}C(CH_2)_nCH_2OH \longrightarrow RC{\equiv}C(CH_2)_nCO_2H$ (n = 0: R = H, $HOCH_2$; n = 1, R = H)	9	28 – 51 (10 – 20)	117, 118
	10	59 (40)	117, 118
$HOCH_2(CH_2)_nCH_2OH \longrightarrow HO_2C(CH_2)_nCO_2H$ (n = 4, 8)	11	77 – 85 (24 – 38)	118
 (n = 1, 2, 3, 7)	12	74 – 84 (74 – 84)	120
	13	72 (11)	120
	14	70 (37)	120
$HOCH_2C{\equiv}CCH_2OH \longrightarrow HO_2CC{\equiv}CCO_2H$	15	55 (39)	117, 118
	16	70 (18)	120
Steroidal 3α- and 3β-alcohols ⟶ 3α- and 3β-ketosteroids	17	28 – 78 (1 – 5)	117, 118
 (R^1 = H, Me, Ph; R^2 = H, All, CH_2OMe)	18	92 – 97 (46 – 64)	121

Table 5 (continued).

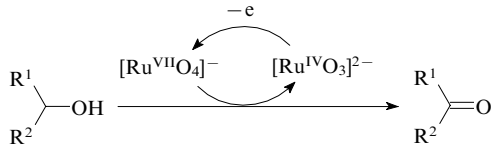
Reaction	Entry	Yield (%)	Ref.
One-phase system [a]			
	19	71 – 96	121
$RCHO \longrightarrow RCO_2H$ (R = Alk, Ar, Alkenyl, cyclo-C_6H_{11})	20	57 – 98	118
Two-phase system [b]			
$RCH_2OH \longrightarrow RCHO + RCO_2H$ [c]	21	32 – 67 (15 – 40)	122
$ArCH_2OH \longrightarrow ArCHO$	22	83 – 86 (43 – 50)	122
$RCH{=}CHCH_2OH \longrightarrow RCH{=}CHCHO$	23	36 – 70 (22 – 50)	122
$Me_2C{=}CH(CH_2)_2\underset{\displaystyle Me}{C}{=}CHCH_2OH \longrightarrow Me_2C{=}CH(CH_2)_2\underset{\displaystyle Me}{C}{=}CHCHO$	24	86 (52)	122
$PhCH{=}CHCH_2OH \longrightarrow PhCH{=}CHCHO$	25	75 (60)	122
$Bu^nOH \longrightarrow Pr^nCO_2H$ [d]	26	(166)	123

Note. The process was conducted in an undivided cell at room temperature. [a] A solution of NaOH, KOH or K_2CO_3 in H_2O or aqueous Bu^tOH; [b] aq. K_2CO_3 – petroleum ether; [c] dodecanoic acid was added, the product ratio was (1.5 – 23) : 1; [d] parallel indirect anodic and cathodic oxidations were used, mediators: Ni(O)OH generated by electrooxidation of an Ni-anode in an alkaline medium and the system H_2O_2/O_2.

and phenyl ketones formed do not undergo subsequent transformations such as the haloform reaction or chlorination of the benzene ring. Under the optimal conditions (pH 7 and 6 – 7 F of electricity), primary aliphatic (including benzylic) alcohols undergo oxidation to carboxylic (benzoic) acids. The latter are also formed from the corresponding aldehydes (Table 4, entries 1, 2 and 20).[107, 178] The structures of the oxidation products (diols) depend on the remoteness of HO groups from one another (Table 4, entries 6 – 11, 27, 28).[107, 116]

The method of indirect oxidation was successfully extended to halogen-substituted alcohols and carbohydrates (Table 4, entries 12 – 15).[110, 111] Due to the ease of isolation of the target products and relatively low cost of their preparation, indirect electrooxidation of glycols, carbohydrates and their derivatives to carbonyl compounds and carboxylic acids has substantial advantages over standard oxidation methods demanding stoichiometric amounts of expensive reagents.

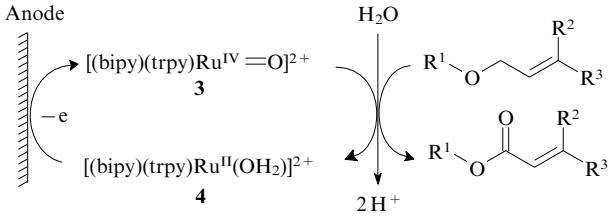
When the electrolysis is performed in the presence of the Ru ions in alkaline medium (for example, in a water – acetonitrile solution of tetrabutylammonium hydroxide) the perruthenate ions $[Ru^{VII}O_4]^-$ are formed. They convert primary alcohols to aldehydes, secondary alcohols to ketones (Table 4, entries 21 – 23).[113, 114] In this case, the mediator pair $[RuO_4]^-/[RuO_3]^{2-}$ is involved in electrooxidation:



R^1, R^2 = H, Alk.

Oxoruthenium ions stabilised by pyridine ligands, for example, $[(bipy)(trpy)Ru^{IV}O]^{2+}$ (**3**) catalyse indirect electrooxidative transformations of alcohols, ethers and phenols in a different manner. Oxidation of substrates with ions **3** occurs as a result of two-electron hydride transfer and the formation of the ruthenium aqua-complex $[(bipy)(trpy)Ru^{II}(OH_2)]^{2+}$ (**4**), which is readily oxidised on the anode (E_{ox} = 0.8 V *vs* SCE). This allows the use of mediator **3** in the amount of 5 mol % – 6.5 mol % and the electrolysis can be performed under the conditions where alcohols, ethers and phenol do not undergo direct electrooxidation. Electrochemical oxidation of allylic ethers catalysed by a mediator pair $[(bipy)(trpy)Ru{=}O]^{2+}/[(bipy)(trpy)Ru(OH_2)]^{2+}$ is presented in Scheme 4.

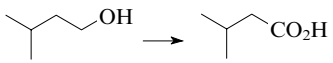
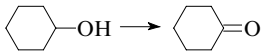
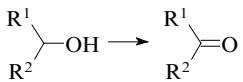
Scheme 4



Butyl acrylate and butyl but-2-enoate (from allyl butyl and but-2-enyl butyl ethers, respectively), 2,3-dihydropyran-4-one (from dihydro-4*H*-pyran), 1,2-benzoquinone (from phenol and allyl phenyl ethers) and 1-hydroxybutan-2(3)-one [from butan-1,2(3)-diol] were synthesised using the ruthenium redox pair **3**/**4** (Table 4, entries 24 – 26).[115]

One of the novel promising trends in organic electrosynthesis is associated with the design of modified electrodes with redox mediators immobilised on the surface, which can permanently be regenerated in the course of electrolysis

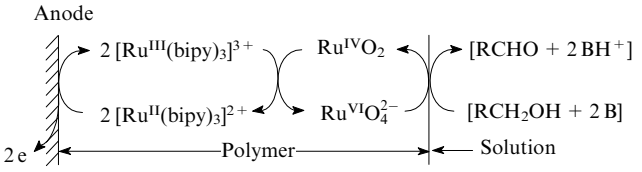
Table 6. Synthesis of aldehydes, ketones and carboxylic acids by indirect anodic oxidation of alcohols, carbohydrates and their derivatives in the presence of redox systems based on metal ions.

Reaction	Entry	Yield (%)	Mediator	Conditions			Ref.
				process	cell	electrolyte	
$MeCH(OH)CO_2Et \longrightarrow MeC(O)CO_2Et$	1	> 78	Mn^{III}/Mn^{II}	B	UC	H_2SO_4, H_2O	124
$HOCH_2CH(OH)CH_2OH \longrightarrow HOCH_2CH(OH)CHO$	2	91 (> 90)	Mn^{III}/Mn^{II}	B	UC	H_2SO_4, H_2O	125
$Bu^nOH \longrightarrow Pr^nCHO$	3	–	Mn^{III}/Mn^{II}	B	UC	H_2SO_4, H_2O	126
$RCH{=}CHCH_2OH \longrightarrow RCH{=}CHCHO$ (R = Alk, Ph)	4	73 – 100	MnO_2 or Ce^{4+}/Ce^{3+}	B	UC	H_2SO_4, H_2O, hexane	127, 128
$PhCH_2OH \longrightarrow PhCHO$	5	78	MnO_2	B	UC	H_2SO_4, H_2O, hexane	127
$PhCH(OH)R \longrightarrow PhC(O)R$ (R = Alk, CH_2CO_2Et)	6	76 – 100	MnO_2	B	UC	H_2SO_4, H_2O, hexane	127
	7	> 95	Cr^{VI}/Cr^{III}	–	UC	H_2SO_4, H_2O [a]	129
	8	(72)	Cr^{VI}/Cr^{III}	B	UC	H_2SO_4, H_2O	130
$ROCH_2Ar \longrightarrow ROH + ArCHO$	9	77 – 91	Mn^{III}/Mn^{II}	A	DC	H_2SO_4, H_2O, CCl_4	131
(R = Alk)	10	–	see [b]	A	DC	H_2SO_4, H_2O [a]	65
Aldopentoses, ketohexoses $\longrightarrow$ 2-osuloses	11	48 – 55	Cu^{II}/Cu^{I}	A	UC	MeOH, H_2O, AcOH	132
$4\text{-}XC_6H_4CH_2OH \longrightarrow 4\text{-}XC_6H_4CHO$ (X = H, Me, MeO, Cl)	12	65 – 98	$Pd(OAc)_2$ – benzoquinone	A	DC	DMF, $Bu_4^nNBF_4$	133
							
(R^1 = Alk, Ar; R^2 = H, Me, PhC(O), $HOCH_2$, Ph;	13	58 – 100	$Pd(OAc)_2$ – benzoquinone	A	DC	DMF, $Bu_4^nNBF_4$	133
$R^1 - R^2 = (CH_2)_6$)	14	29	$Pd(OAc)_2$ – benzoquinone	A	DC	DMF, $Bu_4^nNBF_4$	133
$PhCH{=}CHCH_2OH \longrightarrow PhCH{=}CHCHO$	15	64	$Pd(OAc)_2$ – benzoquinone	A	DC	DMF, $Bu_4^nNBF_4$	133

[a] Tetrabutylammonium hydrosulfate or perchlorate was used as a phase-transfer catalyst; [b] double mediatory system based on chromium(III) and silver (I) ions.

and catalyse oxidation of organic compounds. Among them are carbon felt electrodes modified by polypyrrole films with immobilised cationic groups and dispersed microparticles of ruthenium dioxide. These microparticles appeared to be convenient and efficient mediators of mild electrooxidation of primary alcohols to aldehydes in a water–organic medium (Scheme 5).[134–137]

Scheme 5



Immobilised cations $[Ru(bipy)_3]^{3+}$ act as electron carriers in the generation of the RuO_4^{2-} ions, which possess higher oxidation ability. Under the optimum conditions, polypyrrole films stand >10 000 catalytic cycles without loss of catalytic activity. The lifetime of these modified electrodes is determined by the rate of loss of the RuO_4^{2-} ions.

Hydroxide nickel anodes are also used as electrodes with immobilised redox mediators, which are permanently regenerated in the course of electrolysis and catalyse electrooxidation of organic compounds.[117–123] Under the conditions of amperostatic electrolysis in an undivided cell in an aqueous alkaline medium, $Ni^{III}(O)OH$ is generated on the anode surface as a black film. Nickel oxyhydroxide acts as an electrogenerated oxidant of organic substrates transforming primary alcohols and aldehydes into carboxylic acids, secondary alcohols into ketones, γ-substituted lactones into the corresponding oxocarboxylic acids, hydroxy-substituted steroids into steroidal ketones and carboxylic acids (Table 5).

Electrochemical oxidation of steroidal alcohols is selective;[117,118] the reactivities of hydroxyl groups decrease in the series: 3β-OH ≈ 3α-OH > 17β-OH ≫ 20β-OH > 11β-OH. Such a significant difference in the reactivities of the OH groups is explained by the arrangement of the hydroxyl groups in the positions 11β, 17β and 20β at the side of the steroid molecule, which is more sterically hindered and less favourable for adsorption on the anode and for the interaction with $Ni^{III}(O)OH$. Special features of the electrogenerated mediator $Ni^{III}(O)OH$ as an oxidant are also manifested in their inertness to ethers, C=C double bond and aromatic ring.

Indirect oxidation of alcohols at the nickel anode is conducted under the conditions of amperostatic electrolysis in an undivided cell in an alkaline medium at pH 10–14. Both one- or two-phase system and low-density current, not exceeding 0.5 mA cm^{-2} are used. At higher current density, the current efficiency of the target products sharply decreases due to competitive electrolysis of water.

The rate-determining stage of indirect anodic oxidation of alcohols in the presence of Ni(O)OH is the generation of radicals upon abstraction of the H atom from the adsorbed alcohol by nickel oxyhydroxide. Subsequent oxidation of radicals at the anode or under the action of $Ni^{III}(O)OH$ results in the formation of final products, aldehydes, ketones and carboxylic acids:

$$Ni(OH)_2 \xrightarrow[-e]{} Ni(O)OH + H^+,$$

$$R^1CH(OH)R^2 + Ni(O)OH \rightleftharpoons [Ni(O)OH \cdot R^1CH(OH)R^2]_{ads},$$

$$[Ni(O)OH \cdot R^1CH(OH)R^2]_{ads} \longrightarrow [R^1\dot{C}(OH)R^2] + Ni(OH)_2,$$

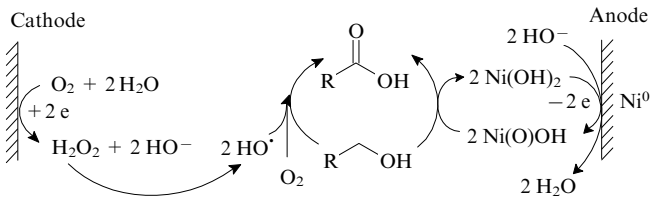
$$[R^1\dot{C}(OH)R^2] \xrightarrow[-H^+]{} R^1C(O)R^2 \xrightarrow{(R^2 = H)} R^1CO_2H.$$

Lengthening of the hydrocarbon chain and increase in the molecular mass of alcohols lower the adsorption capacity on the anode. This substantially slows down the process; for this reason, electrooxidation of alcohols containing six and more carbon atoms is carried out with heating. Substituents that sterically shield the hydroxyl group also exert an 'inhibitory' effect. For this reason, primary alcohols are oxidised easier than secondary alcohols; normal alcohols and unsubstituted cycloalkanols are oxidised easier than their 2-alkyl-substituted analogues. Thus, hexan-1-ol, octan-1-ol, decane-1,10-diol and cyclohexanol are oxidised 1.5, 3, 5 and 10 times faster than hexan-3-ol, 2-ethyloctan-1-ol, decan-1-ol and 2-ethylcyclohexanol, respectively. For 2-ethylhexane-1,6-diol, oxidation of the less shielded hydroxyl group in position 6 occurs three times faster than that of the OH group in position 1. The influence of the shielding effect of substituents was manifested to a greater extent in the synthesis of the corresponding hydroxy aldehydes from methyl-α-D-glucoside, glucose and sucrose; these aldehydes are obtained by selective oxidation of the primary hydroxyl groups in the presence of secondary ones.[117]

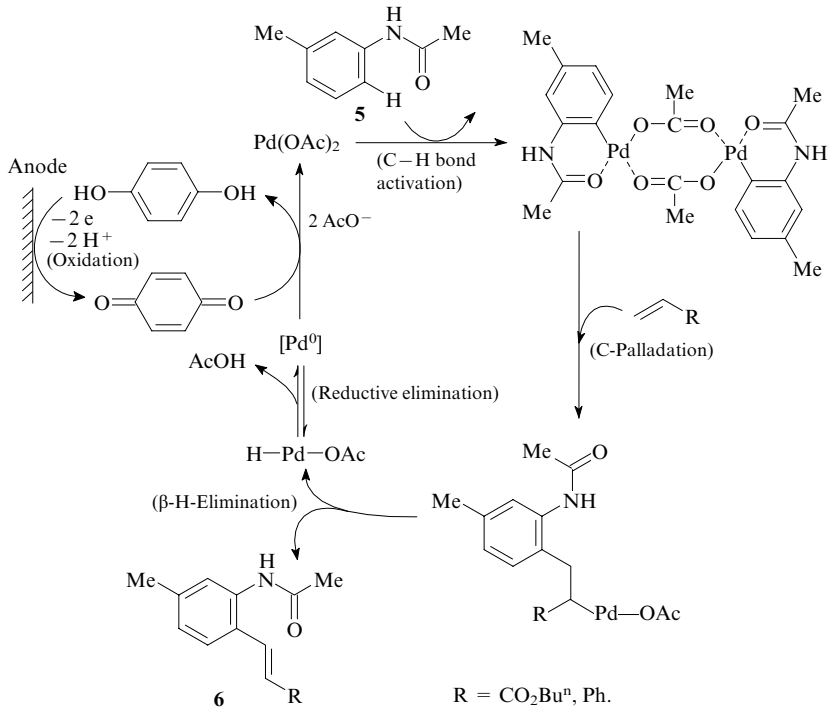
Benzylic and allylic alcohols are selectively oxidised to aldehydes under the conditions of anodic oxidation of alcohols at the hydroxide nickel anode in the two-phase system K_2CO_3 (aq)–petroleum ether. In the case of primary alcohols, the process can be directed to the predominant formation of aldehydes by their extraction in the course of electrolysis into the non-polar organic phase thus preventing further oxidation to carboxylic acids (Table 5, entries 21–25).[122] Oxidation of lipophilic alcohols proceeds more efficiently in the presence of dodecanoic acid, which favours the phase transfer of alcohols from the solution to the anode and removal of the oxidation products from the anode surface.

The efficiency of electrochemical conversion of alcohols into the corresponding carboxylic acids substantially enhances if cathodic current is involved. Thus for the parallel anodic and cathodic oxidation of n-butanol in the undivided cell using Ni(O)OH and H_2O_2 electrogenerated in an alkaline medium in the presence of dioxygen, the current efficiency for butyric acid increases from 80% to 166%.[123] The reactions that occur in this electrochemical system are given in Scheme 6.

Scheme 6



Scheme 7



Redox systems based on the manganese, cerium, chromium and copper ions, as well as the palladium ions in combination with benzoquinone were successfully used as mediators for electrooxidation of alcohols and their derivatives.[65, 124–132] The following processes involving these mediators were developed:

1) an electrocatalytic version of the synthesis of 2-osuloses, intermediates in the preparation of L-ascorbic acid and relative compounds (mediators, copper ions) from aldopentoses and ketohexoses (D-xylose, D-arabinose, D-ribose, *etc.*) (Table 6, entry 11);[132]

2) a general electrochemical method for the selective oxidation of primary and secondary alcohols to carbonyl compounds under anaerobic conditions [mediator, the system $Pd(OAc)_2$–benzoquinone] that prevent the intermediate formation of H_2O_2, which induces side reactions of the products (Table 6, entries 12–15).[133]

Other examples of indirect anodic oxidation of alcohols and their derivatives catalysed by redox systems based on manganese, cerium, chromium and copper ions are presented in Table 6.

5. Electrooxidative transformations of alkenes and alkynes

Indirect electrooxidation of alkenes and alkynes is most efficiently catalysed by mediators based on compounds of palladium,[138–147] ruthenium,[148–152] silver,[153, 154] osmium,[155–158] chromium[159, 160] and some other metals.[161–168] Such reaction as the Wacker electrochemical reaction, epoxidation, allylic oxidation, allylic and vinylic substitution, α,β-dihydroxylation, hydromethoxycarbonylation, double bond oxidative cleavage catalysed by these mediators result in conversion of alkenes to carbonyl compounds, epoxides, esters of mono- and dicarboxylic acids and diols (Table 7). Electrochemical mono- and dimethoxycarbonylation of alkynes catalysed by $Pd(PPh_3)_2(OAc)_2$ and $PdCl_2$ gives alk-2-enoic acids and esters of acetylenecarboxylic and alk-2-enedioic acids. Some examples of these reactions have already been considered in a review,[11] we give these examples as an illustration of electrochemical versions of the reactions widely used in organic synthesis.

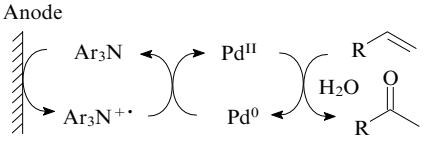
Recently, a series of new preparative methods for electrooxidative conversion of alkenes and alkynes has been developed, which are either alternative to traditional methods or have no corresponding chemical analogies.

1. Electrochemical version of arene vinylation according to the Heck-type reaction (a system Pd^{II}–benzoquinone as a mediator), which extends the application field of this reaction due to activation of C–H bonds of arenes and makes it more environmentally friendly (Table 7, entry 22).[138]

The most successful approach consists of the use of arenes with substituents playing the role of a ligand for additional coordination to Pd^{II} ions. The latter, due to intramolecular interaction, activate the *ortho*-C–H bonds thus favouring its facile vinylation with activated alkene. The overall process is illustrated in Scheme 7. Electrooxidative vinylation of *N*-(3-tolyl)acetamide (**5**) with butyl acrylate ($R = CO_2Bu^n$) and styrene ($R = Ph$) to form 2-vinyl-substituted *N*-acetyl-5-methylanilines **6** is given as an example.

2. Indirect electrochemical oxidation of alkenes catalysed by a double mediator system containing a Pd-complex and tris(4-bromophenyl)amine (Scheme 8).[146]

Scheme 8



Ar = 4-BrC_6H_4.

This is an electrochemical version of the Wacker process eliminating its substantial drawbacks such as side chlorination of parent alkenes and ketones formed, explosibility of gaseous mixtures of alkenes with oxygen, strong corrosion of equipment due to the action of corrosive reaction medium (Table 7, entries 2, 3, 5, 6).

Table 7. Electrooxidative transformations of alkenes and alkynes catalysed by metal and selenium compounds, as well as by mediatory systems based on these compounds (reactions were carried out under constant current).

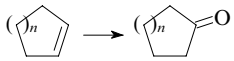
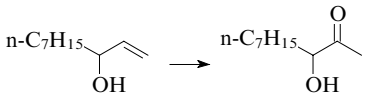
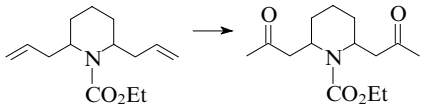
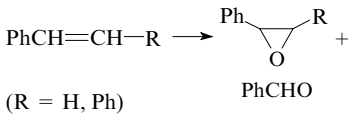
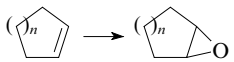
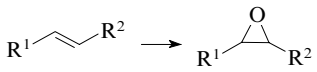
Reaction	Entry	Yield (%)	Mediator [a]	Conditions		Ref.
				cell	electrolyte	
Oxidation of alkenes to ketones (electrolyte Et_4NBF_4 or Et_4NOTs)						
$RCH{=}CH_2 \longrightarrow RC(O)Me$	1	56 – 79 (48 – 59)	$Pd(OAc)_2$ (2) – benzoquinone (20)	DC	MeCN, H_2O	139, 144
(R = Alk, Ph;	2	90 (60 – 90)	$Pd(OAc)_2$ (2) – $(4\text{-}BrC_6H_4)_3N$ (5)	UC	MeCN, H_2O	146
R = $PhCH_2$, cyclo-Alk)	3	57 – 85	$Pd(OAc)_2$ (2) – $(4\text{-}BrC_6H_4)_3N$ (5)	UC	MeCN, H_2O	146
	4	75 – 83 (62 – 96)	$Pd(OAc)_2$ (2) – benzoquinone (20)	DC	MeCN, H_2O	139, 144
(*n* = 1, 2)						
	5	70 (46 – 70)	$Pd(OAc)_2$ (2) – $(4\text{-}BrC_6H_4)_3N$ (5)	UC	MeCN, H_2O	146
	6	74 (47 – 72)	$Pd(OAc)_2$ (2) – $(4\text{-}BrC_6H_4)_3N$ (5)	UC	MeCN, H_2O	146
Epoxidation of alkenes						
 (R = H, Ph)	7	18 – 25 15 – 20	$[Ru(O)(H_2O)_3Cl_2]^+/[Ru(H_2O)_4Cl_2]^+$ (1)	DC	H_2O, Bu^tOH	150
	8	48 – 52	$[Ru(O)(H_2O)_3Cl_2]^+/[Ru(H_2O)_4Cl_2]^+$ (1)	DC	H_2O, Bu^tOH	150
(*n* = 2, 4)						
						
[R^1 = H: R^2 = Me, Et; R^1 = R^2 = Me;	9	80 – 95 (80 – 95)	$[Ag^I(Py)_2]^+$	DC	H_2O, AcOH, CF_3CO_2H	153
R^1 = H, R^2 = C_nH_{2n+1} (*n* = 3 – 12);	10	> 90 (27 – 72)	$[Ag^I(Py)_2]^+$	DC	H_2O, AcOH, CF_3CO_2H	153
R^1 = Me, R^2 = C_nH_{2n+1} (*n* = 2 – 5)]	11	> 90 (82)	$[Ag^I(Py)_2]^+$	DC	H_2O, AcOH, CF_3CO_2H	153
$RCH{=}CH_2 \longrightarrow$  (R = Alk)	12	80 – 87 (21 – 24)	$AgOAc(bipy)_2$ (1 – 5)	DC	MeCN, H_2O, H_2SO_4	154

Table 7 (continued).

