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Electrochemical reactions of alkenes induced by anodic oxidation and their applications in organic synthesis

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Abstract. The main achievements and trends in the use of anodic oxidation and electrochemical reactions of alkenes in organic synthesis are analysed, systematised and generalised. The large potential and advantages of electrochemical methods of synthesis of organic compounds are demonstrated. These methods allow transformation of alkenes into functional derivatives the preparation of which by conventional chemical methods is either difficult or impossible. Primary attention is paid to the influence of the structures of substrates and electrolysis conditions on the regio- and stereoselectivities of the reactions. The bibliography includes 305 references.

I. Introduction

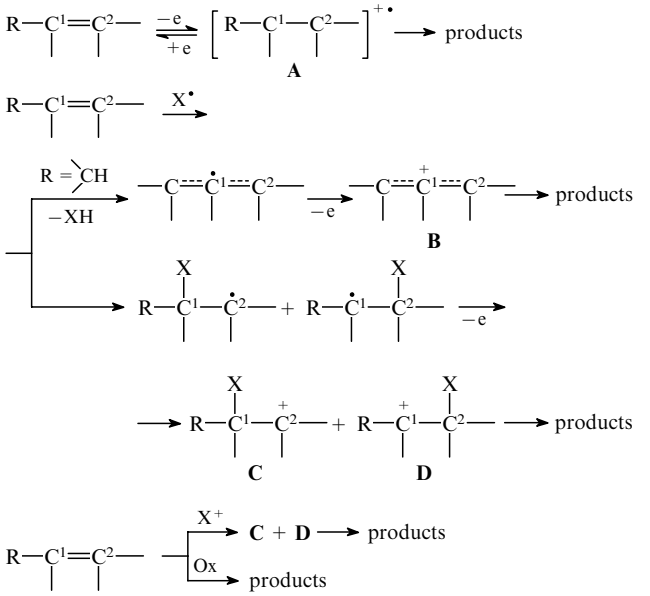
Anodic oxidation and electrochemical reactions of unsaturated organic compounds represent a vigorously developing line of research in organic electrochemistry. These reactions allow transformation of alkenes into functionally substituted compounds the synthesis of which by chemical methods is either impossible or difficult from the experimental standpoint. In many cases, electrochemical reactions are more advantageous from the environmental standpoint than chemical reactions.

This review describes systematically the published data on the reactions of alkenes taking place at the anode and in electrolyte solutions and on the use of these reactions in organic synthesis. More than 200 studies on electrooxidation of alkenes have now been published (most of them, during the last 15 years). There are several reviews [1–18] and monographs [19–23] containing data on the anodic processes involving unsaturated compounds. However, the information on electrooxidation of alkenes presented in these sources is not systematised in any way and does not reflect adequately the knowledge accumulated to date. The present review is meant to fill these gaps, to shed light upon the new trends in the development of alkene reactions induced by anodic oxidation, and to demonstrate the use of these reactions in organic synthesis taking electrooxidation of unsubstituted and functionally substituted alkenes and cycloalkenes, substituted dienes, and some other types of alkenes as examples. The review covers publications of the last two decades and also some earlier studies that have not been reflected adequately in the above-mentioned reviews and monographs.

An alkene can be directly involved in an electrochemical process upon transfer of an electron from its higher occupied molecular orbital at the anode (direct route). Alkenes can also participate in the electrochemical process *via* the reaction with electrogenerated organic or inorganic radicals ($X^{\bullet}$), ions (X^{+}), or oxidants (Ox), which can be formed from the corresponding precursors at potentials lower than the potential of alkene oxidation (indirect route).[24–26] The role of precursors can be played by the solvent, organic or inorganic anions and mediators (Scheme 1).

In accordance with the possibility of electrochemical transformations of alkenes into final products by both direct and indirect routes, the reactions considered in the review are classified into two groups.

Scheme 1



II. Reactions induced by direct anodic oxidation

The efficiency of direct anodic oxidation depends, most of all, on the rate of electron transfer from the alkenes adsorbed on the anode and is determined by their oxidation potentials. The oxidation potentials of the alkenes considered in this Section are listed in Table 1.[27–39]

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Table 1. Potentials of oxidation half-waves ($E_{1/2}$) for alkenes of various types.