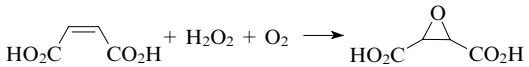
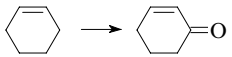
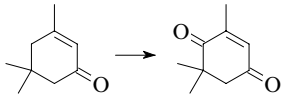
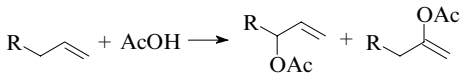
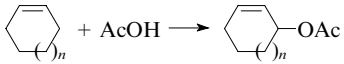
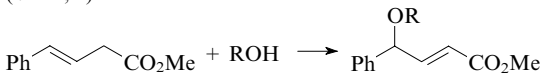
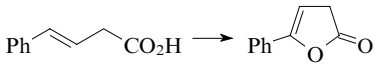
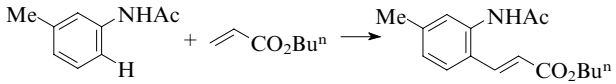
Reaction	Entry	Yield (%)	Mediator [a]	Conditions		Ref.
				cell	electrolyte	
Epoxidation of alkenes						
Esters of alkenoic and alkenedioic acids ⟶ ⟶ Esters of epoxyalkanoic and epoxyalkanedioic acids	13	80 – 87 (21 – 24)	$AgOAc(bipy)_2$ (1 – 5)	DC	MeCN, H_2O, H_2SO_4	154
	14	–	$VO(acac)_2$	–	–	161
Allylic oxidation of alkenes (pH 6.8 – 8.0)						
$ArCH_2CH{=}CH_2 \longrightarrow ArC(O)CH{=}CH_2$	15	65	$[(bipy)(trpy)Ru(O)]^{2+}$/ $[(bipy)(trpy)Ru(OH_2)]^{2+}$ (5 – 6) [b]	DC	H_2O, Bu^tOH	148
	16	47	$[(bipy)(trpy)Ru(O)]^{2+}$/ $[(bipy)(trpy)Ru(OH_2)]^{2+}$ (5 – 6) [b]	DC	H_2O, Bu^tOH	148
	17	14	$[(bipy)(trpy)Ru(O)]^{2+}$/ $[(bipy)(trpy)Ru(OH_2)]^{2+}$ (5 – 6) [b]	DC	H_2O, Bu^tOH	148
Allylic and vinylic substitution of alkenes						
 (R = Alk, cyclo-C_6H_{11}, Ph)	18	64 – 91	$Pd(OAc)_2$ (5) – $Cu(OAc)_2$ (10)	DC	AcOH, MeCN	147
 (n = 1, 2)	19	29 – 72	$Pd(OAc)_2$ (5) – $Cu(OAc)_2$ (10)	DC	AcOH, MeCN	147
 (R = Me, Et, Pr^i, Ac)	20	40 – 62	$(PhSe)_2$ (10) – Et_4NBr (100)	UC	ROH, H_2SO_4	166
	21	–	$(PhSe)_2$ (10) – Et_4NBr (100)	UC	MeCN, H_2SO_4	166
	22	84	$Pd(OAc)_2$ – benzoquinone	DC	AcOH, $Bu^n_4NBF_4$	138

Table 7 (continued).

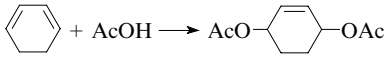
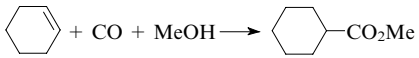
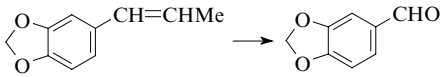
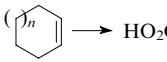
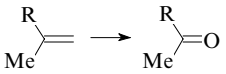
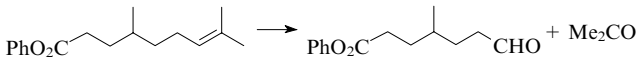
Reaction	Entry	Yield (%)	Mediator [a]	Conditions		Ref.
				cell	electrolyte	
Transformation of alkenes to α,β-diacetates and α,β-diols						
$PhCH{=}CHR \longrightarrow PhCH(OAc)CH(OAc)R$ (R = H, Ph)	23	49 – 60 (22 – 26)	$Mn(OAc)_2$ (10)	UC	AcOH	101
	24	–	$Pd(OAc)_2$ (0.5 – 3) – benzoquinone (3 – 15)	DC	AcOH	140
$R^1CH{=}CR^2R^3 + H_2O \longrightarrow R^1CH(OH)CR^2(OH)R^3$	25	88 – 94 (88 – 94)	OsO_4 (1.6) – BDQP – $K_3Fe(CN)_6$ (40)	DC	H_2O, Bu^tOH, K_2CO_3	155
(R^1 = Alk, Bn, Ph, 2-naphthyl, BnO_2C, PhO_2CCH_2; R^2 = H, Me, EtO_2C, Ph; R^3 = H, Me)	26	75 – 97 (64 – 83)	$K_2OsO_2(OH)_4$ (0.2) – BDQP (1) – $K_3Fe(CN)_6$ (1)	UC	H_2O, Bu^tOH, K_2CO_3	156
	27	84 – 99 (33 – 39)	$K_2OsO_2(OH)_4$ (0.2) – BDQP (1) – I_2 (1)	UC	H_2O, Bu^tOH, K_2CO_3	157
Methoxyhydrocarbonylation of alkenes						
$RCH{=}CH_2 + CO + MeOH \longrightarrow RCHMeCO_2Me + RCH_2CH_2CO_2Me$ [R = C_nH_{2n+1} (n = 6 – 10)]	28	69 – 72 23 – 24	$PdCl_2$ (10)	DC	MeOH	141
	29	50	$PdCl_2$ (10)	DC	MeOH	141
$PhCH{=}CH_2 + CO + MeOH \longrightarrow PhCHMeCO_2Me + Ph(CH_2)_2CO_2Me$	30	56 19	$PdCl_2$ (10)	DC	MeOH	141
Transformation of alkynes to methyl alk-2-ynoates and dimethyl alk-2-enedioates						
$RC{\equiv}CH + CO + MeOH \longrightarrow RC(CO_2Me){=}CCO_2Me$ [R = C_nH_{2n+1} (n = 5 – 12)]	31	25 – 93	$PdCl_2$ (10)	DC	MeOH	142
$R^1{-}C{\equiv}C{-}R^2 + CO + MeOH \longrightarrow MeO_2CC(R^1){=}C(R^2)CO_2Me$ (R^1, R^2 = Alk, Me; Ph, Et)	32	33 – 80	$PdCl_2$ (10)	DC	MeOH	142
$RC{\equiv}CH + CO + MeOH \longrightarrow RC{\equiv}CCO_2Me$ (R = Bu^n, cyclo-Alk, Ph)	33	70 – 87	$Pd(PPh_3)_2(OAc)_2$ (10)	UC	MeOH, MeCN	143
Oxidative cleavage of the C=C bonds in alkenes						
	34	70	$[O{=}RuSiW_{11}O_{39}]^{5-}$ / $[(H_2O)RuSiW_{11}O_{39}]^{5-} - IO_4^-$	UC	H_2O, CH_2Cl_2	149
	35	70	$Cr_2O_7^{2+} + / Cr^{3+}$	DC	H_2O, H_2SO_4	159

Table 7 (continued).

Reaction	Entry	Yield (%)	Mediator [a]	Conditions		Ref.
				cell	electrolyte	
Oxidative cleavage of the C=C bonds in alkenes						
n-$C_8H_{17}CH{=}CH_2 \longrightarrow$ n-$C_8H_{17}CO_2H$	36	79	RuO_4 (2.2) – IO_4^- (90)	DC	MeCN, H_2O, CCl_4	151
 $\longrightarrow$ $HO_2C(CH_2)_{n+3}CO_2H$ (n = 1, 3)	37	62 – 91	RuO_4 (2.2) – IO_4^- (90)	DC	MeCN, H_2O, CCl_4	151
n-$C_8H_{17}CH{=}CH(CH_2)_7CO_2Me \longrightarrow$ $\longrightarrow$ n-$C_8H_{17}CO_2H$ + $HO_2C(CH_2)_7CO_2H$	38	51 – 65 57 – 62	RuO_4 (2.2) – IO_4^- (90)	DC	MeCN, H_2O, CCl_4	151
 [R = $PhO_2C(CH_2)_2$, Ph]	39	< 91 (< 73)	$K_2OsO_2(OH)_4$ (4) – HIO_4 (50)	DC	MeCN, H_2O, CCl_4	158
	40	72 (29)	$K_2OsO_2(OH)_4$ (4) – HIO_4 (50)	DC	MeCN, H_2O, CCl_4	158
ArCH=CHR $\longrightarrow$ ArCHO + RCHO (R = Me, Ph)	41	62 – 66 (< 33)	$K_2OsO_2(OH)_4$ (4) – HIO_4 (50)	DC	MeCN, H_2O, CCl_4	158
4-$MeC_6H_4CH{=}CHC_6H_4Me$-4 $\longrightarrow$ 4-$MeC_6H_4CH{=}CHC_6H_4CO_2H$-4	42	(> 70)	$Cr_2O_7^{2+}/Cr^{3+}$	DC	H_2O, H_2SO_4	160
$R^1CH{=}CHR^2 \longrightarrow R^1CHO + R^2CO_2H$ [R^1 = Alk; R^2 = H, $(CH_2)_7CO_2H$; $R^1 - R^2 = (CH_2)_{10}$]	43	72 – 84 (4 – 5)	O_3/O_2 (PbO_2-anode)	UC	H_2O, AcOEt	152

Note. The following abbreviations are adopted: acac is acetylacetonate, BDQP is 1,4-bis(9-*O*-dihydroquinidine)phthalazine (the Sharpless ligand). [a] The amount of mediator (mol % with respect to the substrate) is given in parentheses; [b] experiments were conducted at controlled potential of 0.8 – 0.95 *vs* SCE.

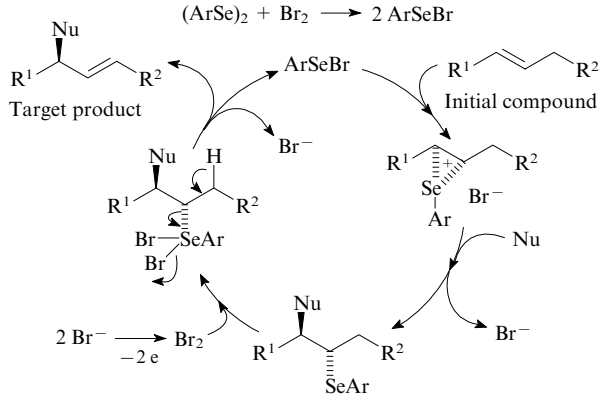
3. Epoxidation of alkenes promoted by the mediator pair $[Ru(O)(H_2O)_3Cl_2]^+/[Ru(H_2O)_4Cl_2]^+$ (Ref. 150), silver pyridine complexes [153, 154] and a mediator system $VO(acac)_2-H_2O_2$ in the presence of O_2 (Table 7, entries 7–14).[161]

4. Pd-catalysed hydromethoxycarbonylation of alkenes, mono- and methoxycarbonylation of alkynes (Table 7, entries 28–33).[141–143]

5. Cleavage of alkene double bonds involving chromium compounds,[159, 160] double mediator systems $RuO_4-IO_4^-$, $[O{=}RuSiW_{11}O_{39}]^{5-}/[(H_2O)RuSiW_{11}O_{39}]^{5-}-IO_4^-$ (Refs 149, 151), $K_2OsO_2(OH)_4-HIO_4$ (Ref. 158) and electrogenerated ozone [152] to form aldehydes, ketones and carboxylic acids (Table 7, entries 34–43).

6. Diaryl diselenide-catalysed enantioselective oxidative substitution of nucleophilic groups for the allylic hydrogen atom of alkenes including the catalytic cycle of electroregeneration of the mediator presented in Scheme 9 (Table 7, entries 20 and 21).[166]

Scheme 9



6. Indirect electrooxidation of other classes compounds

Electrooxidation reactions of miscellaneous organic compounds that involve activated metals as mediators, are summarised in Table 8. On the basis of these reactions, preparative methods for deallylation of allyl ethers under the action of electrogenerated highly active nickel (entries 1, 2);[162] isoprenylation of aldehydes and ketones with 1,4-dibromo-2-bromomethylbut-2-ene promoted by electrogenerated highly active zinc (entries 3, 4);[164] dimerisation of trimethylacetic acid to tetramethyladipic acid under sonication (electrochemical version of the Fenton reaction using the iron anode as a source of Fe^{2+} ions) (entry 5);[167] conversion of (arylthiomethyl)trimethylsilanes to alkoxymethyl aryl sulfides using a macrocyclic nickel polyamine complex (entry 6) were developed.

Particular emphasis should be given to parallel indirect anodic and cathodic oxidation of bis(2-carboxyethyl) sulfide to the corresponding sulfone (entries 7, 8) [169] using the redox systems Os^{VIII}/Os^{VI} as mediators (for anodic oxidation) and tungsten/peroxotungstate $W^{VI}O_4^{2-}/W^{IV}O_2(O_2)_2^{2-}$ (for cathodic oxidation) as mediators. This process was performed in both divided and undivided cells with an overall current efficiency of 161% and 141%, respectively.

The direction of the electrooxidation of thioamides catalysed by bis(*p*-methoxyphenyl) telluride(II) depends on the solvent. Thus in aqueous acetonitrile, nitriles are formed, whereas in ethanol, thiadiazoles are obtained (entries 9, 10).[168]

As an exception, transformation of aryl methyl ketones to α-oxoacetals catalysed by diphenyl diselenide is also included into this Table (entry 11).[165]

IV. Electrooxidation in the presence of halides

Halides are the most well-known and popular inorganic mediators. These mediators are widely used in electrocatalytic oxidation of organic compounds, as well as in electrocatalytic cascade processes of transformations according to the 'domino' principle which were introduced into practice two decades ago. Their advantages include accessibility and low cost, as well as the fact that the majority of the processes catalysed by these mediators are performed in the undivided cell. This substantially simplifies the experimental procedure, its hardware implementation and scaling, which significantly broadens the field of application of electrocatalytic reactions under both industrial and experimental conditions. In particular, in laboratory experiments, standard chemical glass-ware can be used as an undivided cell where electrodes are placed; a common rectifier can serve as a direct-current source.

Pairs I^-/I_2 and Br^-/Br_2 with electrochemically generated iodine and bromine as oxidants are usually employed in mediator pairs. In some cases, chloride ions are also used, though electrogenerated chlorine, being more reactive as compared to bromine and iodine, often causes side reactions, for instance, radical chlorination of organic substrates.

By the beginning of the 1990s, a large series of electrocatalytic reactions with halides as mediators has been studied including the:

— oxidation of furans to 2,5-dihydro-2,5-dimethoxyfurans;

— dimerisation and dehydrodimerisation of CH-acids;

— linear trimerisation and cyclic cyclotrimerisation of CH-acids;

— oxidation of primary alcohols to esters and secondary alcohols to ketones;

— transformation of methyl ketones to carboxylic acid esters (the haloform react ion);

— conversion of alkyl iodides to acetamides;

— epoxidation of alkenes;

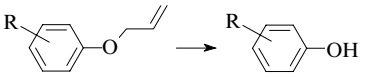
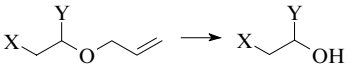
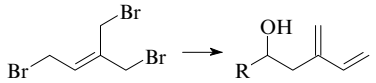
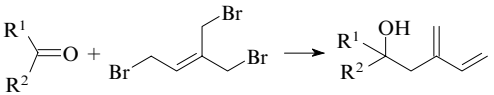
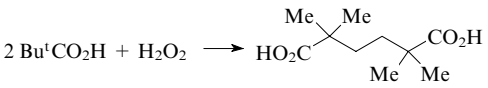
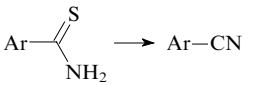
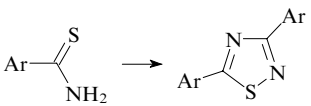
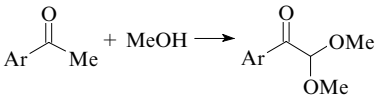
— oxidation of glucose to gluconic acid and other oxidative transformations in carbohydrate chemistry.

The major results of these studies are generalised in reviews [5, 6, 10,] and monographs.[7, 9, 170, 171] A new strategy of electrocatalytic oxidation of CH-acids and electrocatalytic synthesis of functionally substituted cyclopropanes from CH-acids or from carbonyl compounds is presented in the resumptive publication.[172] In this chapter, papers are considered concerning halide-catalysed electrochemical transformations of carbonyl compounds and CH-acids, as well as aldehydes, ketones and activated alkenes in their joint electrolysis with CH-acids that have been published over recent 15 years. These reactions provide a wide variety of valuable organic compounds in high yields and selectivities.

1. Anodic oxidation of carbonyl compounds catalysed by halide anions

Electrocatalytic oxidation of alkyl aryl ketones in methanol with a mediator system NaI–NaOH gives α-hydroxy ketals in high yields (Table 9, entry 1).[173] The electrode reactions of alkyl aryl ketones are specific for this mediator system and include the formation of iodine at the anode and

Table 8. Transformation of organic compounds involving electrochemically activated metals, tellurium compounds and diphenyl diselenide.

Reaction	Entry	Yield (%)	Mediator	Conditions			Ref.
				process	cell	electrolyte	
 [R = MeO_2C, Ac, N≡C, HC(O), Cl, Br, MeO, PhO, $EtO_2CCH{=}CH$]	1	72 – 100	Ni (anode)	B	UC	DMF, AcONa	162
 (X, Y = H, Ar)	2	69 – 70	Ni (anode)	B	UC	DMF, AcONa	162
RCHO +  (R = H, Alk, Ph, $CH_2{=}CH$, $Me_2C{=}CH$, $PhCH{=}CH$)	3	34 (R = H) 67 – 99	Zn (anode)	B	UC	DMF	164
 [R^1 = Me, R^2 = Et, Ph, $CH_2{=}CH$; R^1 – R^2 = $(CH_2)_5$]	4	23 – 83	Zn (anode)	B	UC	DMF	164
	5	34	Fe (anode)	A [a]	UC	H_2O, H_2O_2, H_2SO_4	167
$ArSCH_2SiMe_3$ + ROH ⟶ $ArSCH_2OR$ (Ar = Ph, 4-MeC_6H_4; R = Me, $CH_2{=}CH$)	6	33 – 41	Ni^{III}/Ni^{II}	A	DC	MeCN, ROH	163
$(EtO_2C)_2S$ ⟶ $(EtO_2C)_2S{=}O$	7	(141)	Os^{VIII}/Os^{VI}	A	UC	H_2O	169
	8	(161)	$WO_4^{2-}/WO_2(O_2)_2^{2-}$	A	DC	H_2O	169
 (Ar = Ph, 4-ClC_6H_4, 4-$MeOC_6H_4$)	9	63 – 80	$(4\text{-}MeOC_6H_4)_2Te^{IV}/(4\text{-}MeOC_6H_4)_2Te^{II}$	A	DC	MeCN, H_2O	168
 (Ar = Ph, 4-ClC_6H_4, 4-$MeOC_6H_4$)	10	71 – 77	$(4\text{-}MeOC_6H_4)_2Te^{IV}/(4\text{-}MeOC_6H_4)_2Te^{II}$	A	DC	EtOH, H_2O	168
 (Ar = Ph, 4-HOC_6H_4, 4-$MeOC_6H_4$, 1- and 2-naphthyl)	11	57 – 73	$(PhSe)_2$	A	DC	MeOH	165

[a] Sonication.

Table 9. Electrooxidative transformations of carbonyl compounds and their derivatives mediated by halide ions (undivided cell).

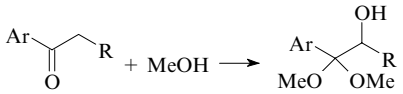
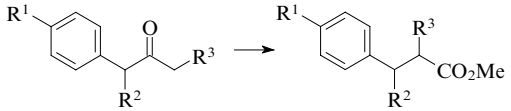
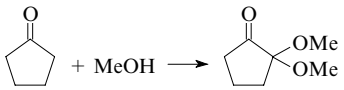
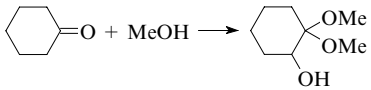
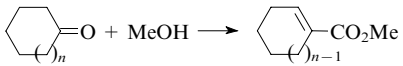
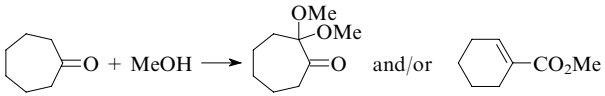
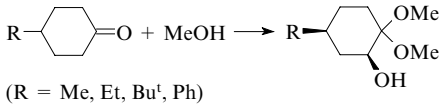
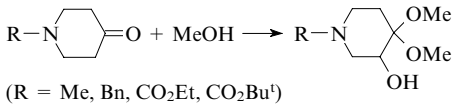
Reaction	Entry	Yield (%)	Mediator	Reaction medium	Ref.
 (Ar = Ph, 4-MeC$_6$H$_4$, 6-MeO-2-naphthyl; R = Alk)	1	75–85 (65–75)	I^-	MeOH, NaOH	173, 174
 (R^1 = H, MeO, Cl; R^2, R^3 = H, Me)	2	80–90	Br^-, I^-	MeOH, NaOH	175
 [R^1, R^2 = n-C$_n$H$_{2n+1}$ (n = 1–3, 5, 7), Bu^i]	3	70–80 (60–70)	Br^-, I^-	MeOH, NaOH	176, 177
	4	80 (80)	I^-	MeOH, NaOH	178, 179
	5	85 (60)	I^-	MeOH, NaOH	178, 179
 (n = 3, 7)	6	65–90 (65–90)	I^-	MeOH, NaOH	178, 179
	7	80–85 (80–85)	I^-	MeOH, NaOH	178, 179
 (R = Me, Et, Bu^t, Ph)	8	70–80 (50–60)	Br^-, I^-	MeOH, NaOH	180, 181
 (R = Me, Bn, CO_2Et, CO_2Bu^t)	9	70–95	Br^-, I^-	MeOH, NaOH	182

Table 9 (continued).

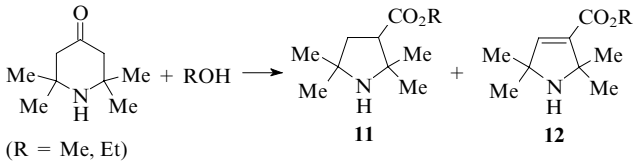
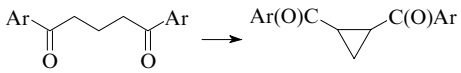
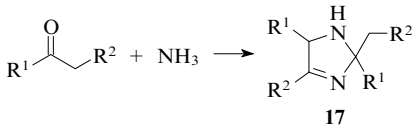
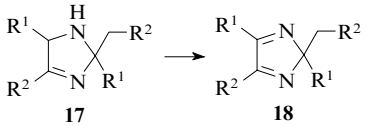
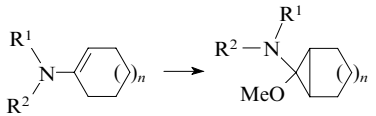
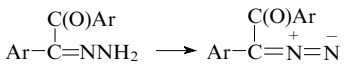
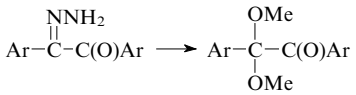
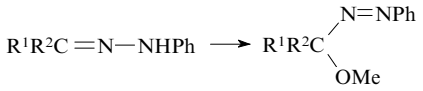
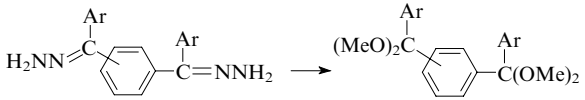
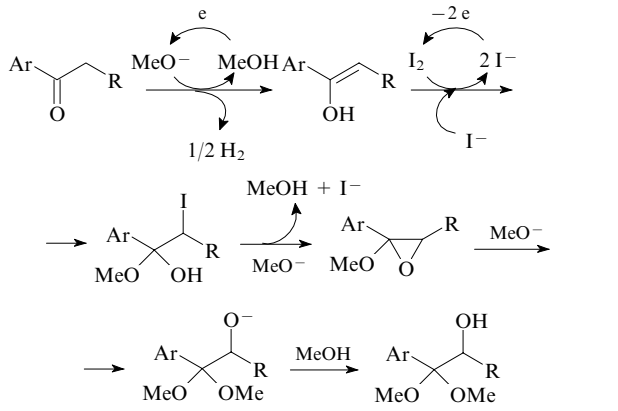
Reaction	Entry	Yield (%)	Mediator	Reaction medium	Ref.
 (R = Me, Et)	10	75 – 90	Br^-, I^-	ROH, MeONa	182
11 + MeOH ⟶ **12**	11	68 (40)	I^-	MeOH, MeONa	182
 [Ar = RC_6H_4 (R = 4-Me, 4-MeO, 4-BuO, 4-PhO, 4-Cl , 4-Br), $3,4\text{-}Me_2C_6H_3$, 4-MeO-3-MeC_6H_3, 2-MeO-5-MeC_6H_3]	12	76 – 89 (63 – 72)	I^-	MeOH, MeONa	183
$ArC(O)Me + 2\,CN^- \longrightarrow ArC(O)CH(CN)_2$ [Ar = 4-RC_6H_4 (R = H, Me, MeO, Cl, NO_2)]	13	54 – 89 (30 – 48)	I^-	MeOH, NaCN	184
$ArC(O)C(O)Ar + MeOH \longrightarrow 2\,ArCO_2Me$ [Ar = RC_6H_4 (R = H, 2- and 4-Me, MeO, Cl, 4-Bu^t); Ar = 2-furyl, 2-thienyl, 2-pyridyl]	14	46 – 94 (12 – 50) 43 – 86 (17 – 43)	I^-	MeOH, NaCN	185
 [R^1, R^2 = H, Alk; $R^1 - R^2 = (CH_2)_4$]	15	76 (74)	I^-	MeOH, NH_3	186
	16	43 – 88 (20 – 57)	I^-	MeOH, NH_3	186
 [n = 1, 2; R^1, R^2 = Me, Et, Ph; $R^1 - R^2 = (CH_2)_m$ (m = 4, 5); $(CH_2)_2O(CH_2)_2$]	17	63 – 74 (63 – 74)	I^-	MeOH, MeONa	187
 [Ar = 4-RC_6H_4 (R = H, Me, MeO, Cl)]	18	76 – 90 (76 – 82)	I^-	MeOH, MeONa	188

Table 9 (continued).

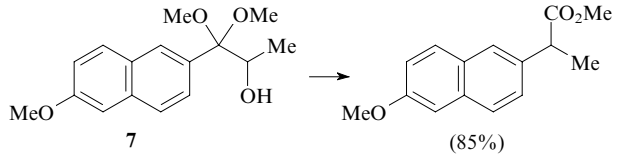
Reaction	Entry	Yield (%)	Mediator	Reaction medium	Ref.
 [Ar = 4-RC_6H_4 (R = H, Me, MeO, Cl)]	19	75 – 83 (72 – 80)	Br^-	MeOH, MeONa	188
 [R^1, R^2 = H, Alk; $R^1 - R^2$ = $(CH_2)_n$ (n = 5, 7, 8)]	20	44 – 74 (30 – 72)	I^-	MeOH	189
 [Ar = 4-RC_6H_4 (R = H, Me, OMe, Cl) (m- and p-isomers)]	21	60 – 75 (40 – 75) 60 – 85 (47 – 62)	I^-	MeOH, MeONa	190

hydrogen evolution at the cathode to generate the methoxide ions (Scheme 10).

Scheme 10



Further, α-iodination of alkyl aryl ketones and addition of the methoxide anion to the carbonyl group occur in solution. The subsequent intramolecular cyclisation to form intermediate epoxide and its opening with the second equivalent of the methoxide anion result in α-hydroxy ketals, which are electrochemically inert under these conditions. These type of ketals are convenient starting compounds for the synthesis of 2-arylpropionic acids, a well-known class of non-steroidal analgesic and antiinflamatory drugs. Thus 2-(6-methoxy-2-naphthyl)propionic acid, the active component of the antirheumatic drug Naprosyn, was synthesised from α-hydroxy ketal **7**.[174]



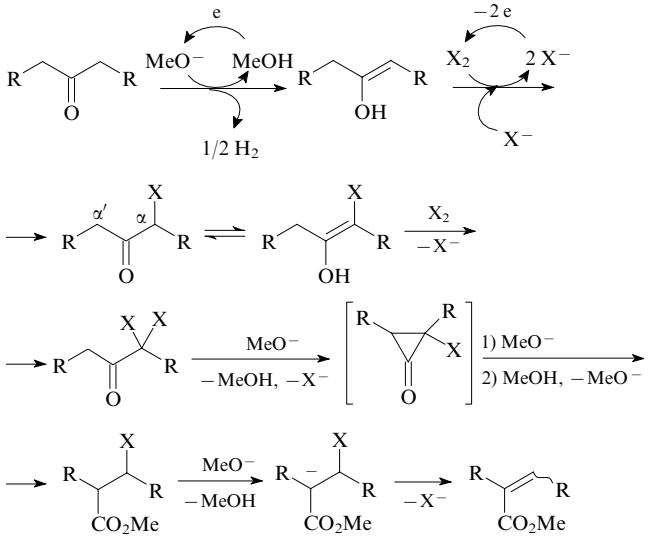
The direction of electrochemical conversion of alkyl benzyl ketones is governed by the presence of the benzylic hydrogen atom in their structure. These ketones undergo the Favorsky rearrangement to yield methyl β-arylalkanecarboxylates (Table 9, entry 2).[175]

In the oxidation under the similar conditions, dialkyl ketones undergo (in high current efficiency and substance yield) the electrocatalytically induced Favorsky rearrangement to α,β-unsaturated carboxylates (Scheme 11; Table 9, entry 3).[176, 177]

Thus the direction of ketone oxidation depends on their structures. It is believed [173] that the attack by the methoxide anion on the carbonyl group of alkyl aryl ketones is facilitated by its higher reactivity due to conjugation with the aromatic ring. As a consequence, the initially formed α-haloaryl alkyl ketone transforms to α-hydroxy ketal. In the case of alkyl benzyl ketones, the presence of the acidic methylene group causes the preferential α′-deprotonation of α-halogenoketone and the Favorsky rearrangement to give β-alkanecarboxylic acids. In the case of dialkyl ketones under similar conditions, the preferential direction of the reaction is α,α-dihalogenation followed by the Favorsky rearrangement to form esters of alk-2-enoic acids.

Under the conditions of electrochemical oxidation, alicyclic ketones with 5–12-membered rings also react in different manners (Table 9, entries 4–7).[178, 179] Thus cyclopentanone transforms into 2,2-dimethoxycyclopentanone cyclohexanone transforms to α-hydroxycyclohexanone

Scheme 11

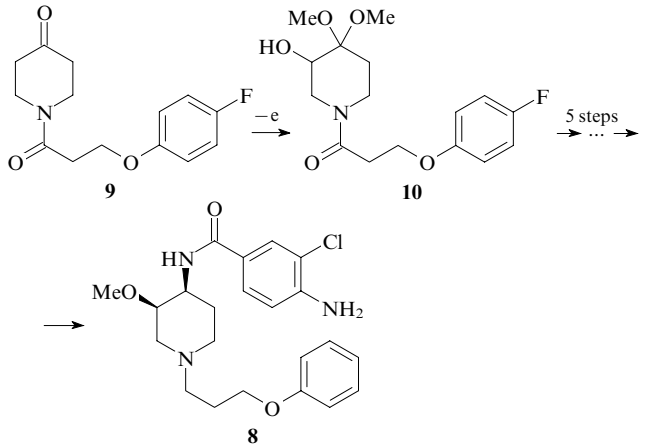


ketal, 8- and 12-membered cycloalkanones transform preferably to methyl esters of cycloalkene-1-carboxylic acids. Cycloheptanone having intermediate reactivity forms either α-hydroxycycloheptanone ketal or methylcyclohexene-1-carboxylate depending on the reaction conditions.

Electrooxidation of 4-substituted cyclohexanones occurs stereoselectively to give 5-substituted *cis*-2,2-dimethoxycyclohexanols (Table 9, entry 8).[180, 181] This is the first example of stereoselective indirect electrooxidation of ketones. Electrocatalytic oxidation of *N*-substituted piperidin-4-ones occurs similarly to yield *N*-substituted α-hydroxypiperidinone ketals preferably as conformers with the axial hydroxyl group (Table 9, entry 9).[182]

The efficiency of this process is increased in the presence of a base. The development of the electrocatalytic method for the oxidation of piperidin-4-ones permitted optimisation of the synthesis of compound **8**, the base of the progastrokinetic drug Cisapride.[174]

The key step of the chemical synthesis of compound **8** is oxidative conversion of *N*-acylated piperidin-4-one **9** to α-hydroxy ketal **10** under the action of $PhI(OAc)_2$ (yield 36%). The yield of product **10** in the electrocatalytic synthesis that obviates the application of expensive $PhI(OAc)_2$ was 68%.



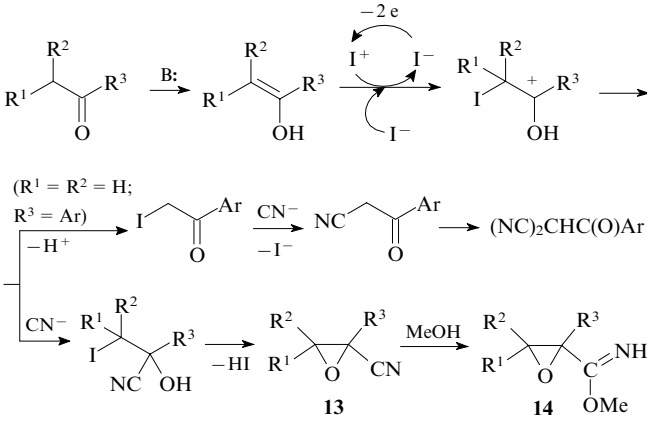
Halide-mediated indirect electrooxidation of triacetoneamine implies the electrocatalytic version of the Favorsky rearrangement. As a result, 2,2,5,5-tetramethylpyrrolidine-3-carboxylates (**11**) and -2,5-dihydro-1*H*-pyrrole-3-carboxylates (**12**) are formed (Table 9, entries 10, 11).[182]

The stereochemical effect of four methyl groups is the main reason for the change in the direction of this process as compared to oxidation of *N*-substituted piperidin-4-ones. The alcohol structure and the amount of the base with respect to substrate influence the ratio of esters **11** and **12**. The electrocatalytically induced Favorsky rearrangement of triacetoneamine provides a convenient one-step synthesis of esters **11** and **12**, which are the starting compounds for the synthesis of biologically active iminoxyl radicals.[174]

1,3-Diaroylpropanes cyclise to 1,2-diaroylcyclopropanes in the iodide-mediated electrooxidation in high yields (Table 9, entry 12).[183]

In addition to the systems MHal–MOH (Hal = Br, I; M = Na, K), halide ions in combination with sodium cyanide or ammonia were used as catalysts for indirect ketone oxidation. The structures of the reaction products formed in the presence of the system KI–NaCN are determined by the structures of the parent ketones. For instance, alkanones convert first to oxiranecarbonitriles **13** and then partially to oxiranecarboximidates **14** (Scheme 12), whereas acetophenones transform to benzoylmalononitriles (Table 9, entry 13).[184]

Scheme 12

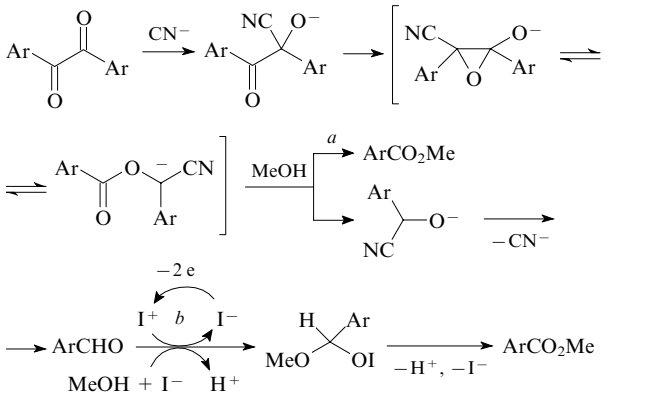


R^1–R^3	Yield (%)	
	13	**14**
R^1 = H, Me, Et, Ph; R^2 = H, Me; R^3 = Me, Pr^n, Ph, Bn	47–75	14–32
R^1 = H, R^2–R^3 = $(CH_2)_4$	12	57

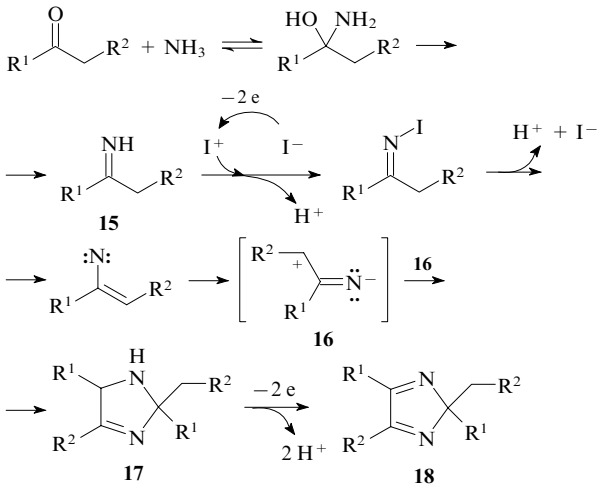
Under similar conditions, aromatic 1,2-diketones give esters of arylenecarboxylic acids according to two routes: chemical (route *a*) and electrochemical (route *b*) (Scheme 13; Table 9, entry 14).[185]

Passage of 0.6–1.0 F mol^{-1} of electricity converts alkanones into 2,2-dialkyl-2,5-dihydro-1*H*-imidazoles **17** in the presence of ammonia and KI *via* the ketimines **15** and subsequent electrooxidative cyclocoupling of intermediate **16** (Scheme 14). An increase in the amount of electricity passed to 3.4–4.4 F mol^{-1} results in the transformation of dihydroimidazoles **17** into the corresponding 2*H*-imidazoles **18** (Table 9, entries 15, 16).[186]

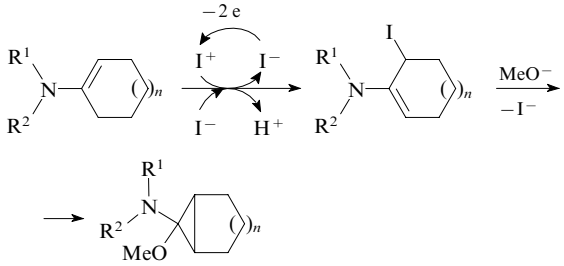
Scheme 13



Scheme 14



Iodide-catalysed indirect electrooxidation of ketone derivatives, for example, cycloalkanone enamines results in bicyclic hemiacetals (Table 9, entry 17).[187]



Under similar conditions, benzil monohydrazones transform to aroylaryldiazomethanes, whereas bromide-catalysed electrochemical process results in benzil monoacetals (Table 9, entries 18, 19).[188] Electrooxidation of phenylhydrazones of aldehydes and ketones gives methoxy(phenylazo)alkanes; in the case of dihydrazones of diaroylbenzenes, diaroylbenzene bis(diketals) are formed (Table 9, entries 20, 21).[189,190]

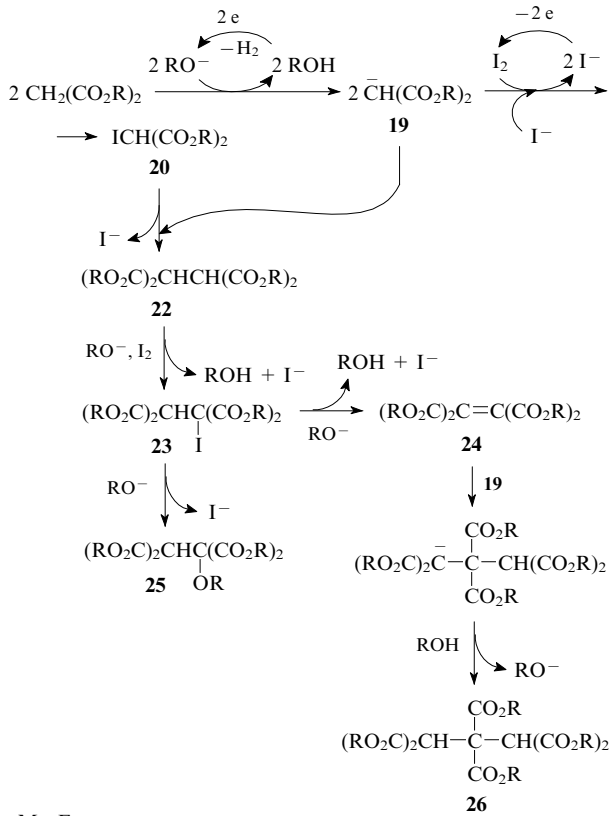
2. Electrosynthesis of esters of polycarboxylic acids and substituted cyclopropanes

Along with carbonyl compounds and their derivatives, CH-acids (diethyl malonate, ethyl acetoacetate and cyanoacetic esters, malononitrile, their derivatives, *etc*.) are the promising objects for electrocatalytic transformations involving

halide mediators. They were studied as substrates taken alone and in combination with carbonyl compounds and activated alkenes. In the 1980s, the ability of diethyl malonate and ethyl cyanoacetate to undergo halide-assisted electrooxidation to give derivatives of aliphatic and alicyclic polycarboxylic acids with high selectivity was demonstrated.[191–210] Later it was established that electrolysis of these esters with carbonyl compounds resulted in esters and nitriles of 3-mono- and 3,3-disubstituted cyclopropanepolycarboxylic acids,[211–215], while in the case of activated alkenes, in functionally substituted cyclopropanes and cyclic systems containing cyclopropane, as well as the pyrroline or pyrrolidone fragments.[216–226] The second type processes are examples of a basically novel approach to the construction of the cyclopropane ring.

Electrochemical transformations of CH-acids catalysed by alkaline metal halides start from their cathodic activation due to the interaction with cathode-generated alkoxy anions (when the reaction is carried out in alcohols) or with alkali metals (when electrolysis is performed in aprotic solvents) with the simultaneous generation of a chemical oxidant, *viz*., halogen molecule, on the anode. In the subsequent stage of the process, the halogen oxidises (in solution) the activated CH-acid, then, depending on the electrolysis conditions, dehydrodimerisation, dehydrogenation, condensation or cyclisation of intermediates occurs to form the final products. During two recent decades, simple and efficient methods for electrosynthesis of esters of unsubstituted and substituted ethane-1,1,2,2-tetracarboxylic, ethylenetetracarboxylic, propane -1,1,2,2,3,3-hexacarboxylic, 3,3-dimethoxyalkane-1,1-dicarboxylic acids; nitriles of 1,2-diarylethylene-1,2-dicarboxylic acids, 3,4-diacetylhexane-2,5-dione (Table 10, entries 1–9), as well as esters of unsubstituted, 2-mono- and 2,2-disubstituted cyclopropane-1,1,3,3-tetracarboxylic, cyclobutane- and cyclopentane-1,1,2,2-tetracarboxylic, cyclopropane-1,1,2,2,3,3-hexacarboxylic, 1,2,3-tricyano-cyclopropane-1,2,3-tricarboxylic acids (Table 10, entries 10–14) have been developed on the base of diethyl malonate, ethyl acylacetate and ethyl cyanoacetate, malononitrile and their derivatives.

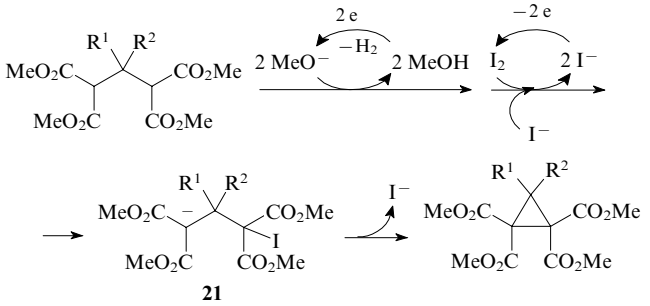
Scheme 15



R = Me, Et.

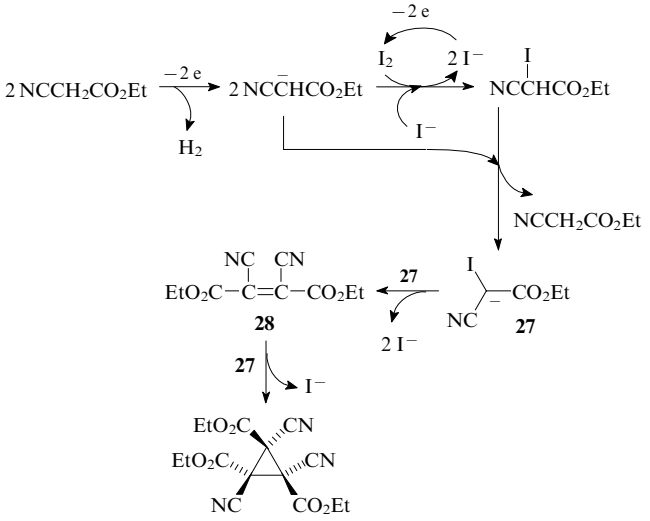
The mechanism of formation of some of these compounds is presented in Scheme 15 (transformation of malonates in their profound electrooxidation in alcohols in the presence of iodides[194]) and Scheme 16 (electrochemical cyclisation yielding esters of substituted propane-1,1,3,3-tetracarboxylic acids[203]).

Scheme 16



Both processes start with electrogeneration of alkoxy anions and molecular iodine. Then these reactants consecutively deprotonate and iodinate the starting compounds to form the corresponding secondary intermediates **19**–**21**. The intermediates **19** and **20** undergo coupling into intermediate esters of ethanetetracarboxylic (**22**), iodoethanetetracarboxylic (**23**) and ethylenetetracarboxylic (**24**) acids involving electrogenerated RO^- and I_2 and intermediates **19** affording alternatively esters of alkoxy-1,1,2,2-tetracarboxylic (**25**) and propane-1,1,2,2,3,3-hexacarboxylic (**26**) acids (Scheme 15). Electrochemical cyclotrimerisation of ethyl cyanoacetate to triethyl *trans*-1,2,3-tricyanocyclopropane-1,2,3-tricarboxylate in acetone occurs according to the similar scheme (Scheme 17).[210] (Note that electrolysis in alcohols leads to the formation of a mixture of oligomers at low substrate conversion).

Scheme 17



In final steps of this process, the intermediate formation of anions of ethyl iodocyanoacetate (**27**), diethyl 1,2-dicyanoethylene-1,2-dicarboxylic acid (**28**) (as a result of homocondensation of anions **27**) and cyclocondensation of ester

Table 10. Electrochemical synthesis of esters of aliphatic and alicyclic polycarboxylic acids from CH-acids mediated by halide ions (undivided cell).

Reaction	Entry	Yield (%)	Mediator	Conditions	Ref.
Transformations of dialkyl malonate, alkyl acylacetates and alkyl cyanoacetates					
$2\,CH_2(CO_2Me)_2 \longrightarrow (MeO_2C)_2CHCH(CO_2Me)_2$	1	94	NaBr	MeOH, −20 °C	194
$2\,CH_2(CO_2Me)_2 + MeOH \longrightarrow (MeO_2C)_2CHC(OMe)(CO_2Me)_2$	2	58	Bu_4NI	MeOH	194
$RC(O)CH_2CO_2Et \longrightarrow EtO_2CCH(R(O)C)-CH(C(O)R)CO_2Et$ (R = Me, Ph)	3	94–100	NaI	Me_2CO, −20 °C	197
$(MeO_2C)_2CHCH(CO_2Me)_2 \longrightarrow (MeO_2C)_2C{=}C(CO_2Me)_2$	4	~100 (61)	NH_4I	MeOH, 0 °C	192–194, 201
$3\,CH_2(CO_2Me)_2 \longrightarrow (MeO_2C)_2CH-C(CO_2Me)_2-CH(CO_2Me)_2$	5 6	90 (60) 98 (87)	LiBr LiI	MeOH, 50 °C MeOH, 50 °C	195, 196 195, 196
$R^1C(CO_2Me)=C(CO_2Me)CH_2R^2 + MeOH \longrightarrow MeO(OMe)C(CO_2Me)CHR^2CHR^1CO_2Me$ (R^1 = H, Me, Et; R^2 = H, Me)	7	76–89	NaI	MeOH	200
$2\,ArCH_2CN \longrightarrow NC(Ar)C(Ar)CN$ [Ar = RC_6H_4 (R = H, CN, Cl, Br, F)]	8	60–85 (40–70)	NaBr	MeOH, 0 °C	199
$MeC(O)CH_2C(O)Me \longrightarrow [MeC(O)]_2CH-CH[C(O)Me]_2$	9	95	NaI	Me_2CO, 0 °C	198
$3\,CH_2(CO_2Me)_2 \longrightarrow$ cyclopropane-1,1,2,2-tetracarboxylate	10	60	NaBr	MeOH, 50 °C	201, 202
$(MeO_2C)_2CH-C(R^1)(R^2)-CH(CO_2Me)_2 \longrightarrow$ cyclopropane-1,1,2,2-tetracarboxylate (R^1 = R^2 = H, Me, CO_2Me; R^1 = H, R^2 = Alk, CO_2Me, Ar, Het)	11	68–98	NaI	MeOH	203–205, 210
$MeO_2C-CH(CO_2Me)-(CH_2)_n-CH(CO_2Me)-CO_2Me \longrightarrow$ bicyclo[n+1].1.0 tetracarboxylate (n = 1–3)	12	75–98	NaI	MeOH	206, 207

Table 10 (continued).

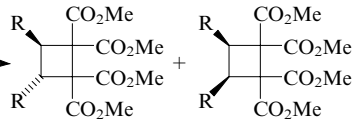
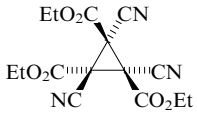
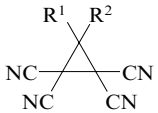
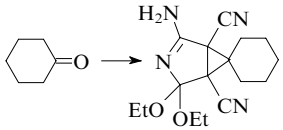
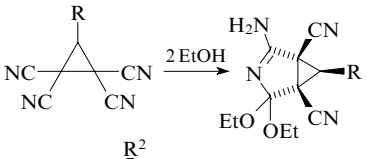
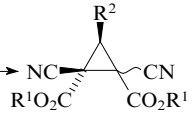
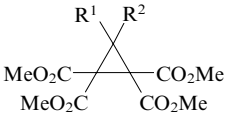
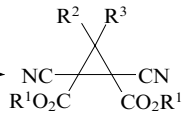
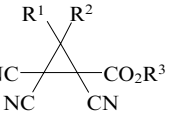
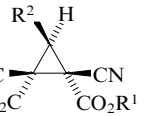
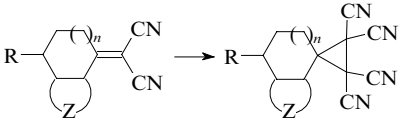
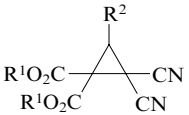
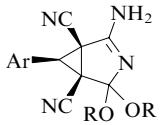
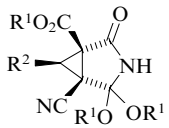
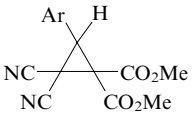
Reaction	Entry	Yield (%)	Mediator	Conditions	Ref.
Transformations of dialkyl malonate, alkyl- and acyl acetates alkyl cyanoacetates					
$RCH{=}C(CO_2Me)_2 \longrightarrow$  (R = Alk, Ar)	13	52–73	NaI	MeOH	207, 208
$3\,NCCH_2CO_2Et \longrightarrow$ 	14	75–80	NaI	Me_2CO	210
Electrosynthesis of substituted cyclopropanes					
$CH_2(CN)_2 + R^1C(O)R^2 \longrightarrow$  [R^1 = Me, R^2 = Alk; $R^1-R^2 = (CH_2)_n$ (n = 4, 6); R^1 = H: R^2 = H, Alk, Ar]	15	60–96	NaBr	EtOH	211, 214
$CH_2(CN)_2 +$ 	16	62	NaBr	EtOH	211
$CH_2(CN)_2 + RCH{=}O \longrightarrow$  (R = H, Alk, Ar)	17	56–97	NaBr	EtOH, 0–10 °C	212, 215
$NCCH_2CO_2R^1 + R^2CH{=}O \longrightarrow$  (R^1 = Me, Et; R^2 = Ar)	18	57–98	NaBr	R^1OH	213
$CH_2(CO_2Me)_2 + R^1R^2C{=}C(CO_2Me)_2 \longrightarrow$  [R^1 = Me, Pr^n, Ph, CO_2Me; R^2 = H, CO_2Me; $R^1-R^2 = (CH_2)_5$]	19	59–95 (63–76)	NaBr	MeOH	216
$NCCH_2CO_2R^1 + R^2R^3C{=}C(CN)CO_2R^1 \longrightarrow$  [R^1 = Me, Et; R^2 = Alk, cyclo-Pr; R^3 = Me, Pr^n; $R^2-R^3 = (CH_2)_n$ (n = 5, 6)]	20	67–95	NaBr	R^1OH, 10 °C	217

Table 10 (continued).

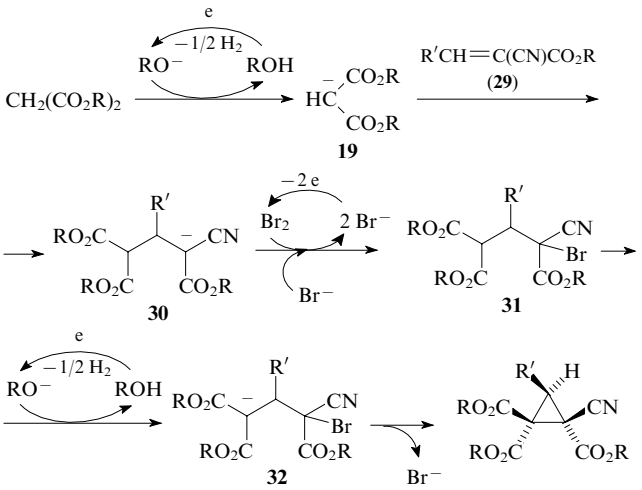
Reaction	Entry	Yield (%)	Mediator	Conditions	Ref.
Electrosynthesis of substituted cyclopropanes					
$CH_2(CN)_2 + R^1R^2C{=}C(CN)CO_2R^3 \longrightarrow$  [R^1 = Me, Pr^n; R^2 = Alk, Ph; $R^1 - R^2 = (CH_2)_n$ (n = 4, 6); R^3 = Me, Et]	21	62 – 78 (52 – 65)	NaBr	R^3OH, 10 °C	214
$CH_2(CO_2R^1)_2 + R^2CH{=}C(CN)CO_2R^1 \longrightarrow$  (R^1 = Me, Et; R^2 = Alk, Ar)	22	75 – 90 (50 – 60)	NaBr	R^1OH, 50 °C	218, 223
$CH_2(CN)_2 +$  (R = H, Me, Bu^t, Ph; n = 0, 1, 2, 7; R = H, n = 0, 1; Z = 4 H, benzo)	23	51 – 88	NaBr	EtOH	219
$CH_2(CO_2R^1)_2 + R^2CH{=}C(CN)_2 \longrightarrow$  (R^1 = Me, Et; R^2 = Alk, Ar)	24	60 – 90	NaBr	MeOH, 0 °C	220
$CH_2(CN)_2 + ArCH{=}C(CN)_2 \xrightarrow{2\,ROH}$  [Ar = XC_6H_4 (X = H, 4-Me, 4-Bu^t, 4-MeO, 2-Cl, 4-Cl, 3-Br, 4-I, 4-NO_2)]	25	63 – 82	NaBr	MeOH, 0 °C	221
$CH_2(CO_2R^1)_2 + R^2CH{=}C(CN)_2 \longrightarrow$  (R^1 = Me, Et; R^2 = Alk, Ar)	26	50 – 70	NaBr	MeOH, 10 °C	222
$CH_2(CN)_2 + CH_2(CO_2Me)_2 + ArCHO \longrightarrow$  [Ar = RC_6H_4 (R = H, Me, MeO, Cl, Br, F)]	27	40 – 60	NaBr	MeOH, 0 °C	224

28 and anions **27** with the elimination of the iodide anion take place.

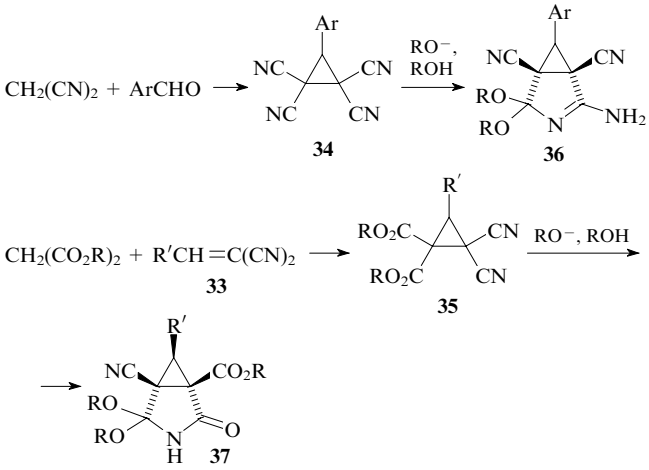
During the recent decade, a new approach to the construction of the cyclopropane ring based on electrolysis of CH-acids with carbonyl compounds and activated alkenes has been developed.[211–225] Using this approach, efficient methods for electrosynthesis of nitriles and esters of unsubstituted, 3-mono- and 3,3-disubstituted cyclopropane-1,1,2-tricarboxylic, cyclopropane-1,1,2,2-tetracarboxylic, as well as unsubstituted, 3-mono- and 3,3-disubstituted cyclopropane-1,2-dicarboxylic acids containing pyrroline and pyrrolidone fragments have been developed (Table 10, entries 15–27). Some of these methods of electrosynthesis are stereoselective. Thus joint electrolysis of dialkyl malonates and alkyl alkylidenecyanoacetates in alcohols in the presence of NaBr occurs with high current efficiency to give exclusively alkyl 3-substituted 2-cyanocyclopropane-1,1,2-tricarboxylates with *trans* arrangement of the CN and CO_2R groups (Scheme 18; Table 10, entry 22).[218, 223]

In this process, after electrogeneration of alkoxy anions and molecular bromine, dialkyl malonate transforms into anion **19** under the action of RO^- (in solution), which further adds to alkylidenecyanacetate (**29**). Then the anionic adduct **30** formed is brominated by electrogenerated bromine. Subsequent deprotonation of the bromination product **31** by the alkoxy anion and cyclisation of anion **32** with the elimination of the Br anion result in the target esters with the *trans* arrangement of the CN and CO_2R groups (Scheme 18). It is believed[218] that the halogenation step is responsible for the stereoselectivity of the ester formation.

Scheme 18



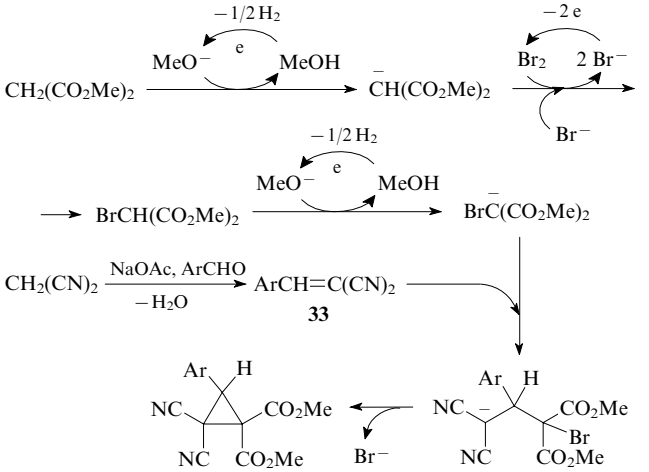
Only one of two possible stereoisomers is formed in the electrochemical reaction of benzaldehydes with malononitrile and dialkyl malonates with arylidene- or alkylidenemalononitriles **33** catalysed by NaBr or by the mediator system NaBr–NaOAc (Table 10, entries 17 and 26). The former process affords nitriles of 3-arylcyclopropane-1,1,2,2-tetracarbonitriles (**34**); the latter yields esters of 3-alkyl-2,2-dicyanocyclopropane-1,2-dicarboxylic acids (**35**). Chain alcoholysis under electrochemical conditions catalysed by electrogenerated alkoxy anions results in the easy conversion of compounds **34**, **35** into bicyclic pyrrolines (**36**) and pyrrolidones (**37**), respectively, containing *cis* ester and nitrile groups in the cyclopropane ring.[212, 215, 222]



Easy transformation of intermediates **34** and **35** into bicyclic products **36** and **37** is caused by the presence of the geminal cyano groups, which substantially differ in their reactivity due to steric effect. It is sufficient to pass 0.05–0.2 F mol^{-1} of electricity to perform this process.[225, 226] The structures of products presented in Schemes 16–18 and compounds **36** and **37** were established by X-ray diffraction analysis.[204, 210, 218, 221, 223, 225]

Progress in the development of halide-catalysed organic electrosynthesis is mainly associated with the development of the principle of one-pot multicomponent cascade assembling of the cyclopropane ring from three different substrates, benzaldehydes, dialkyl malonates and malononitrile (Table 10, entry 27).[224] This 'domino'-type cascade process starts from the condensation of ArCHO with $CH_2(CN)_2$ catalysed by sodium acetate and continues like electrochemical reaction of diethyl malonate with arylidenemalononitrile (Scheme 19).[220]

Scheme 19



Summarising the state-of-the-art studies on the application of indirect anodic oxidation of organic compounds using halides as mediators, it can be stated that substantial progress has been achieved in the last two decades. The most important result is the design of one-pot methods for the synthesis of a wide range of valuable compounds using accessible reactants and electric current as a cheap oxidant, which are efficient, easily adaptable technologically, environmentally acceptable, and, in some of cases, have no analogues in organic chemistry.

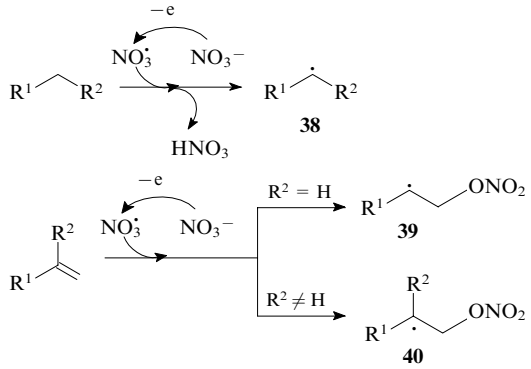
V. Electrooxidation in the presence of other inorganic reagents

1. Electrooxidative periodate cleavage of alcohols

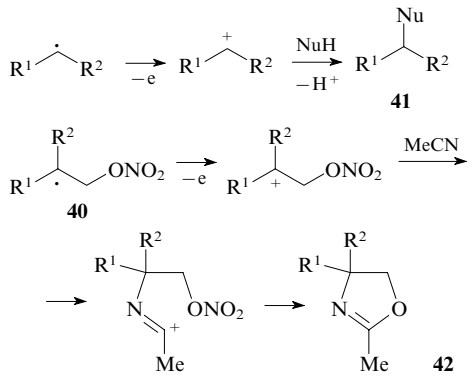
Oxidative cleavage of vicinal diols, hydroxy ketones and amino alcohols under the action of electrogenerated periodate ions in aqueous and water-organic media exceeds substantially in efficiency the chemical version of this reaction (Table 11, entries 1–6).[227–230] A method for utilisation of biomass formed in the fermentation of glucose and xylose has been developed based on this electrochemical reaction. In particular, hardly utilisable butane-2,3-diol in dilute aqueous solutions transforms to readily isolable acetaldehyde with 80% current efficiency.[227,228] The two-phase version of this method using a phase-transfer catalyst allows efficient electrooxidative cleavage of water-insoluble vicinal diols, hydroxy ketones and aminoethanols.

2. Oxidation of substrates by electrogenerated nitrate radicals

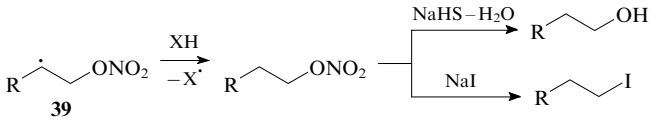
Alkanes, ethers, aldehydes and alkenes are oxidised by electrogenerated nitrate radicals through hydrogen abstraction or addition to C=C bonds. These reactions result in secondary radicals **38**–**40**.



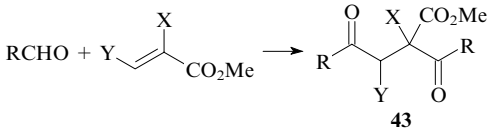
The process is usually carried out in a water–organic medium using *tert*-butyl alcohol or acetonitrile as an organic co-solvent in an inert atmosphere (except for linear alkanes, which are electrooxidised in an oxygen atmosphere). Under these conditions, subsequent electrooxidations of radicals **38**, **40** and reactions of carbocationic intermediates formed with nucleophiles (NuH) afford products **41**, **42**;



the abstraction of hydrogen atoms from proton donors XH by radicals **39** results in labile alkyl nitrates. The latter transform into alcohols or iodides upon treatment with aqueous sodium hydrogen sulfide or sodium iodide.



Among products **41** prepared in this way, isomeric ketones,[240] carboxylic acids and cycloalkanones, α,γ-alkanediols and α-diketones, acetals, alcohols, alkyl iodides and oxazolines are noteworthy (Table 11, entries 7–15).[231–233] Acyl radicals generated under the above conditions give esters of diacyl-substituted propionic and succinic acids (**43**) in the presence of active receptors, in particular, esters of acrylic, methacrylic, maleic and itaconic acids.[231,234]



X = H: Y = H, CO_2Me; Y = H: X = Me, CH_2CO_2Me.

3. Oxidation of substrates with hydrogen peroxide electrogenerated *in situ* from dioxygen

The unique property of H_2O_2 as an intermediate of indirect cathodic oxidation consists in its environmental safety. This peculiarity, as well as lower cost of electricity compared to chemical oxidants, simplicity of electrochemical generation, possibility to obtain H_2O_2 *in situ* from dioxygen give reason to consider mediator systems based on hydrogen peroxide as the most promising and efficient among similar reagents. The most important achievements in application of these systems for indirect electrooxidation are reviewed.[241,242] The most substantial is the application of gas-diffuse hydrophobised electrodes prepared from technical carbon (electrocatalyst) and polytetrafluoroethylene (hydrophobiser-binder).[243] This graphitised carbon electrode allows the formtion of highly developed surface of contact between three phases (electrocatalyst, aqueous electrolyte and gaseous reagent at zero pressure drop), enables good contact between the reagent and electrolyte, which increases the rate of electrogeneration of H_2O_2 by more than two orders of magnitude at current efficiency of 95%–99%.[244] Using electrogeneration of H_2O_2 *in situ* from dioxygen, efficient methods for electrosynthesis of formic,[244] malic[235,236] and 2,5-dihydrobenzoic[237] acids by cathodic oxidation of formaldehyde, maleic and salicylic acids, respectively, as well as the synthesis of salts of humic and polycarboxylic acids[244] from coal organic matter have been developed. In addition, parallel cathodic and anodic oxidation of organic substrates was successfully used for the synthesis of benzaldehyde from toluene,[37] anthraquinone from anthracene,[76] butyric acid from n-butanol,[123] nitrones from secondary amines,[238] sulfones from sulfoxides[239,245] and sulfoxides from sulfides[169] (Table 11, entries 18–26). This method is also used for electrochemical treatment of waste water from organic

Table 11. Indirect anodic and cathodic oxidation of organic compounds mediated by inorganic redox systems.

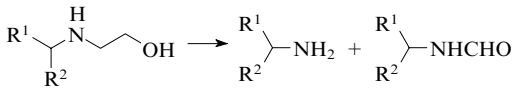
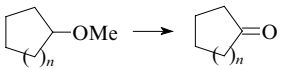
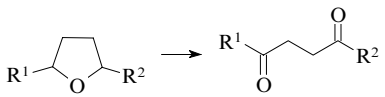
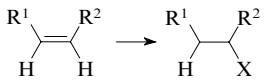
Reaction	Entry	Yield (%)	Conditions		Ref.
			cell	electrolyte	
IO_4^-/IO_3^- as a mediator (20 mol % – 40 mol %)					
$MeCH(OH)CH(OH)Me \longrightarrow 2\,MeCHO$	1	(80) [a]	DC	H_2O	227, 228
	2	(100) [b]	DC	H_2O	228
$PhCH(OH)CH(OH)Ph \longrightarrow 2\,PhCHO$	3	~100	DC	CH_2Cl_2, H_2O, $Bu_4^nNHSO_4$	229, 230
$PhCH(OH)C(O)Ph \longrightarrow PhCHO + PhCO_2H$	4	48	DC	CH_2Cl_2, H_2O, $Bu_4^nNHSO_4$	229, 230
$n\text{-}C_8H_{17}CH(OH)CH(OH)(CH_2)_7CO_2H \longrightarrow n\text{-}C_8H_{17}CHO + OCH(CH_2)_7CO_2H$	5	90	DC	CH_2Cl_2, H_2O, $Bu_4^nNHSO_4$	229, 230
	6	58 – 70	DC	CH_2Cl_2, H_2O	230
[R^1 = Ph, 4-MeC_6H_4, 4-ClC_6H_4; R^2 = H, Me; $R^1 - R^2 = (CH_2)_5$]					
$NO_3^{\bullet}/NO_3^-$ as a mediator					
$RCH_2OMe \longrightarrow RCO_2H$ (R = Alk)	7	69 – 77	UC	MeCN, H_2O	231
 (n = 1, 2)	8	~90	UC	MeCN, H_2O	231
 (R^1, R^2 = Alk)	9	~92	UC	MeCN, H_2O	231
$2\,RCHO \longrightarrow R{-}C(=O){-}C(=O){-}R$ (R = Alk)	10	~20	UC	MeCN, H_2O	231
$RCH_2OH + MeOH \longrightarrow RCH(OMe)_2$ (R = Alk)	11	62 – 73	UC	MeOH	232
	12	52 – 78 (X = OH)	UC	MeCN, Et_2O, H_2O	233
	13	67 – 70 (X = I)	UC	MeCN, Et_2O, H_2O	233
[R^1 = Bu^n, n-C_7H_{15}; $R^1 - R^2 = (CH_2)_n$ (n = 4, 6); X = OH, I]					

Table 11 (continued).

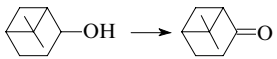
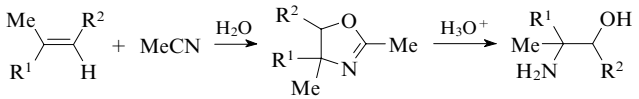
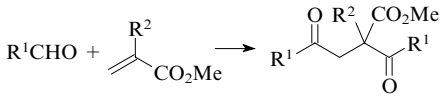
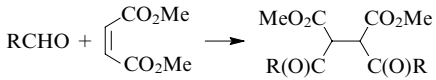
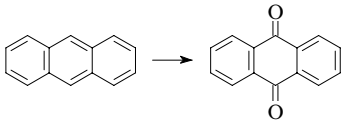
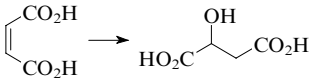
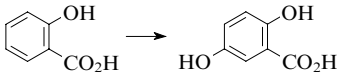
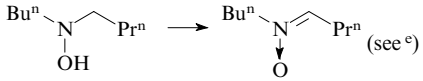
Reaction	Entry	Yield (%)	Conditions		Ref.
			cell	electrolyte	
$NO_3^{\bullet}/NO_3^-$ as a mediator					
	14	70	UC	MeCN, Et_2O, H_2O	233
 ($R^1 = R^2 = Me$; $R^1 = H$, $R^2 = Et$)	15	69 – 77	UC	MeCN, Et_2O, H_2O	231, 233
 (R^1 = Et, Pr^n, Pr^i; R^2 = H, Me, CH_2CO_2Me)	16	40 – 58	UC	MeCN, H_2O [c]	231, 234
 (R = Alk)	17	47	DC	MeCN, H_2O [c]	234
H_2O_2/O_2 – M (M = Mn, V, W, Os) as a mediator					
PhMe ⟶ PhCHO (see [d])	18	(171)	DC	H_2SO_4, H_2O	37
	19	98 (152)	UC	H_2SO_4, H_2O, $CHCl_3$	76
Bu^nOH ⟶ Pr^nCO_2H (see [d])	20	(166)	UC	KOH, H_2O	123
	21	56 – 58	DC	H_2SO_4, H_2O	235, 236
	22	–	DC	H_2O	237

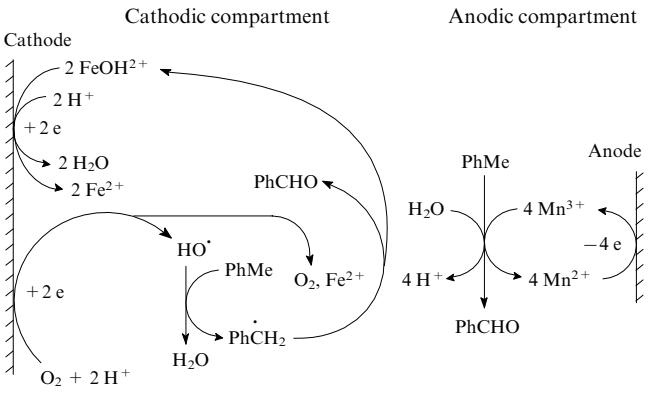
Table 11 (continued).

Reaction	Entry	Yield (%)	Conditions		Ref.
			cell	electrolyte	
H_2O_2/O_2 – M (M = Mn, V, W, Os) as a mediator					
 (see [e])	23	(177 – 182)	UC	Na_2HPO_4, H_2O	238
$R_2S \longrightarrow R_2SO_2$ (see [d]) (R = Me, $HOCH_2CH_2$, $HO_2CCH_2CH_2$)	24	(141 – 161)	UC or DC	H_2O	169
$R_2SO \longrightarrow R_2SO_2$ (see [e, f]) (R = Me, $HOCH_2CH_2$, $HO_2CCH_2CH_2$)	25	64 – 71	UC or DC	KH_2PO_4, H_2O	239
$R_2S \longrightarrow R_2SO$ (see [e, f]) (R = Me, $HOCH_2CH_2$, $HO_2CCH_2CH_2$)	26	73 – 75	UC or DC	KH_2PO_4, H_2O	239

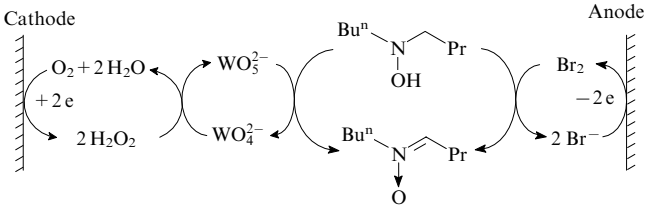
[a] 'In-cell'-process; [b] 'ex-cell'-process; [c] the amount of passed electricity is 10 F mol^{-1}; [d] parallel indirect anodic and cathodic oxidation using redox pairs Mn^{3+}/Mn^{2+} and V^{5+}/V^{4+} (entry 18), V^{5+}/V^{4+} and H_2O_2/O_2 (entry 20), WO_4^{2-}/WO_5^{2-} and Br^-/Br_2 (entry 23), Os^{VIII}/Os^{IV} and $WO_4^{2-}/WO_2(O_2)_2^{2-}$ (entry 24); [e] the amount of passed electricity is 2 F mol^{-1}; [f] indirect cathodic oxidation involving redox pair HWO_4^-/HWO_5^-.

toxicants.[242, 245] These are exemplified by two processes, *viz*., parallel electrosynthesis of benzaldehyde from toluene in the anodic and cathodic compartments of the divided cell (Scheme 20) and of nitrones from secondary amines in the undivided cell (Scheme 21).

Scheme 20



Scheme 21



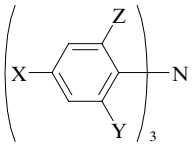
Benzaldehyde and nitrones are obtained with current efficiencies of 171% and 182%.[37, 238]

VI. Electrooxidation in the presence of organic mediators

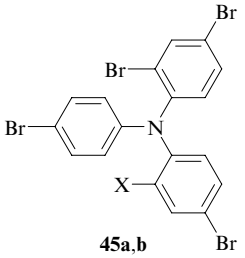
Organic mediators for electrooxidation are of interest due to their accessibility and ease of structural modification of molecules.

1. Indirect electrooxidation involving triarylamine mediators

By the early 1980s, electrooxidation reactions catalysed by organic mediators have not attracted attention of electrochemists. There existed a concept on low catalytic efficiency of these mediators, because their active forms, *viz*., the corresponding radical cation, are usually unstable, readily react with nucleophiles and thus escape the electroregeneration cycle. Only after *para*- and *ortho*-substituted triarylamine radical cations highly stable against nucleophiles had been prepared, organic mediators (for example, compounds **44** and **45**) found use in indirect electrooxidation.[6]



44a–f



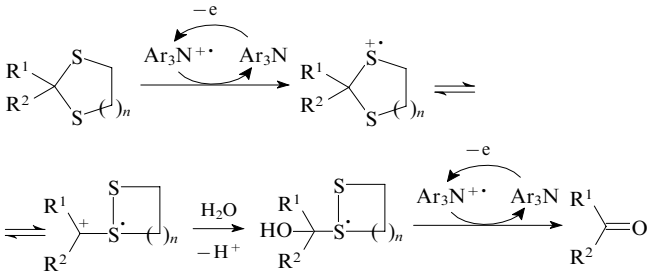
45a,b

Compound	X	Y	Z	E°_{ox}/V§
44a	MeO	H	H	0.76
44b	Br	H	H	1.30
44c	Br	Br	H	1.74
44d	Me	NO_2	H	1.80
44e	NO_2	H	H	1.80
44f	Br	Br	Br	1.96
45a	H	–	–	1.42
45b	Br	–	–	1.56

Oxidation potential (E°_{ox}) and stability of triarylamine mediators depend substantially on the nature of substituents in the *para*- and *ortho*-positions. The E°_{ox} value can vary from 0.76 to 1.96 V, while the turnover number, for example, for tris(2,4-dibromophenyl)amine (**44c**), reaches 2500.[6, 246]

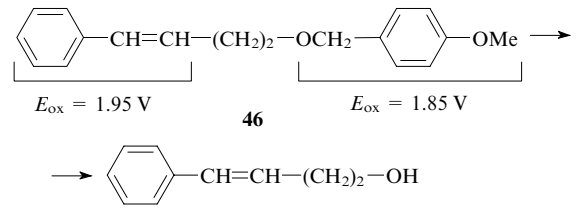
In contrast to mediators based on metals in high oxidation states, electrogenerated triarylamine radical cations show much more pronounced ability to form metastable complexes with substrates. This facilitates oxidative processes and allows oxidation of substrates having oxidation potential up to 1 V, higher than that of the mediator E°_{ox}, under milder conditions and with higher selectivity.[6]

Indirect electrooxidation involving triarylamine mediators can be used for selective oxidative removal of protecting groups. For example, 1,3-dithianes and 1,3-dithiolanes are converted in ketones including steroidal hydroxy ketones (Table 12, entries 1, 2). The mechanism of this process can be presented as follows:



n = 1, 2.

Under electrochemical conditions, the anisylmethyl protection was removed from the OH group of 4-phenylbut-3-enol; oxidation potential values for the electrophore fragments in compound **46** differ only by 100 mV.[6]



46

This method was also used for selective removal of *S*-protecting groups from cysteine residues with formation of disulfide bridges (Table 12, entry 3).[6]

§ Hereinafter E°_{ox} are given *vs* SHE.

Table 12. Indirect anodic oxidation of organic substrates in the presence of triarylamine mediators.

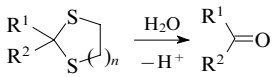
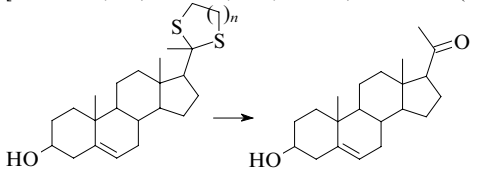
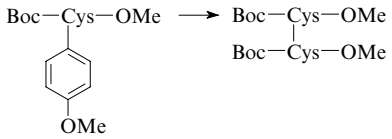
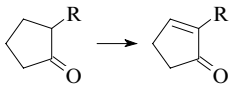
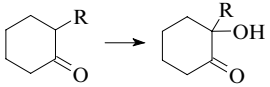
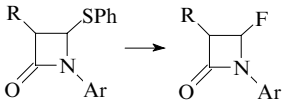
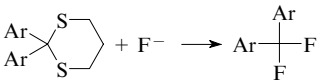
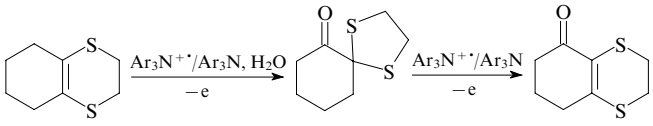
Reaction	Entry	Yield (%)	Triarylamine	Conditions		Ref.
				cell	electrolyte	
Synthesis of ketones and cystine with selective removal of protecting groups						
 [R^1 = Alk, Ph; R^2 = H, Alk, EtO_2C; R^1-R^2 = $(CH_2)_5$; n = 1, 2]	1	70–95	$(4\text{-}MeC_6H_4)_3N$	DC	MeCN, H_2O, $LiClO_4$, $NaHCO_3$	6
 (n = 1, 2)	2	~100	$(4\text{-}AcC_6H_4)_4N$	DC	MeCN, H_2O, $LiClO_4$, $NaHCO_3$	6
	3	91	$(4\text{-}BrC_6H_4)_4N$	DC	MeCN, H_2O, $LiClO_4$, $NaHCO_3$	6
Synthesis of ketones, enones, α-hydroxy ketone, esters and orthoesters by indirect anodic oxidation of cycloalkanones, alkenes and acetals						
 (R = Me, Bu^t)	4	30–53	$(2,4\text{-}Br_2C_6H_3)_3N$	DC	MeCN, H_2O	247
 (R = Me, Ph)	5	46–47	$(2,4\text{-}Br_2C_6H_3)_3N$	DC	MeCN, H_2O	247
$RCH{=}CH_2 + H_2O \longrightarrow RC(O)Me$ (R = $PhCH_2$, cyclo-Alk)	6	57–85	$(4\text{-}BrC_6H_4)_3N$ [a]	UC	MeCN, H_2O	146
$4\text{-}RC_6H_4Me + MeOH \longrightarrow 4\text{-}RC_6H_4CO_2Me$ (R = H, Me, Bu^t, Cl, Br)	7	71–95	$(2,4\text{-}Br_2C_6H_3)_3N$	UC	MeOH, CH_2Cl_2	248
$4\text{-}RC_6H_4CH(OMe)_2 + MeOH \longrightarrow 4\text{-}RC_6H_4C(OMe)_3$	8	78–93	$(2,4\text{-}Br_2C_6H_3)_3N$	UC	MeOH, H_2Cl_2	248

Table 12 (continued).

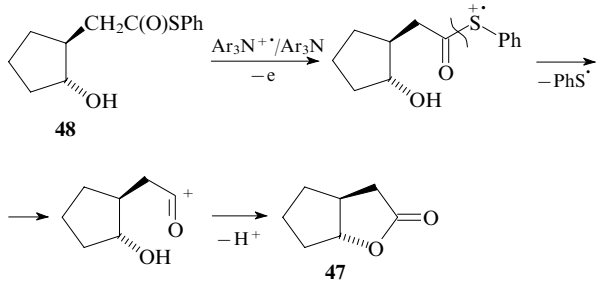
Reaction	Entry	Yield (%)	Triarylamine	Conditions		Ref.
				cell	electrolyte	
Synthesis of fluorinated organic compounds						
 [R = H, $SiBu^tMe_2$; Ar = 4-XC_6H_4 (X = H, Me, Br)]	9	66 – 100	(2,4-$Br_2C_6H_3)_3N$	DC	MeCN, $Et_3N \cdot 3\,HF$	249
PhC(O)SAr ⟶ PhC(O)F [Ar = 4-XC_6H_4 (X = H, Cl, MeO)]	10	60 – 69	(2,4-$Br_2C_6H_3)_3N$	DC	MeCN, CH_2Cl_2, $Et_3N \cdot 3\,HF$	250
$R^1C(SPh)_2R^2$ ⟶ $R^1CF_2R^2$ [R^1, R^2 = 4-XC_6H_4 (X = H, F, Cl)]	11	58 – 83	(4-$BrC_6H_4)_3N$ or (2,4-$Br_2C_6H_3)_3N$	DC	MeCN, CH_2Cl_2, $Et_3N \cdot 3\,HF$	251
 [Ar = 4-XC_6H_4 (X = H, Cl, F)]	12	87 – 98	see [b]	DC	MeCN, $Et_3N \cdot 3\,HF$	252
	13	63 – 99	see [c]	DC	MeCN, CH_2Cl_2, $Et_3N \cdot 3\,HF$	253
	14	61 – 86	see [d]	DC	MeCN, CH_2Cl_2, $Et_3N \cdot 3\,HF$	254
Electrooxidative versions of alkene ozonolysis						
4-$XC_6H_4CH{=}CHC_6H_4Y$-4 + H_2O ⟶ 4-XC_6H_4CHO + 4-YC_6H_4CHO (X, Y = H, CF_3, CN, CHO)	15	93 – 96	(2-NO_2-4-$MeC_6H_3)_3N$	UC	MeCN, CH_2Cl_2, $Et_3N \cdot 3\,HF$	255
3,5-$(CF_3)_2C_6H_3CH{=}CHC_6H_3(CF_3)_2$-3,5 ⟶ 3,5-$(CF_3)_2C_6H_3CH{=}O$	16	95	(2-NO_2-4-$MeC_6H_3)_3N$	UC	MeCN, CH_2Cl_2, $Et_3N \cdot 3\,HF$	255

[a] In the presence of $Pd(OAc)_2$; [b] mediator is pair 4-$MeOC_6H_4IF_2$/4-$MeOC_6H_4I$; [c] mediator is pair Br^+/Br^-; [d] mediator is system 4-$MeOC_6H_4I - Cl^-$.

Triarylamine mediators demonstrated high catalytic activity in such electrooxidative processes as the rearrangement of organosulfur compounds [6]

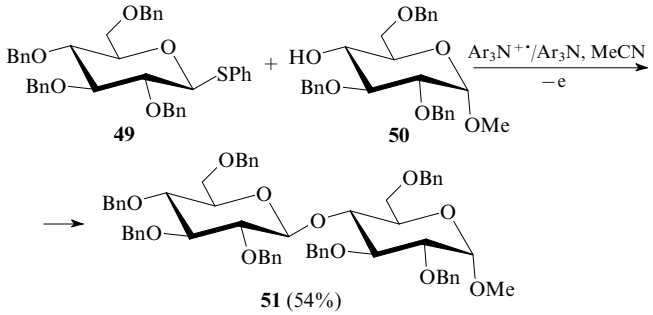


and the synthesis of poorly accessible *trans*-cyclopentano-γ-lactone (**47**) from *S*-phenyl-*trans*-2-hydroxycyclopentylthioacetate (**48**).[6]



Electrooxidative α,β-dehydrogenation of cyclopentanones, α-hydroxylation of cyclohexanones (Table 12, entries 4, 5) [247] and alkene oxygenation catalysed by triarylamine **44b** together with palladium (see Section III.5) should be also mentioned.[146]

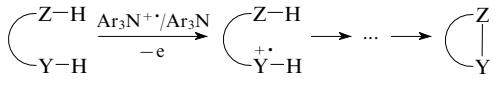
S-Glycosides (**49**) glycosylate *O*-glycosides (**50**) in an undivided cell to form the corresponding β-*O*-linked disaccharide (**51**).[256]



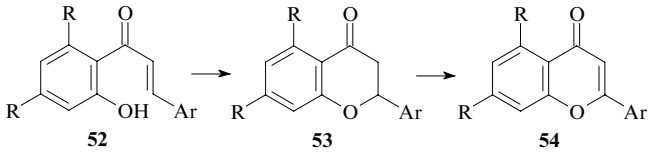
Ar = $(4\text{-}BrC_6H_4)_3N$.

A possibility to perform oxidation of organic substrates catalysed by triarylamine mediators in methanol in an undivided cell became an important phase in the development and application of the method. Methyl benzoates and trimethyl orthobenzoates were obtained in this way (Table 12, entries 7, 8).[248]

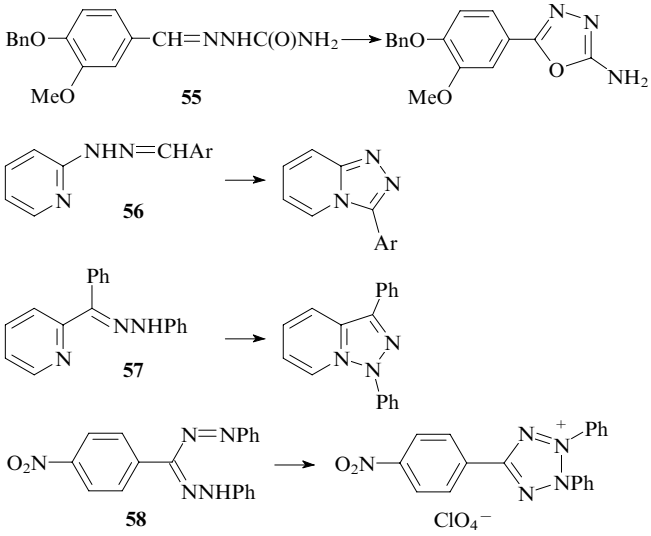
Triarylamine mediators have found application in electrosynthesis of heterocyclic compounds. This method is based on triarylamine-catalysed electrochemical formation of heteroatom-centred radical cations capable of cyclisation.[257]



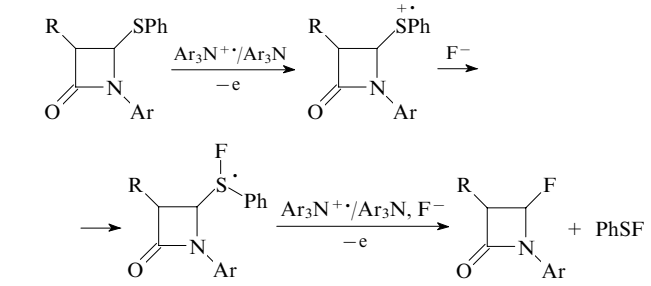
This approach was used for the synthesis of flavonoids **53**, **54** from hydroxychalcones **52** [257] and



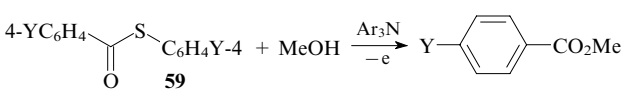
of nitrogen-containing heterocycles from the corresponding azomethines **55**–**58**.[258]



A striking effect was achieved when using triarylamine mediators in the electrosynthesis of fluorinated β-lactams (Table 12, entry 9) that served as 'building blocks' for the construction of carbohydrates and amino acids. Triethylamine salt ($Et_3N \cdot 3\,HF$) was used as a fluorinating agent. Electrooxidation of β-phenylsulfenyl-β-lactams in the presence of 10 mol% $(2,4\text{-}Br_2C_6H_3)_3N$ (**44c**) resulted in the target product in a yield of 83%, electricity consumption per 1 mol of the starting lactam being 2.9 F mol^{-1} (Ref. 249). In the absence of the mediator, a strong anode passivation was observed, electricity consumption was higher, 6.9 F mol^{-1}, the lactam yield was only 37%. The mechanism of this process involving the mediator **44c** can be presented as follows:

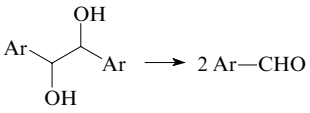


Electrochemical desulfidation of *S*-aryl thiobenzoates and dithioacetals catalysed by triarylamine mediators occurs similarly (Table 12, entries 10, 11).[250,251] Note that in the presence of methanol, methoxydesulfidation of *S*-aryl thiobenzoates (**59**) occurs.[259]

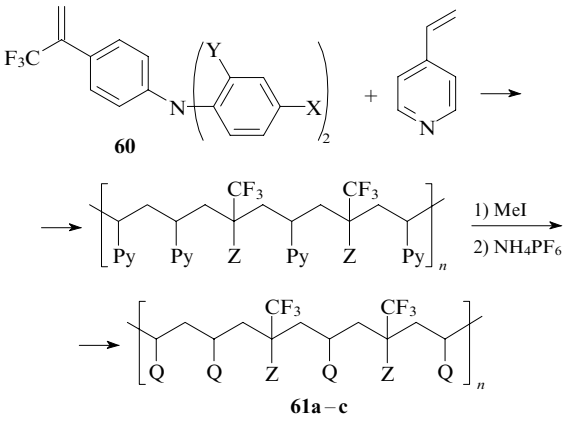


Introduction of a fluorine atom into organic molecule by alternative chemical methods usually requires the application of highly toxic reagents, that is why the potential of electrochemical synthesis of fluorinated products is obvious. Indirect electrooxidative difluorodesulfidation of dithioacetals also proceeds in the presence of 4-methoxyphenyl iodide, a double mediator system 4-methoxyphenyl iodide–chloride anions and a pair Br^+/Br^- (entries 12–14 are included into Table 12 for the sake of comparison).[252–254]

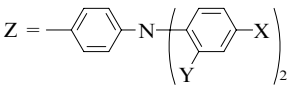
Recently, an easily accessible triarylamine mediator, tris(2-nitro-4-methylphenyl)amine, has allowed the development of electrocatalytic versions of the cleavage of alkenes substituted with electron-withdrawing groups (Table 12, entry 15) and glycols, which is difficult to perform under the action of chemical oxidants.[255]



Polyelectrolytes with incorporated triarylamine fragments well soluble in stardard organic solvents, made an important contribution to the development of electrooxidation processes catalysed by triarylamine mediators.[260] These polymers were obtained by copolymerisation of diaryl-4-(1-trifluoromethylvinyl)arylamines (**60**) with 4-vinylpyridine followed by treatment of the copolymer with methyl iodide and ammonium hexafluorophosphate. Mediators **61** were tested using indirect electrooxidation of $PhCH_2OH$ to PhCHO as a model.



X = Br: Y = H (**a**), Br (**b**); X = Y = NO_2 (**c**); Py is 4-pyridyl;

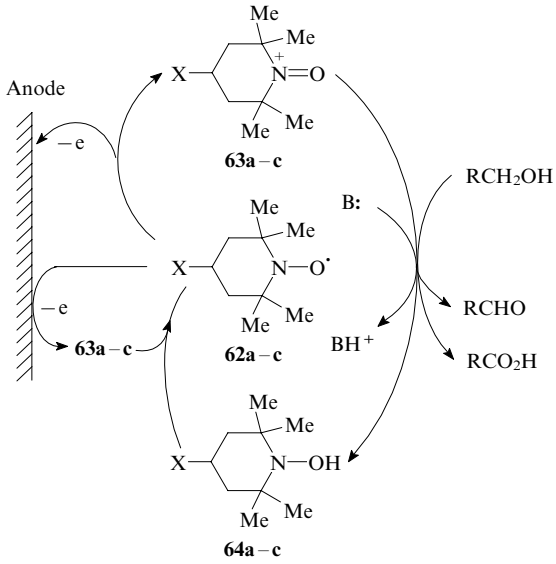


Due to homogeneous distribution in solution, polymeric mediators **61** favour efficient electron transfer between their oxidised forms and substrates and eliminate diffusion limitations typical of electrochemical processes. In addition, the advantage of redox catalysts bound to the polymeric matrix consists in a possibility of their fairly easy isolation from the reaction mixture by ultrafiltration or sedimentation; also no additional electrolyte is required. These benefits substantially simplify purification and regeneration of the mediator. Before polyelectrolytes **61** have been synthesised polymeric triarylamines were applied exclusively as redox polymeric coatings deposited on the electrode surface. However, due to low stability, limited permeability and slow charge transfer through the polymeric film, these coating appeared to be unsuitable for electrocatalytic synthesis.

2. Oxidation using stable 2,2,6,6-tetramethylpyridinyl-1-oxyl radicals as mediators

The catalytic effect of 2,2,6,6-tetramethylpiperidinyl-1-oxyl radicals **62a–c** in indirect electrooxidation of organic substrates is connected with the transformation of these radicals to oxoammonium cations **63a–c** as a result of one-electron transfer. The latter are electroregenerated highly reactive reagents that induce rapid abstraction of the hydride ion from compounds to be oxidised, in particular, primary alcohols, in the presence of bases (Scheme 22).[6, 261, 262]

Scheme 22



X = H (**a**), $PhCO_2$ (**b**), AcNH (**c**).

Application of TEMPO and its derivatives as mediators permits the synthesis of aldehydes at a substantially lower anodic potential (0.4 V) than the oxidation potential of alcohols (>2 V). Electrolysis of acetonitrile solutions of alcohols in an undivided cell prevents further oxidation of the aldehydes formed to carboxylic acids and ensures efficient and selective transformation of primary alcohols to the corresponding aldehydes (Table 13, entry 1).[261]

In the case of electrooxidation of primary alcohols in aqueous and water-organic solutions in an undivided cell, hydration of the aldehydes formed leads to its rapid transformation into the corresponding acids. Thus under these conditions mono- (**65**) and disaccharides (**66**, **67**) are oxidised to uronic acids **68–70**.[262–264]

Table 13. Indirect anodic oxidation of organic compounds in the presence of TEMPO-based mediatory systems.

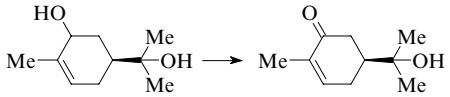
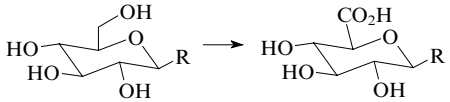
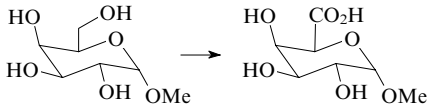
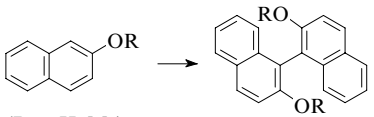
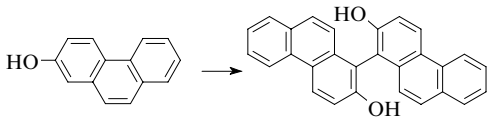
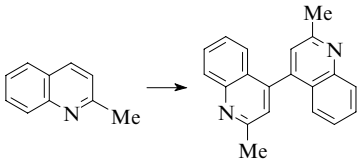
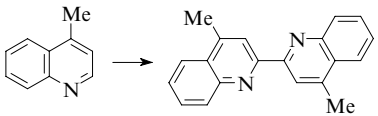
Reaction	Entry	Yield (%)	Mediator	Conditions		Ref.
				cell	electrolyte	
Synthesis of aldehydes, ketones and carboxylic acids by indirect anodic oxidation of alcohols in a homogeneous medium						
4-$XC_6H_4CH_2OH$ ⟶ 4-XC_6H_4CHO (X = H, Me, MeO)	1	71 – 85 (52 – 63)	**62a**	DC	MeCN	261
	2	76	**62a**	DC	MeCN, H_2O	263
 (R = MeO, n-$C_8H_{17}O$, N_3)	3	58 – 85	**62a**	DC	MeCN, H_2O	264, 265
	4	53	**62a**	DC	MeCN, H_2O	264
Synthesis of (het)arene dimers						
 (R = H, Me)	5	96 – 98	**62c** [a]	DC	MeCN	266
	6	94	**62c** [a]	DC	MeCN	267
	7	> 92	**62c** [a]	DC	MeCN	268
	8	> 92	**62c** [a]	DC	MeCN	268

Table 13 (continued).

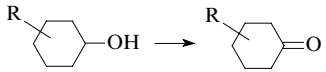
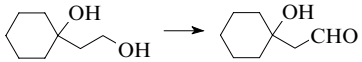
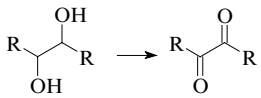
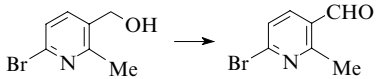
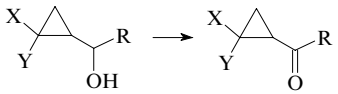
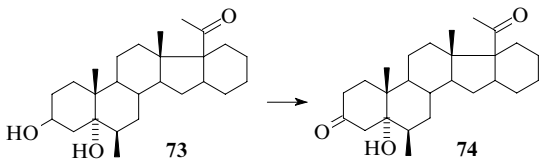
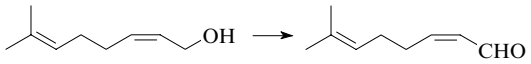
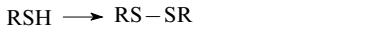
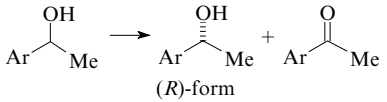
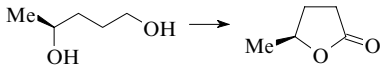
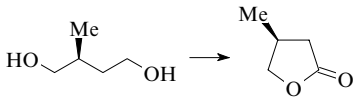
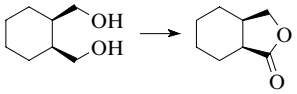
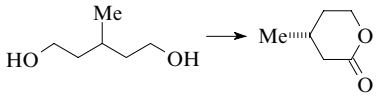
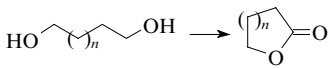
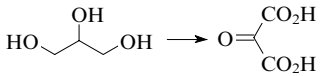
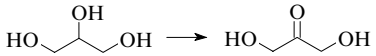
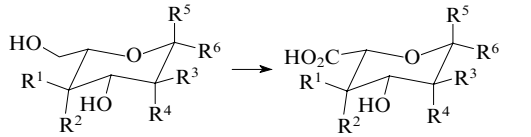
Reaction	Entry	Yield (%)	Mediator	Conditions		Ref.
				cell	electrolyte	
Synthesis of aldehydes and ketones by indirect anodic oxidation of alcohols in a two-phase system						
$R^1R^2CHOH \longrightarrow R^1R^2C(O)$ (R^1 = Alk, Ph; R^2 = H, Alk)	9	93–97	**62b** – Br^-	UC	H_2O, CH_2Cl_2	269–271
 (R = 4-Bu^t, 2-OAc)	10	93–97	**62b** – Br^-	UC	H_2O, CH_2Cl_2	269, 270
	11	87	**62b** – Br^-	UC	H_2O, CH_2Cl_2	269, 270
$R-C\equiv C-CH_2OH \longrightarrow R-C\equiv C-CHO$ (R = Alk)	12	90	**62b** – Br^-	UC	H_2O, CH_2Cl_2	269, 270
 (R = Alk)	13	85	**62b** – Br^-	UC	H_2O, CH_2Cl_2	269, 270
$ArCH_2OH \longrightarrow ArCHO$ [Ar = 4-XC_6H_4 (X = Bu^t, MeO, NO_2); 2-$PhOC_6H_4$, 3,4,5-$(MeO)_3C_6H_2$]	14	76–93	**62b** – $Bu_4^nNBr_3$	DC [b]	H_2O, CH_2Cl_2	272
	15	94	**62b** – $Bu_4^nNBr_3$	DC [b]	H_2O, CH_2Cl_2	272
	16	90	**62b** – $Bu_4^nNBr_3$	DC [b]	H_2O, CH_2Cl_2	272
$Cl(CH_2)_4OH \longrightarrow Cl(CH_2)_3CHO$	17	70–90	**62b** – Br^-	UC	$NaHCO_3$, H_2O, CH_2Cl_2	273
3-$PhOC_6H_4CH_2OH \longrightarrow$ 3-$PhOC_6H_4CHO$	18	85	**62b** – Br^-	UC	$NaHCO_3$, H_2O, CH_2Cl_2	273
 [X, Y = H, Cl, Br; R = H, $CH_2CH(OEt)_2$]	19	56–98	**62b** – Br^-	UC	$NaHCO_3$, H_2O, CH_2Cl_2	273
 **73** **74**	20	88	**62b** – Br^-	UC	$NaHCO_3$, H_2O, CH_2Cl_2	274

Table 13 (continued).

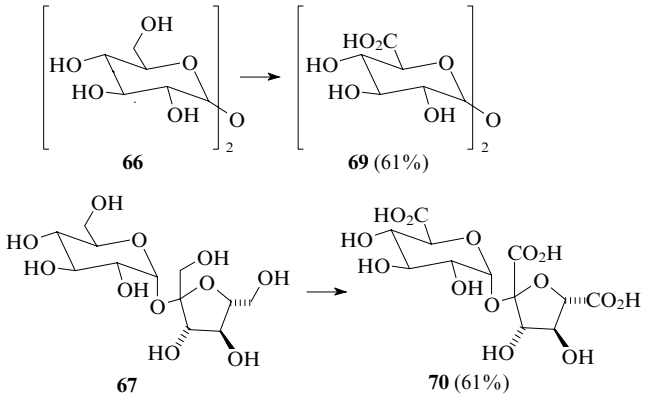
Reaction	Entry	Yield (%)	Mediator	Conditions		Ref.
				cell	electrolyte	
Indirect anodic oxidation involving TEMPO analogues						
	21	100 (80 – 90)	**62b** – Br^- (see [a])	DC	MeCN	275, 276
 (R = Alk)	22	100 (> 90)	**62b** – Br^- (see [a])	DC	MeCN	277
 [Ar = Ph, 4-XC_6H_4 (X = Me, Cl, MeO)]	23	53	**62b** – Br^- + **77** [a]	DC	MeCN	278
	24	100	**76** – Br^-	DC	MeCN	279
	25	80 – 91	PE-*N*-Oxyl [c]	DC	MeCN	280
	26	42 – 88	(*S*)-**78** – Br^-	UC	H_2O, $NaHCO_3$	281
	27	48	**62c** – Br^- + **77** [a]	DC	MeCN	282
	28	95 (96)	**76** – Br (see [a])	DC	MeCN	283
	29	94	**62c** – Br^- + **77** [a]	DC	MeCN	282
	30	92	**76** – Br (see [a])	DC	MeCN	283
	31	92	(*S*)-**78** – Br^-	UC	H_2O, $NaHCO_3$, NaBr	281
	32	96	**62c** – Br^- + **77** [a]	DC	MeCN	282
	33	96 (97)	**76** – Br^-	DC	MeCN	283
 (n = 1, 2)	34	72 – 84	(*S*)-**78** – Br^-	UC	H_2O, $NaHCO_3$	281
	35	–	**62a** – Br^-	UC	H_2O, NaCl	284
	36	–	**62a**	UC	H_2O, $NaHCO_3$	285

[a] TEMPO immobilised on the surface of a graphite felt anode was used; [b] 'ex-cell' process; [c] polyethylene granules with TEMPO immobilised on the surface.



65 **68** (45% – 96%)

R^1, R^2 = R^3, R^4 = H or OH; R^5 = H,
R^6 = $Me(CH_2)_nO$ (n = 0, 7, 11); R^5 = OH, R^6 = H.

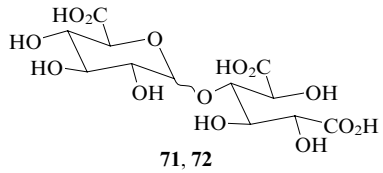


66 **69** (61%)

67 **70** (61%)

Oligo- and polysaccharides, (for example, potato starch) as well as alkyl glycosides and β-D-glycopyranosyl azide undergo similar transformations (Table 13, entries 3, 4).[264, 265]

Acids **71** and **72** were obtained with high current efficiencies (95%) from maltose and cellobiose, respectively, in the divided cell (electrolyte was aqueous acetonitrile).[263]



71, **72**

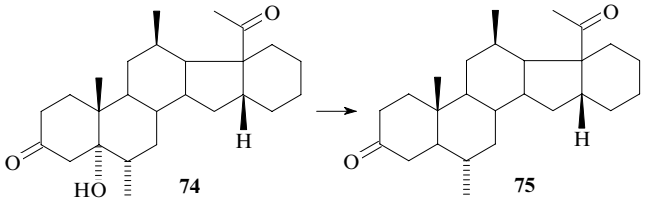
Isomers: α (**71**), β (**72**).

TEMPO-catalysed indirect anodic oxidation of naphthols, phenanthrol, alkyl aryl ethers, methylquinolines and phenanthrene resulted in the corresponding dimers. For example, 1-naphthol or its methyl ether give a mixture of isomeric products containing hydroxy or methoxy groups in positions 2,2′, 2,4′ and 4,4′;[266] 2,2′-dihydroxy- and 2,2′-dimethoxy-substituted dimers were obtained from 2-naphthol and its methyl ether, 2,2′-dihydroxy-1,1′-biphenanthrene was prepared from 2-phenanthrol, 2,2′-dimethyl-2,2′(4,4′)-dimethyl-4,4′(2,2′-)biquinolines were obtained from 2(4)-methylquinolines (Table 13, entries 5 – 8).[266 – 268]

Further studies on TEMPO-catalysed indirect electrooxidation of organic compounds were directed to increasing its efficiency due to increase in mediator turnover numbers and improvement of experimental procedure, as well as to the preparation of chiral compounds. As a result, two groups of electrochemical processes have been developed. Processes performed in the two-phase water-organic systems using double mediator systems including TEMPO as the key component belong to the first group.[269 – 274, 286] Processes using TEMPO deposited on anodes (usually of graphite felt) coated with polymeric polypyrrole or polyacrylic acid films [274 – 283, 287 – 289] carried out in the presense of chiral bases belong to the second group.[278 – 281] In the latter case, chiral products are formed as a result of rapid selective oxidation of one of enantiomeric forms.

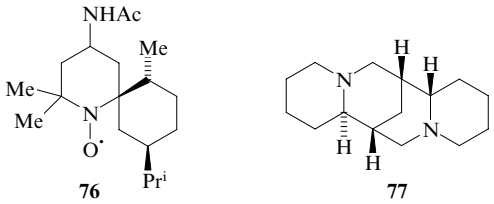
The following electrochemical processes implemented recently can be mentioned as achievements in the field of indirect electrooxidation using TEMPO-type *N*-oxyl mediators:

1. Electrooxidative dehydrogenation of alcohols under the action of the double mediator system TEMPO – NaBr in a two-phase water-organic medium. This reaction was successfully used for the preparation of a wide range of aldehydes and ketones, for example, 4-chlorobutanal, formylcyclopropanes, 3-phenoxybenzaldehyde (Table 13, entries 17 – 19),[273] for the synthesis of C_{10} aldehyde components of analogues of juvenile hormones methoprene and hydroprene,[271] as well as for the selective transformation of 6β-methyl-3β,5α-dihydroxy-16α,17α-cyclohexanopregnan-20-one (**73**) into 6β-methyl-5α-hydroxy-16α,17α-cyclohexanopregnane-3,20-dione (**74**) (Table 13, entry 20). The latter is of interest as an intermediate in the synthesis of progestine (**75**), a medicine for curing hormonal disorders.[274]



74 **75**

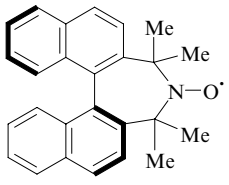
2. Asymmetrical lactonisation of diols based on their indirect anodic oxidation by an *N*-oxyl mediator immobilised on the graphite anode coated with polyacrylic film. Both a chiral radical (for example, piperidinoxyl **76**) and achiral TEMPO in combination with a chiral base, alkaloid sparteine (**77**) (Table 13, entries 23, 24, 27, 28) were used as mediators.[278, 279, 282, 283]



76 **77**

3. Oxidation of alcohols to carbonyl compounds in a disperse system consisting of *N*-oxyl-immobilised polyethylene grains and aqueous solution of $NaHCO_3$ and NaBr.[280]

4. Kinetic separation of enantiomeric forms of secondary alcohols due to faster anodic oxidation of one of the forms involving a chiral mediator For instance, in the indirect electrooxidation of racemic 1-arylethanols in the presence of *N*-oxyl (*S*)-**78**, (*S*)-enantiomers transform into ketones, while (*R*)-enantiomers remain unoxidised (Table 13, entry 26).[281]



(*S*)-**78**

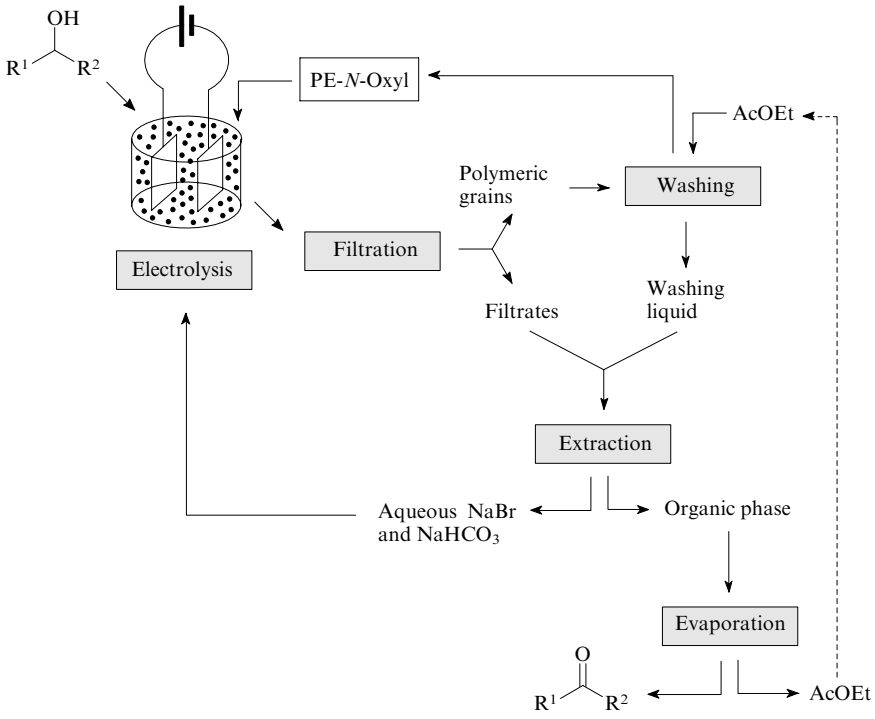


Figure 1. Schematic diagram for alcohol electrooxidation in disperse system.

5. Electrooxidative transformation of glycerol to ketomalonic acid or (at controlled potential of 1.1 V) to 1,3-dihydroxypropan-2-one (Table 13, entries 35, 36).[284, 285]

The singularity of the third and fourth processes consists of the use of organic solvent-free heterogeneous disperse systems, which includes PE-*N*-oxyl as a disperse phase and aqueous solution of $NaHCO_3$ and NaBr as a disperse medium of the system. They can be effected as closed ecologically clean processes with multiple use of the disperse system. Another distinguished feature of these methods is the simplicity of isolation of the target products (Fig. 1).

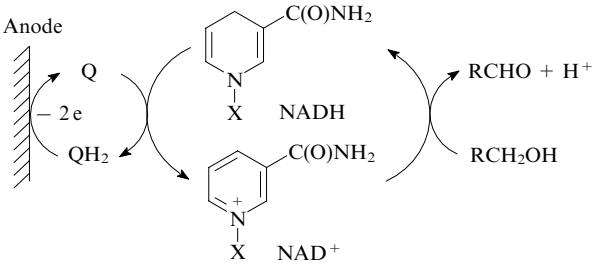
Selective transformation of glycerol to 1,3-dihydroxypropan-2-one (dihydroxyacetone) is topical because of growing excess of the former and the necessity in the latter. Glycerol is formed as a by-product in the production of biodiesel fuel. Dihydroxyacetone is used in the synthesis of fungicides and as a tanning agent in cosmetic industry. In particular, it is the main active ingredient in sun-protecting cosmetics. The presence of three hydroxyl groups of similar reactivities in the glycerol molecule complicates significantly its transformation to dihydroxyacetone under the action of common chemical oxidants due to their further facile oxidation. Potential-controlled electrooxidation of glycerol (its conversion does not exceed 25%) allows the synthesis of dihydroxyacetone in a yield comparable with that in the enzymatic synthesis.At higher conversion, the ketone undergo oxidation to result preferentially in hydroxypyruvic acid, $HOCH_2C(O)CO_2H$. No transformation of dihydroxyacetone to the acid occurs under the conditions of controlled potential (1.1 V).

3. Electrochemical transformations using other type mediators

N-Hydroxyphthalimide,[290–292] quinones,[293] ferrocenylethylamine,[294] aromatic sulfides and disulfides[295, 296] belong to miscellaneous organic mediators. Triphenylstannane manifested high efficiency as a mediator for electrooxidative initiation of radical-chain reactions (Table 14).[297] Low turnover number of these mediators, usually not exceeding 10, is a reason for their substantially lower catalytic efficiency as compared to that of triarylamines and *N*-oxyl radicals. For this reason, we consider only the most spectacular examples of the processes involving these mediators. Indirect electrooxidation is usually conducted in a non-aqueous medium due to the interaction of oxidised forms of organic mediators with water and their limited solubility in aqueous media.

Among reactions mediated by heterocyclic quinones (Q), electrooxidation of the reduced form of nicotinamide dinucleotide (NADH) is noteworthy. This way of regeneration of NAD^+ was the background for the design of the electroenzymatic method for alcohol oxidation (Scheme 23).[293, 294]

Scheme 23



The addition of 2,2,2-trifluoroethanol to the solvent that was used in electrochemical oxidation of secondary alcohols to ketones with thioanisole as a mediator resulted in an unusual effect (Table 14, entries 6, 7).[295]

Table 14. Electrochemical transformations involving *N*-hydroxyphthalimide (HPI), sulfides and triphenylstannane as mediators.

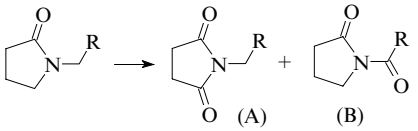
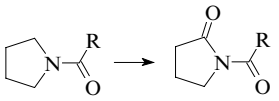
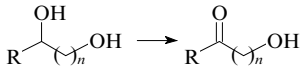
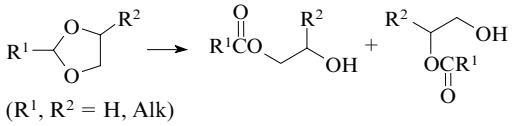
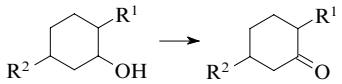
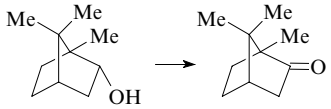
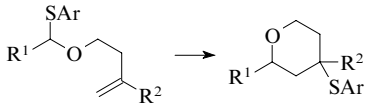
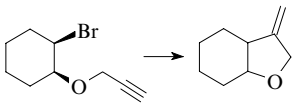
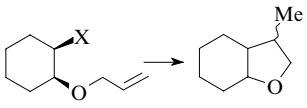
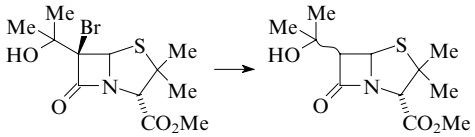
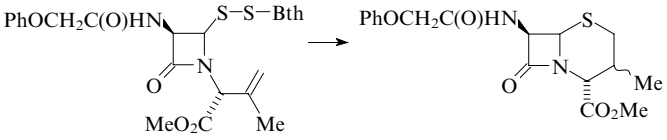
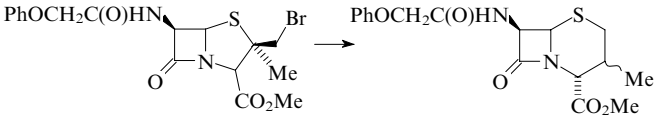
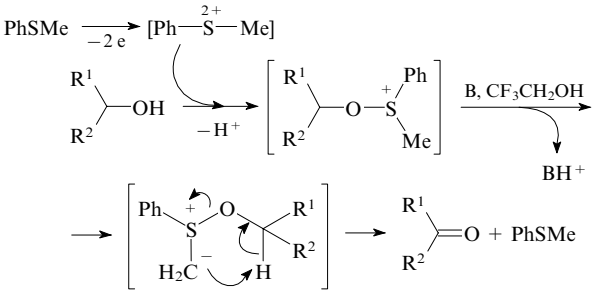
Reaction	Entry	Yield (%)	Mediator	Conditions		Ref.
				cell	electrolyte	
 (R = H, Me, Ph)	1	47–81 (A) 11–34 (B)	HPI	DC	MeCN, Py [a]	290
 (R = Me, Ph)	2	79–80	HPI	DC	MeCN, Py [a]	290
 (R = Me, *n* = 2;	3	90	HPI	UC	MeCN, Py	291
R = Ph, *n* = 1)	4	51	HPI	UC	MeCN, Py	291
 (R^1, R^2 = H, Alk)	5	–	HPI	UC	MeCN, Py	291
 (R^1, R^2 = H, Alk)	6	79–80	PhSMe	UC	MeCN, CF_3CH_2OH	295
	7	85	PhSMe	UC	MeCN, CF_3CH_2OH	295
 [R^1 = H, n-C_7H_{15}, cyclo-C_6H_{11}, Ph, Bn, $MeO(CH_2)_2$; R^2 = H, Me]	8	51–73	$(4\text{-}FC_6H_5)_2S_2$	DC	CH_2Cl_2, $Bu^n_4NB(C_6F_5)_4$	296
	9	65	Ph_3SnH	UC	THF	297
 (X = Br, I)	10	63–65	Ph_3SnH	DC	THF	297
	11	98	Ph_3SnH	DC	THF	297

Table 14 (continued).

Reaction	Entry	Yield (%)	Mediator	Conditions		Ref.
				cell	electrolyte	
 (Bth is benzothiazol-2-yl)	12	80	Ph_3SnH	DC	THF	297
	13	80	Ph_3SnH	DC	THF	297

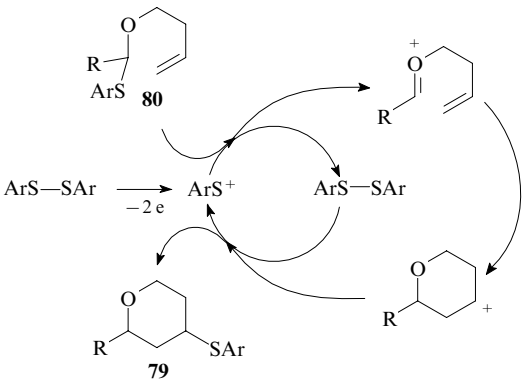
[a] In the presence of oxygen.



The presence of the equimolar amount of thioanisole increased substantially alcohol conversion and yields of the target ketones. For example, the conversion of octan-2-ol increased from 28% to 91%, while the yield of octan-2-one increased from 10% to 86%. In the absence of thioanisole and 2,2,2-trifluoroethanol, only 15% alcohol conversion and 3% ketone yield were achieved.

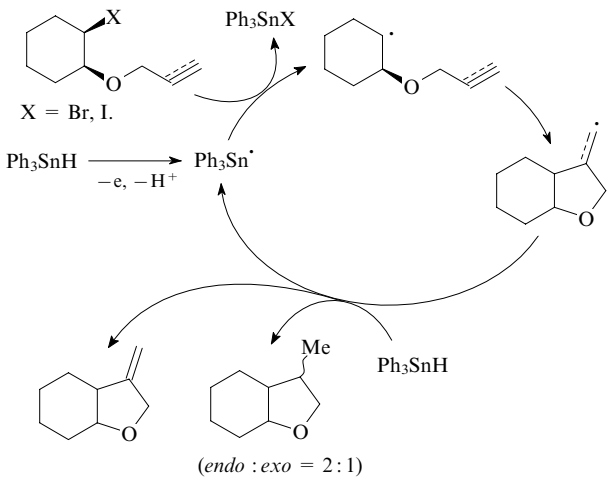
4-Arylthiotetrahydropyrans **79** were obtained by electrochemical generation of arylthio cations from diaryl disulfides followed by the reactions of ArS^+ with *O*-alkenyl-*S*-arylhemithioacetals and ArSSAr (Table 14, entry 8).[296] On the basis of this reaction, a novel concept of cationic chain cyclisation of *O*-homoallyl-*S*-arylhemithioacetals **80** was suggested and developed, this being alternative to the free-radical cyclisation of organic compounds (Scheme 24).

Scheme 24



Among the most important processes catalysed by tin compounds, cyclisation of 2-propargyl(allyl) halocyclohexyl ethers to 3-methylidene- or 3-methyl-substituted octahydrobenzofurans (Scheme 25; Table 14, entries 9, 10), as well as conversion of β-lactam derivatives are noteworthy (Table 14, entries 11–13).[297]

Scheme 25



VII. Conclusion

This review reflects the state of the art in organic electrosynthesis based on indirect anodic and cathodic oxidation of organic compounds. Impetuous growth of the number of publications devoted to the development of synthetic methods based on these processes observed in the last decades demostrates great interest in this technique. The main advantages include the increase in selectivity of substrate conversion to the target products, a decrease in energy consumption due to acceleration of electrode reactions and, the most important, a decrease in negative environmental effect due to a substantial decrease in amounts of side products and wastes. These advantages create the prerequisites for the application of organic electrosynthesis on industrial scale. Since electric current is an accessible and cheap oxidant, further progress in the development of novel methods of organic electrosynthesis, in the design of more advanced and promising electrochemical versions of known chemical reactions, as well as the discovery of processes having no analogues in classical organic chemistry can be expected in the nearest future.

References

1. S Torii *Electroorganic Synthesis. Methods and Applications (Ser. Monographs in Modern Chemistry)* (Tokyo, Weinheim: Wiley-VCH, Kodansha, 1985) Vol. 15
2. K Uoshida *Elektrooxidation in Organic Chemistry* (New York: Wiley, 1984)
3. D Pletcher *Industrial Electrochemistry* (London: Chapman and Hall, 1990)
4. S Torii, T Inokuchi *Yuki Gosei Kagaku Kyokaishi (J. Synth. Org. Chem. (Japan))* **43** 533 (1985); *Chem. Abstr.* **103** 61299 (1985)
5. T Shono *Tetrahedron* **40** 811 (1984)
6. E Steckhan *Top. Curr. Chem.* **142** 1 (1987)
7. *Recent Advances in Electroorganic Synthesis* (Ed. S Torii) (Tokyo, Amsterdam, New York: Kodansha, Elsevier, 1987)
8. *Organic Electrochemistry* (Eds M M Baizer, H Lund) (New York: Marcel Dekker, 1983)
9. *Organic Electrochemistry* (Eds H Lund, O Hammerich) (New York: Marcel Dekker, 2001)
10. Yu G Budnikova, G K Budnikov *Zh. Obshch. Khim.* **65** 1517 (1995) [a]
11. Yu N Ogibin, G I Nikishin *Usp. Khim.* **70** 619 (2001) [*Russ. Chem. Rev.* **70** 543 (2001)]
12. T V Magdesieva, K P Butin *Usp. Khim.* **71** 255 (2002) [*Russ. Chem. Rev.* **71** 223 (2002)]
13. G Kreysa, H Medin *J. Appl. Electrochem.* **16** 757 (1986)
14. R P Kreh, R M Spotnitz, J T Lundquist *Tetrahedron Lett.* **28** 1067 (1987)
15. R P Kreh, R M Spotnitz, J T Lundquist *J. Org. Chem.* **54** 1526 (1989)
16. D Pletcher, E M Valdes *Electrochim. Acta* **33** 499 (1988)
17. D Pletcher, E M Valdes *Electrochim. Acta* **33** 509 (1988)
18. H Wendt, S Bitterlich, in *Dechema Monographien (Organische Electrochemie – Angewandte Chemie)* Bd. 125 (Weinheim: Wiley-VCH ,1992) S. 613
19. M Morita, T Masatani, Y Matsuda *Bull. Chem. Soc. Jpn.* **66** 2747 (1993)
20. M Morita, S Kitamura, M Ishikawa, Y Matsuda *Electrochemistry* **62** 1206 (1994)
21. J J Lozar, A J Savall *Ind. Eng. Chem. Res.* **34** 3149 (1995)
22. Y Zeng *Hunan Shifan Daxue Ziran Kexue Xuebao* **16** 338 (1993); *Chem. Abstr.* **120** 333591 (1994)
23. Z Ding *Huaxue Shiji* **18** 210 (1996); *Chem. Abstr.* **126** 81198 (1997)
24. T Tzedakis, A J Sevall *J. Appl. Electrochem.* **27** 589 (1997)
25. W-L Deng, H-Z Liu, Y-T Yang, G-X Wang *Jingxi Huagong* **16** 29 (1999); *Chem. Abstr.* **131** 249477 (1999)
26. G Boulanger, D Ducharme, M Petitclerc, A Velin *Electrochemistry* **62** 1217 (1994)
27. K Jayaraman,V Devadoss, A Kulandai, S Thamizharasi, S Krishnamoorthy, R K Srinivasan, S Chidambaram *Bull. Electrochem.* **15** 300 (1999)
28. Y-m Zhao, G-j Liu, T-l Luo, Z-x Li *Jingxi Huagong* **17** 217 (2000); *Chem. Abstr.* **133** 323267 (2000)
29. T Vijayabarathi, D Velayutham, M Noel *Bull. Electrochem.* **18** 49 (2002)
30. R-S Hu, H-K Zhang, D-P Gu *Jingxi Huagong* **20** 169 (2003); *Chem. Abstr.* **140** 6367 (2004)
31. R-S Hu, Y-Y Gu, D-P Zhu, X Liu *Jingxi Huagong* **20** 239 (2003); *Chem. Abstr.* **140** 113187 (2004)
32. R-S Hu, X Liu, H-K Zhang, D-P Gu *Hebei Shifan Daxue Xuebao, Ziran Kexueban* **27** 602 (2003); *Chem. Abstr.* **141** 71320 (2004)
33. D-P Gu, R-S Hu, X Liu, Y-J Zhang *Jingxi Huagong* **21** 53 (2004); *Chem. Abstr.* **141** 351700 (2004)
34. S-J Liu, R-S Hu *Hebei Keji Daxue Xuebao* **26** 28 (2005); *Chem. Abstr.* **144** 441387 (2006)
35. H Wendt, H Schneider *J. Appl. Electrochem.* **16** 134 (1986)
36. H Wendt, H Schneider, in *Recent Advances in Electroorganic Synthesis* (Ed. S Torii) (Tokyo, Amsterdam, New York: Kodansha, Elsevier, 1987) p. 453
37. J-J Jow, A-C Lee, T-C Chou *J. Appl. Electrochem.* **17** 753 (1987)
38. C Comninellis *Chimia* **40** 413 (1986)
39. C Comninellis, E Plattner *J. Appl. Electrochem.* **17** 1315 (1987)
40. P Vaudano *Chimia* **46** 103 (1992)
41. P Vaudano, E Plattner, C Comninellis *Chimia* **49** 12 (1995)
42. W Wang, W Liu, K Ding, D Gu *Xiandai Huagong* **16** (6) 33 (1996); *Chem. Abstr.* **126** 157241 (1997)
43. Z Wang, Y Qiu, X Yan, Q Hua, G Chen, Z Wang *Dianhuaxue* **2** (1) 96 (1996); *Chem. Abstr.* **126** 178112 (1997)
44. Q Wang, C Zhao, Z Zhu *Fujian Shifan Daxue Xuebao, Ziran Kexueban* **13** (3) 41 (1997); *Chem. Abstr.* **128** 294568 (1998)
45. R Wang, H Zhang, X Zhang, D Gu *Hebei Shifan Daxue Xuebao, Ziran Kexueban* **22** 82 (1998); *Chem. Abstr.* **129** 33737 (1998)
46. D Gu, H Zhang, R Wang, W Liu, X Fan, W Zhang *Jingxi Huagong* **15** *(Zengkan)* 265 (1998); *Chem. Abstr.* **130** 116463 (1999)
47. H-K Zhang, Z-B Jia, D-J Jiang, D-P Gu *Hebei Shifan Daxue Xuebao, Ziran Kexueban* **23** 232 (1999); *Chem. Abstr.* **131** 108235 (1999)
48. Z Sun, X Hu, W Hu, D Zhou *Huagong Huanbao* **19** 103 (1999); *Chem. Abstr.* **131** 18814 (1999)
49. H Tan *Huagong Shikan* **13** (3) 9 (1999); *Chem. Abstr.* **131** 243029 (1999)
50. Z-x Li, G-j Liu, T-l Luo, Y-m Zhao, J-z Chen *Zhengzhou Gongye Daxue Xuebao* **20** (4) 74 (1999); *Chem. Abstr.* **133** 60325 (2000)
51. A S Vaze, S B Sawant, V G Pangarkar *J. Appl. Electrochem.* **29** 7 (1999)
52. W-q Lu, Z Cai, G-d Li, H-s Deng, B-r Cheng *Jingxi Huagong* **17** (*Zengkan*) 31 (2000); *Chem. Abstr.* **134** 282387 (2001)
53. Y-x Tao, L-h Zhou, J-n Yang *Gaoxiao Huaxue Gongcheng Xuebao* **14** 597 (2000); *Chem. Abstr.* **134** 312782 (2001)
54. Y-D Teng, S-Z Shang, T-Z Zhang, D-W He *Shenyang Huagong Xueyuan Xuebao* **14** 178 (2000); *Chem. Abstr.* **135** 228442 (2001)
55. Z Sun, X Hu, D Zhou *Gaojishu Tongxun* **11** (2) 98 (2001); *Chem. Abstr.* **135** 128726 (2001)
56. Z Zhang, X Zhu, X He, G-l Wu *Shanghai Daxue Xuebao, Ziran Kexueban* **7** 73 (2001); *Chem. Abstr.* **135** 244001 (2001)
57. Z Sun, X Hu, D Zhou *Huanjing Wuran Yu Fangzhi* **23** 246 (2001); *Chem. Abstr.* **137** 201118 (2002)
58. X-W Kan, H-S Tao, J Du, Y-Y Zhou, B Fang *Youji Huaxue* **23** 1282 (2003); *Chem. Abstr.* **140** 339007 (2004)
59. L-W Bi, X-Z Liu, Z-D Zhao, P-X Xu, F-X Chu *Linchan Huaxue Yu Gongye* **25** 5 (2005); *Chem. Abstr.* **143** 462084 (2005)
60. Y Guo, C Qian *Shanghai Keji Daxue Xuebao* **16** 107 (1993); *Chem. Abstr.* **120** 333658 (1994)
61. V Devadoss, M Noel, K Jayaraman, C A Basha *J. Appl. Electrochem.* **33** 319 (2003)
62. M A Azzem, E Steckhan *Heterocycles* **31** 1959 (1990)
63. G Falgayrac, A J Savall *J. Appl. Electrochem.* **29** 253 (1999)
64. F Lapicque, A Storck *Electrochim. Acta* **30** 1247 (1985)
65. B Yu, H Li *Lanzhou Daxue Xuebao, Ziran Kexueban* **37** 60 (2001); *Chem. Abstr.* **137** 5958 (2002)
66. R-S Hu, X Liu, D-P Gu, Y-J Zhang *Hebei Shifan Daxue Xuebao, Ziran Kexueban* **28** 275 (2004); *Chem. Abstr.* **142** 219013 (2005)
67. R M C Carrijo, J R Romero *Synth. Commun.* **24** 433 (1994)
68. S M de Oliveira, W F de Giovani, J R Romero, J Miller *J. Braz. Chem. Soc.* **3** 70 (1992)
69. Q Yi, X Liu, H Shi, H Song, H Zhao *Huaxue Tongbao* **65** w56/1 (2002); *Chem. Abstr.* **138** 106474 (2003)
70. Q-F Yi, Z-L Yu, M Fan, X-L Zhou, X-P Liu *Yingyong Huaxue* **22** 1127 (2005); *Chem. Abstr.* **145** 147801 (2006)
71. H-Z Ma, B Wang, Y-Q Liang *Catal. Commun.* **5** 617 (2004)
72. V Doiby, C Bonchoule, J Barranlt, M Blanchard *Bull. Soc. Chim. Belg.* **104** 431 (1995)
73. M I Dalrymple, J P Millington *J. Appl. Electrochem.* **16** 885 (1986)
74. E Manda, M Matsumoto, Y Ikeda, T Shimura, in *Recent Advances in Electroorganic Synthesis* (Ed. S Torii) (Tokyo, Amsterdam, New York: Kodansha, Elsevier, 1987) p. 145
75. S Ito, M Iwata, K Sasaki *Tetrahedron* **47** 841 (1991)
76. A C Lee, T-C Chou *J. Appl. Electrochem.* **23** 1259 (1993)

77. R M Spotnitz, R P Kreh, J T Lundquist, P J Press *J. Appl. Electrochem.* **20** 209 (1990)
78. T-C Chou, C-H Cheng *J. Appl. Electrochem.* **22** 743 (1992)
79. R Alkire, O Araujo *J. Electrochem. Soc.* **139** 737 (1992)
80. S Chocron, M Michman *J. Mol. Catal.* **66** 85 (1991)
81. S Chocron, M Michman *J. Mol. Catal.* **83** 251 (1993)
82. A B B Ferreira, H dos Santos Aragao, V F Ferreira *Quim. Nova* **19** 429 (1996)
83. S Harrison, A Theoret *J. New Mater. Electrochem. Syst.* **2** 1 (1999)
84. T Vijayabarathi, R K Srinivasan, M Noel *Bull. Electrochem.* **15** 293 (1999)
85. W Xu, Y Wang *Huaxue Fanying Gongcheng Yu Gongyi* **17** 185 (2001); *Chem. Abstr.* **135** 212575 (2001)
86. D-W Lou, Y-J Yang, N-D Tan, H-J Ji, B Zhu *Jilin Huagong Xueyuan Xuebao* **18** 31 (2001); *Chem. Abstr.* **136** 281097 (2002)
87. Y-E Zhao, H-B Zhang, C-C Sun *Jilin Daxue Xuebao, Lixueban* **40** 215 (2002); *Chem. Abstr.* **138** 106476 (2003)
88. Y Zhao, H Zhang, J Sun *Xiandai Huagong* **21** 31 (2001); *Chem. Abstr.* **136** 285728 (2002)
89. M-L Tsai, N-S Shui, T-C Chou *J. Chin. Inst. Chem. Eng.* **34** 239 (2003); *Chem. Abstr.* **139** 100764 (2003)
90. S Nad, R Breinbauer *Synthesis* 3654 (2005)
91. T Tzedakis, A J Savall, M J Clifton *J. Appl. Electrochem.* **19** 911 (1989)
92. P Pichaichanarong, R M Spotnitz, R P Kreh, S M Goldfarb, J T Lundquist *Chem. Eng. Commun.* **94** 119 (1990)
93. R Shundo, I Nishiguchi, Y Matsubara, M Toyoshima, T Hirashima *Chem. Lett.* **20** 185 (1991)
94. R Shundo, I Nishiguchi, Y Matsubara, T Hirashima *Tetrahedron* **47** 831 (1991)
95. J P Coleman, R C Hallcher, D E McMackins, T E Rogers, J H Wagenknecht *Tetrahedron* **47** 809 (1991)
96. R Shundo, I Nishiguchi, Y Matsubara, T Hirashima *Chem. Lett.* **19** 2285 (1990)
97. R Shundo, I Nishiguchi, Y Matsubara, T Hirashima *Chem. Lett.* **20** 235 (1991)
98. F Bergamini, A Citterio, N Gatti, M Nicolini, R Santi, R Sebastiano *J. Chem. Res. (S)* 364 (1993)
99. R Shundo, Y Matsubara, I Nishiguchi, T Hirashima *Chem. Express* **6** 547 (1991)
100. J-Y Nedelec, I Lachaise, K Nohair, J P Paugam, M Hakiki *Bull. Soc. Chim. Fr.* **132** 843 (1995)
101. R Warsinsky, E Steckhan *J. Chem. Soc., Perkin Trans. 1* 2027 (1994)
102. S Dubey, D Singh, R A Misra *Indian J. Chem., Sect. B* **38** 548 (1999)
103. L Zhou, Z-c Pan, S-h Deng, H-m Huang, Z-o Zeng *Jingxi Huagong* **17** *(Zengkan)* 52 (2000); *Chem. Abstr.* **134** 282392 (2001)
104. J-Y Nédélec, K Nohair *Synlett* 659 (1991)
105. K Nohair, I Lachaise, J-P Paugam, J-Y Nédélec *Tetrahedron Lett.* **33** 213 (1992)
106. Y C Liu, J R Romero *Tetrahedron Lett.* **36** 8757 (1995)
107. S Torii, T Inokuchi, T Sugiura *J. Org. Chem.* **51** 155 (1986)
108. S Rajendran, D C Trivedi *Synthesis* 153 (1995)
109. M-L Tsai, T-C Chou *J. Chin. Inst. Chem. Eng.* **27** 411 (1996)
110. S Torii, T Inokuchi, S Matsumoto, T Saeki, T Oki *Bull. Soc. Chem. Jpn.* **63** 852 (1990)
111. F Ogawa, S Matsumoto, K Kinoshita, Y Saeki, S Takagishi, in *Recent Advances in Electroorganic Synthesis* (Ed. S Torii) (Tokyo, Amsterdam, New York: Kodansha, Elsevier, 1987) p. 157
112. S Torii, T Inokuchi, S Matsumoto, T Saeki, T Oki *Bull. Soc. Chem. Jpn.* **62** 2108 (1989)
113. S Torii, A Yoshida *Chem. Lett.* **24** 369 (1995)
114. S-M Lin, T-C Wen *J. Appl. Electrochem.* **25** 73 (1995)
115. J L Campos, W F De Giovani, J R Romero *Synthesis* 597 (1990)
116. M Navarro, W F De Giovani, J R Romero *Tetrahedron* **47** 851 (1991)
117. H-J Schifer, U Feldhues, H Kaulen, H Ruholl In *Recent Advances in Electroorganic Synthesis* (Ed. S Torii) (Tokyo, Amsterdam, New York: Kodansha, Elsevier, 1987) p. 161
118. H-J Schifer *Top. Curr. Chem.* **142** 101 (1987)
119. A J Rethinam, C J Kennedy *J. Appl. Electrochem.* **34** 371 (2004)
120. H Ruholl, H-J Schifer *Synthesis* 54 (1988)
121. H Ruholl, H-J Schifer *Synthesis* 408 (1987)
122. R Schneider, H-J Schifer *Synthesis* 742 (1989)
123. Y-L Chen, T-C Chou *J. Appl. Electrochem.* **26** 543 (1996)
124. C-t Zhao, Z-s Zhu, Q-p Wang, J-b Weng *Jingxi Huagong* **17** *(Zengkan)* 61 (2000); *Chem. Abstr.* **134** 282394 (2001)
125. X-J Wan , M-Y Song, R Wu, D-B Chu *Yingyong Huaxue* **20** 578 (2003); *Chem. Abstr.* **139** 325002 (2003)
126. Z Liu, W-Q Xiao *Huaxue Yanjiu* **14** 51 (2003); *Chem. Abstr.* **139** 179787 (2003)
127. S Tsuboi, N Ishii, T Sakai, I Tari, M Utaka *Bull. Chem. Soc. Jpn.* **63** 1888 (1990)
128. S Zhang, Y Zang, G Zhang, Z Li, G Wang *Huaxue Shiji* **20** 252 (1998); *Chem. Abstr.* **129** 282571 (1998)
129. C Zhao, Z Zhu *Dianhuaxue* **5** 310 (1999); *Chem. Abstr.* **131** 315179 (1999)
130. Z Liu, Y-M Li *Hedieng Huaxue* **10** 140 (2002); *Chem. Abstr.* **137** 191946 (2002)
131. B Yu, H Li, Z-Y Ding, Q Li, G-L Wang, G-L Li, K Cai *Youji Huaxue* **15** 429 (1995); *Chem. Abstr.* **123** 269234 (1995)
132. P A Garcia Ruiz, A Zapata, F V Barba, J R G Ochoa *J. Appl. Electrochem.* **23** 851 (1993)
133. C Amatore, C Cammoun, A Jutand *Synlett* 2173 (2007)
134. S Cosnier, A Deronzier, J-F Roland *J. Mol. Catal.* **71** 303 (1992)
135. W F De Giovani, A Deronzier *J. Electroanal. Chem.* **337** 285 (1992)
136. F Geneste, C Moinet *New J. Chem.* **28** 722 (2004)
137. F Geneste, C Moinet *J. Electroanal. Chem.* **594** 105 (2006)
138. C Amatore, C Cammoun, A Jutand *Adv. Synth. Catal.* **349** 292 (2007)
139. J Tsuji, M Minato *Tetrahedron Lett.* **28** 3683 (1987)
140. J-E Bäckvall *Pure Appl. Chem.* **64** 429 (1992)
141. D D M Wayner, F W Hartstock *J. Mol. Catal.* **48** 15 (1988)
142. F W Hartstock, L B McMahon, I P Tell *Tetrahedron Lett.* **34** 8067 (1993)
143. I Chiarotto, I Carelli *Synth. Commun.* **32** 881 (2002)
144. D C Miller, D D M Wayner *Can. J. Chem.* **70** 2485 (1992)
145. F W Hartstock, D G Herrington, L B McMahon *Tetrahedron Lett.* **35** 8761 (1994)
146. T Inokuchi, L Ping, F Hamaue, M Izawa, S Torii *Chem. Lett.* **23** 121 (1994)
147. F W Hartstock, D D M Wayner *Tetrahedron Lett.* **35** 8137 (1994)
148. J M Madurro, G Chiericato Jr, W F De Giovani, J R Romero *Tetrahedron Lett.* **29** 765 (1988)
149. E Steckhan, C Kandzia *Synlett* 139 (1992)
150. M M T Khan, A P Rao, S H Mehta *J. Mol. Catal.* **73** 263 (1993)
151. U-S Biumer, H-J Schifer *Electrochim. Acta* **48** 489 (2003)
152. U-S Biumer, H-J Schifer *J. Appl. Electrochem.* **35** 1283 (2005)
153. J M van der Eijk, T J Peters, N de Wit, H A Colijn *Catal. Today* **3** 259 (1988)
154. C Kandzia, E Steckhan *Tetrahedron Lett.* **35** 3695 (1994)
155. A R Amundsen, E N Balko *J. Appl. Electrochem.* **22** 810 (1992)
156. S Torii, P Liu, H Tanaka *Chem. Lett.* **24** 319 (1995)
157. S Torii, P Liu, N Bhuvaneswari, C Amatore, A Jutand *J. Org. Chem.* **61** 3055 (1996)
158. H Tanaka, R Kikuchi, M Baba, S Torii *Bull. Chem. Soc. Jpn.* **68** 2989 (1995)
159. Y-L Liu, L Zhang, B Zhang, D-S Mei, Q-L Zhong, J-Y Liu, Y-H Wang *Jingxi Huagong* **21** 684 (2004); *Chem. Abstr.* **142** 261323 (2005)
160. K-x Wang, G-x Wang *Jingxi Huagong* **17** *(Zengkan)* 67 (2000); *Chem. Abstr.* **134** 282395 (2001)
161. X Liu, R-Z Wang, D-P Gu, X-C Zhang, Y-J Zhang, R-S Hu *Hebei Shifan Daxue Xuebao, Ziran Kexueban* **28** 596 (2004); *Chem. Abstr.* **143** 367152 (2005)

162. A Yasuhara, A Kasano, T Sakamoto *J. Org. Chem.* **64** 4211 (1999)
163. T Takiguchi, T Nonaka *Chem. Lett.* **16** 1217 (1987)
164. M Tokuda, N Mimura, T Karasawa, H Fujita, H Suginome *Tetrahedron Lett.* **34** 7607 (1993)
165. D S Smith, J Winnick, Y Ding, L A Bottomley *Electrochim. Acta* **43** 335 (1998)
166. O Niyamura, M Cox, T Wirth *Synlett* 251 (2006)
167. D H Bremner, A E Burgess, F-B Li *Green Chem.* **3** 126 (2001)
168. T Matsuki, N X Hu, Y Aso, T Otsubo, F Ogura *Bull. Chem. Soc. Jpn.* **61** 2117 (1988)
169. W Li, T Nonaka *Jingxi Huagong* **15** *(Zengkan)* 280 (1998); *Chem. Abstr.* **130** 116466 (1999)
170. A P Tomilov, M Ya Fioshin, V A Smirnov *Elektrokhimicheskii Sintez Organicheskikh Veshchestv* (Electrochemical Synthesis of Organic Substances) (Leningrad: Khimiya, 1976)
171. *Novel Trends in Electroorganic Synthesis* (Ed. S Torii) (Berlin: Springer, 1998)
172. M N Elinson, S K Fedukovich, T L Lizunova, G I Nikishin *Elektrokhimiya* **32** 42 (1996) [b]
173. M N Elinson, S K Feducovich, A S Dorofeev, A N Vereshchagin, G I Nikishin *Tetrahedron* **56** 9999 (2000)
174. A S Dorofeev, Candidate Thesis in Chemical Sciences, Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, 2007
175. M N Elinson, S K Fedukovich, A S Dorofeev, A N Vereshchagin, G I Nikishin *Izv. Akad. Nauk, Ser. Khim.* 216 (2003) [c]
176. F Barba, M N Elinson, J Escudero, M Guirado, S K Feducovich *Electrochim. Acta* **43** 973 (1998)
177. M N Elinson, S K Fedukovich, T A Zaimovskaya, A S Dorofeev, A N Vereshchagin, G I Nikishin *Izv. Akad. Nauk, Ser. Khim.* 946 (2003) [c]
178. F Barba, M N Elinson, J Escudero, S K Feducovich *Tetrahedron Lett.* **37** 5759 (1996)
179. F Barba, M N Elinson, J Escudero, S K Feducovich *Tetrahedron* **53** 4427 (1997)
180. M N Elinson, S K Feducovich, D E Dmitriev, A S Dorofeev, A N Vereshchagin, G I Nikishin *Tetrahedron Lett.* **42** 5557 (2001)
181. M N Elinson, S K Fedukovich, D E Dmitriev, A S Dorofeev, A N Vereshchagin, G I Nikishin *Izv. Akad. Nauk, Ser. Khim.* 1365 (2002) [c]
182. M N Elinson, A S Dorofeev, S K Feducovich, R F Nasybullin, E F Litvin, M V Kopyshev, G I Nikishin *Tetrahedron* **62** 8021 (2006)
183. M Okimoto, Y Takahashi, T Kakuchi *Bull. Chem. Soc. Jpn.* **76** 207 (2003)
184. M Okimoto, T Chiba *J. Org. Chem.* **58** 6194 (1993)
185. M Okimoto, Y Nagata, S Sueda, Y Takahashi *Synth. Commun.* **33** 3771 (2003)
186. T Chiba, H Sakagami, M Murata, M Okimoto *J. Org. Chem.* **60** 6764 (1995)
187. T Chiba, I Saitoh, M Okimoto, T Tanase, S Yano *J. Org. Chem.* **64** 2516 (1999)
188. M Okimoto, Y Takahashi *Bull. Chem. Soc. Jpn.* **75** 2059 (2002)
189. M Okimoto, Y Nagata, Y Takahashi *Bull. Chem. Soc. Jpn.* **76** 1447 (2003)
190. M Okimoto, K Numata, K Tomozawa, T Shigemoto, M Hoshi, Y Takahashi *Aust. J. Chem.* **58** 560 (2005)
191. M Okimoto, K Numata, Y Takahashi *Pol. J. Chem.* **79** 1477 (2005)
192. G I Nikishin, M N Elinson, S K Fedukovich *Izv. Akad. Nauk SSSR, Ser. Khim.* 2154 (1984) [c]
193. M N Elinson, S K Fedukovich, G I Nikishin *Izv. Akad. Nauk SSSR, Ser. Khim.* 96 (1988) [c]
194. M N Elinson, S K Fedukovich, G I Nikishin *Izv. Akad. Nauk SSSR, Ser. Khim.* 2534 (1988) [c]
195. M N Elinson, S K Fedukovich, G I Nikishin *Izv. Akad. Nauk SSSR, Ser. Khim.* 352 (1989) [c]
196. S K Fedukovich, M N Elinson, G I Nikishin *Izv. Akad. Nauk, Ser. Khim.* 620 (1997) [c]
197. M N Elinson, T L Lizunova, G I Nikishin *Izv. Akad. Nauk SSSR, Ser. Khim.* 2536 (1991) [c]
198. M N Elinson, T L Lizunova, G I Nikishin *Izv. Akad. Nauk, Ser. Khim.* 154 (1992) [c]
199. M N Elinson, A S Dorofeev, S K Feducovich, P A Belyakov, G I Nikishin *Eur. J. Org. Chem.* 3023 (2007)
200. G I Nikishin, M N Elinson, S K Feducovich *Tetrahedron Lett.* **32** 799 (1991)
201. M N Elinson, S K Fedukovich, T L Lizunova, G I Nikishin *Elektrokhimiya* **28** 575 (1992) [b]
202. G I Nikishin, M N Elinson, S K Fedukovich *Izv. Akad. Nauk SSSR, Ser. Khim.* 1919 (1986) [c]
203. M N Elinson, S K Fedukovich, G I Nikishin *Izv. Akad. Nauk SSSR, Ser. Khim.* 288 (1987) [c]
204. M N Elinson, S K Fedukovich, S V Lindeman, M S Aleksanyan, Yu T Struchkov, G I Nikishin *Izv. Akad. Nauk SSSR, Ser. Khim.* 1603 (1989) [c]
205. M N Elinson, S K Fedukovich, S V Lindeman, M S Aleksanyan, Yu T Struchkov, G I Nikishin *Izv. Akad. Nauk SSSR, Ser. Khim.* 2783 (1990) [c]
206. M N Elinson, S K Fedukovich, B I Ugrak, G I Nikishin *Izv. Akad. Nauk, Ser. Khim.* 2332 (1992) [c]
207. G I Nikishin, M N Elinson, S K Feducovich, B I Ugrak, Yu T Struchkov, S V Lindeman *Tetrahedron Lett.* **33** 3223 (1992)
208. M N Elinson, S K Feducovich, A A Zakharenkov, B I Ugrak, G I Nikishin, S V Lindeman, Yu T Struchkov *Tetrahedron* **51** 5035 (1995)
209. M Okimoto, Y Takahashi *Synthesis* 2215 (2002)
210. M N Elinson, T L Lizunova, M O Dekaprilevich, Yu T Struchkov, G I Nikishin *Mendeleev Commun.* 192 (1993)
211. G I Nikishin, M N Elinson, T L Lizunova, B I Ugrak *Tetrahedron Lett.* **32** 2655 (1991)
212. M N Elinson, T L Lizunova, B I Ugrak, G I Nikishin *Mendeleev Commun.* 191 (1993)
213. M N Elinson, T L Lizunova, B I Ugrak, M O Decaprilevich, G I Nikishin, Yu T Struchkov *Tetrahedron Lett.* **34** 5795 (1993)
214. M N Elinson, S K Feducovich, T L Lizunova, G I Nikishin *Tetrahedron* **56** 3069 (2000)
215. M N Elinson, S K Fedukovich, T A Zaimovskaya, A N Vereshchagin, G I Nikishin *Izv. Akad. Nauk, Ser. Khim.* 663 (2005) [c]
216. M N Elinson, S K Feducovich, S G Bushuev, A A Zakharenkov, D V Pashchenko, G I Nikishin *Mendeleev Commun.* 15 (1998)
217. M N Elinson, S K Fedukovich, S G Bushuev, D V Pashchenko, G I Nikishin *Izv. Akad. Nauk, Ser. Khim.* 1165 (1998) [c]
218. M N Elinson, S K Feducovich, Z A Starikova, O S Olessova, A N Vereshchagin, G I Nikishin *Tetrahedron Lett.* **41** 4937 (2000)
219. M N Elinson, S K Fedukovich, A N Vereshchagin, A S Dorofeev, D E Dmitriev, G I Nikishin *Izv. Akad. Nauk, Ser. Khim.* 2117 (2003) [c]
220. M N Elinson, S K Fedukovich, T A Zaimovskaya, A N Vereshchagin, S V Gorbunov, G I Nikishin *Izv. Akad. Nauk, Ser. Khim.* 1547 (2005) [c]
221. M N Elinson, S K Feducovich, Z A Starikova, A N Vereshchagin, G I Nikishin *Tetrahedron* **60** 11743 (2004)
222. M N Elinson, S K Feducovich, Z A Starikova, A N Vereshchagin, S V Gorbunov, G I Nikishin *Tetrahedron Lett.* **46** 6389 (2005)
223. M N Elinson, S K Feducovich, Z A Starikova, A N Vereshchagin, P A Belyakov, G I Nikishin *Tetrahedron* **62** 3989 (2006)
224. M N Elinson, S K Feducovich, A N Vereshchagin, S V Gorbunov, P A Belyakov, G I Nikishin *Tetrahedron Lett.* **47** 9129 (2006)
225. M N Elinson, T L Lizunova, B I Ugrak, S V Lindeman, M O Decaprilevich, K M Turdybekov, Yu T Struchkov, G I Nikishin *Mendeleev Commun.* 157 (1993)

226. M N Elinson, S K Fedukovich, T A Zaimovskaya, A N Vereshchagin, G I Nikishin *Izv. Akad. Nauk, Ser. Khim.* 2122 (2003) [c]
227. T Yoshiyama, T Nonaka, M M Baizer, T-C Chou *Bull. Soc. Chem. Jpn.* **58** 201 (1985)
228. T Yoshiyama, T-C Chou, T Fuchigami, T Nonaka, M M Baizer *Electrochemistry* **53** 989 (1985)
229. F N Khan, C N Pillai, K M Bharanidharan, P J Ramabai, M Yesuraman, S Ananthan *Bull. Electrochem.* **15** 298 (1999)
230. F N Khan, R Jayakumar, C N Pillai *J. Mol. Catal. A: Chem.* **195** 139 (2003)
231. T Shono, S Kashimura, T Soejima, K Ohta, Y Yamaguchi, in *Recent Advances in Electroorganic Synthesis* (Ed. S Torii) (Tokyo, Amsterdam, New York: Kodansha, Elsevier, 1987) p. 41
232. S Kashimura, M Ishifune, H Maekawa, Y Yamaguchi, Y Murai, S Kitajima, T Shono *Denki Kagaku Oyobi Kogyo Butsuri Kagaku* **65** 479 (1997); *Chem. Abstr.* **127** 81071 (1997)
233. T Shono, M Chuankammerdkarn, H Maekawa, M Ishifune, S Kashimura *Synthesis* 895 (1994)
234. T Shono, T Soejima, K Takigawa, Y Yamagachi, H Maekawa, S Kashimura *Tetrahedron Lett.* **35** 4161 (1994)
235. N V Chaenko, N I Pavlenko, V L Kornienko *Khim. Inter. Ustoich. Razv.* **10** 497 (2002) [d]
236. G V Kornienko, N V Chaenko, I S Vasil'eva, V L Kornienko *Elektrokhimiya* **40** 148 (2004) [b]
237. S Ai, Q Wang, H Li, L Jin *J. Electroanal. Chem.* **578** 223 (2005)
238. W Li, T Nonaka *Chem. Lett.* **26** 1271 (1997)
239. W Li, T Nonaka *Chem. Lett.* **26** 387 (1997)
240. R Tomat, A Rigo *J. Appl. Electrochem.* **16** 8 (1986)
241. D Pletcher *Acta Chem. Scand.* **53** 745 (1999)
242. V L Kornienko *Khim. Inter. Ustoich. Razv.* **10** 391 (2002) [d]
243. V L Kornienko, G A Kolyagin, Yu V Saltykova *Zh. Prikl. Khim.* **72** 353 (1999) [e]
244. V L Kornienko, G A Kolyagin, I S Vasil'eva *Khim. Inter. Ustoich. Razv.* **7** 681 (1999) [d]
245. N V Chaenko, V L Kornienko, N I Pavlenko *Khim. Inter. Ustoich. Razv.* **12** 233 (2004) [d]
246. S Dappelheld, E Steckhan, K-H G Brinkhaus, T Esch *Chem. Ber.* **124** 2557 (1991)
247. M Schulz, R Kluge, L Sivilai, B Kamm *Tetrahedron* **46** 2371 (1990)
248. K -H G Brinkhaus, E Steckhan, D Degner *Tetrahedron* **42** 553 (1986)
249. T Fuchigami, M Tetsu, T Tajima, T Ishii *Synlett* 1269 (2001)
250. Y Shen, K Suzuki, M Atobe, T Fuchigami *J. Electroanal. Chem.* **540** 189 (2003)
251. T Fuchigami, K Mitomo, H Ishii, A Konno *J. Electroanal. Chem.* **507** 30 (2001)
252. T Fuchigami, T Fujita *J. Org. Chem.* **59** 7190 (1994)
253. T Fujita, T Fuchigami *Tetrahedron Lett.* **37** 4725 (1996)
254. T Fuchigami, M Sano *J. Electroanal. Chem.* **414** 81 (1996)
255. X Wu, A P Davis, A J Fry *Org. Lett.* **9** 5633 (2007)
256. A Marra, J-M Mallet, C Amatore, P Sinay *Synlett* 572 (1990)
257. I Tabaković *Top. Curr. Chem.* **185** 87 (1997)
258. J Gunić, I Tabaković, Z Sanićanin *Electrochim. Acta* **35** 225 (1990)
259. Y Shen, H Hattori, K Ding, M Atobe, T Fuchigami *Electrochim. Acta* **51** 2819 (2006)
260. R Wend, E Steckhan *Electrochim. Acta* **42** 2027 (1997)
261. A Deronzier, D Limosin, J-C Moutet *Electrochim. Acta* **32** 1643 (1987)
262. K Schnatbaum, H-J Schäfer *Synthesis* 864 (1999)
263. D Liaigre, T Breton, E M Belgsir *Electrochem. Commun.* **7** 312 (2005)
264. E M Belgsir, H-J Schäfer *Electrochem. Commun.* **3** 32 (2001)
265. M Schämann, H-J Schäfer *Eur. J. Org. Chem.* 351 (2003)
266. Y Kashiwagi, H Ono, T Osa *Chem. Lett.* **22** 81 (1993)
267. Y Kashiwagi, H Ono, T Osa *Chem. Lett.* **22** 257 (1993)
268. T Osa, Y Kashiwagi, Y Yanagisawa, J M Bobbitt *J. Chem. Soc., Chem. Commum.* 2535 (1994)
269. T Inokuchi, S Matsumoto, T Nisiyama, S Torii *Synlett* 57 (1990)
270. T Inokuchi, S Matsumoto, S Torii *J. Org. Chem.* **56** 2416 (1991)
271. G D Gamalevich, G M Zhdankina, G V Krishtal', G I Nikishin, Yu N Ogibin, E P Serebryakov *Zh. Org. Khim.* **33** 525 (1997) [f]
272. T Inokuchi, S Matsumoto, M Fukushima, S Torii *Bull. Chem. Soc. Jpn.* **64** 796 (1991)
273. Yu N Ogibin, A Kh Khusid, G I Nikishin *Izv. Akad. Nauk, Ser. Khim.* 941 (1992) [c]
274. Yu N Ogibin, I S Levina, A V Kamernitsky, G I Nikishin *Mendeleev Commun.* 184 (1995)
275. T Osa, U Akiba, I Segawa, J M Bobbitt *Chem. Lett.* **17** 1423 (1988)
276. T Osa, Y Kashiwagi, K Mukai, A Ohsawa, J M Bobbitt *Chem. Lett.* **19** 75 (1990)
277. Y Kashiwagi, A Ohsawa, T Osa, Z Ma, J M Bobbitt *Chem. Lett.* **20** 581 (1991)
278. Y Kashiwagi, Y Yanagisawa, F Kurashima, J-i Anzai, T Osa, J M Bobbitt *Chem. Commun.* 2745 (1996)
279. Y Kashiwagi, F Kurashima, J-i Anzai, T Osa, J M Bobbitt *Tetrahedron Lett.* **40** 6469 (1999)
280. H Tanaka, J Kabota, S-j Itogawa, T Ido, M Kuroboshi, K Shimamura, T Uchida *Synlett* 951 (2003)
281. H Tanaka, Y Kawakami, K Goto, M Kuroboshi *Tetrahedron Lett.* **42** 445 (2001)
282. Y Yanagisawa, Y Kashiwagi, F Kurashima, J-i Anzai, T Osa, J M Bobbitt *Chem. Lett.* **25** 1043 (1996)
283. Y Kashiwagi, F Kurashima, S Chiba, J-i Anzai, T Osa, J M Bobbitt *Chem. Commun.* 114 (2003)
284. R Ciriminna, M Pagliaro *Adv. Synth. Catal.* **345** 383 (2003)
285. R Ciriminna, G Palmisano, C D Pina, M Rossi, M Pagliaro *Tetrahedron Lett.* **47** 6993 (2006)
286. T Inokuchi, S Matsumoto, S Torii *Denki Kagaku* **51** 910 (1993); *Chem. Abstr.* **120** 162903 (1994)
287. F Kurashima, Y Kashiwagi, C Kikuchi, J-i Anzai, T Osa *Heterocycles* **50** 79 (1999)
288. Y Kashiwagi, F Kurashima, J-i Anzai, T Osa *Heterocycles* **51** 1945 (1999)
289. Y Kashiwagi, K Uchiyama, F Kurashima, C Kikuchi, J-i Anzai *Chem. Pharm. Bull.* **47** 1051 (1999)
290. M Masai, S Hara, S Ozaki *Chem. Pharm. Bull.* **34** 975 (1986)
291. M Masai, in *Recent Advances in Electroorganic Synthesis* (Ed. S Torii) (Tokyo, Amsterdam, New York: Kodansha, Elsevier, 1987) p. 137
292. J Liang, J Li, B Zhou, S Qin *Huaxue Yanjiu Yu Yingyong* **16** 597 (2004); *Chem. Abstr.* **144** 390211 (2003)
293. S Itoh, H Fukushima, M Kamatsu, Y Ohshiro *Chem. Lett.* **21** 1583 (1992)
294. T Osa, Y Kashiwagi, Y Yanagisawa *Chem. Lett.* **23** 367 (1994)
295. Y Matsumura, M Yamada, N Kise, M Fujiwara *Tetrahedron* **51** 6411 (1995)
296. K Matsumoto, S Fujie, K Ueoka, S Suga, J-i Yoshida *Angew. Chem., Int. Ed.* **47** 2506 (2008)
297. H Tanaka, H Suga, H Ogawa, A K M Abdul Hai, S Torii, A Jutand, C Amatore *Tetrahedron Lett.* **33** 6495 (1992)

[a] — *Russ. J. Gen. Chem. (Engl. Transl.)*
[b] — *Russ. J. Electrochem. (Engl. Transl.)*
[c] — *Russ. Chem. Bull., Int. Ed. (Engl. Transl.)*
[d] — *Chem. Sust. Develop. (Engl. Transl.)*
[e] — *Russ. J. Appl. Chem. (Engl. Transl.)*
[f] — *Russ. J. Org. Chem. (Engl. Transl.)*