Alkene	$E_{1/2}$ /V	Electrolyte	Solvent	Electrode	Ref.
Alkenes and cycloalkenes					
Alk-1-enes	2.7 – 2.8	Et_4NBF_4	MeCN	Pt	27 – 31
Alk-2-enes	2.2 – 2.3	Et_4NBF_4	MeCN	Pt	27 – 31
2-Methylbut-2-ene	1.65	Bu_4NClO_4	MeCN	Pt	32
2,3-Dimethylbut-2-ene	1.29	Bu_4NClO_4	MeCN	Pt	32
Cyclohexene	2.14	$LiClO_4$	MeCN	Pt	28, 32
1-Methylcyclohexene	1.70	$LiClO_4$		Pt	32
α-Pinene	1.3 – 1.4	$LiClO_4$	MeCN	Pt	30
Norbornene	2.02	$LiClO_4$	MeCN	Pt	30
Arylalkenes and arylcycloalkenes					
Styrene	1.45	$NaClO_4$	MeOH	C	33
	1.95 – 2.05	Et_4NBF_4	MeCN	Pt	33
2-Phenylpropene	1.37	$NaClO_4$	MeOH	C	33
	1.80 – 1.89	Et_4NBF_4	MeCN	Pt	27
1-Phenylpropene	1.50	$LiClO_4$	MeCN	Pt	27
1,1-Diphenylethylene	1.48 – 1.55	Bu_4NClO_4	MeCN	Pt	32, 35
1-Methoxyphenylethylene	0.90	$NaClO_4$	MeOH	C	34
4-Methylstyrene	1.38	Et_4NClO_4	MeCN	Pt	35
4-Methoxystyrene	1.15	Et_4NClO_4	MeCN	Pt	35
4-Chlorostyrene	1.76	Et_4NClO_4	MeCN	Pt	35
Allylbenzene	1.89	$LiClO_4$	MeCN	Pt	36
3-Methoxy-3-phenylprop-1-ene	1.95	$LiClO_4$	MeCN	Pt	36
1-Methoxy-3-phenylprop-1-ene	1.42	$LiClO_4$	MeCN	Pt	36
cis-Stilbene	1.38	$NaClO_4$	MeOH	C	27
trans-Stilbene	1.19	$NaClO_4$	MeOH	C	27
1-Phenylcyclohexene	1.36	$NaClO_4$	MeOH	C	32
Indene	1.25	$NaClO_4$	MeOH	C	28, 29
Acenaphthene	0.95	$NaClO_4$	MeCN	Pt	27
Acenaphthylene	1.32	Et_4NClO_4	MeCN	Pt	37
Enol ethers and esters					
1-Ethoxycycloalkenes	0.95 – 1.00	$NaClO_4$	MeOH	glass carbon	38
1-Methoxyhex-1-ene	1.04	$NaClO_4$	MeOH	glass carbon	38
1-Acetoxy-2-methylcyclopentene	1.18	$LiClO_4$	MeCN	Pt	39

Note. Hereinafter, the oxidation potentials are given in the unified scale *versus* a silver halide electrode at 25 °C; the potentials determined *versus* saturated calomel and standard hydrogen reference electrodes were decreased by 0.30 and 0.54 V, respectively.

The high oxidation potentials of alkenes with a terminal double bond hamper their direct anodic oxidation. The replacement of hydrogen atoms at double bonds by alkyl or other electron-donating groups decreases the oxidation potential and thus facilitates this process. To reach the anodic potentials at which alkenes undergo effective direct oxidation, tetrafluoroborates are used as supporting electrolytes and acetonitrile, 2,2,2-trifluoroethanol, trifluoroacetic acid or fluorosulfonic acid are used as solvents. Oxidation of activated alkenes, for example, styrenes and enol ethers (or esters), is normally carried out in methanol and ethanol, which are the best solvents for most of the electrochemical processes considered in this review. In undivided cells, these protic solvents suppress side cathodic reactions of alkenes due to easy discharge of protons. Owing to their versatile solvent capacity, they permit the use of high concentrations of the electrolyte and the organic substrate.

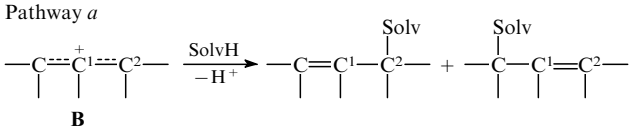
The transformation route of radical cations **A** (see Scheme 1) depends on their reactivity with respect to other compounds present in the reaction mixture. In most cases, radical cations behave as proton donors or electrophiles and react with nucleophiles or bases. They can also be oxidised or be involved in radical dimerisation, recombination, disproportionation and addition processes. The most typical reactions of the radical cations electrogenerated from alkenes are considered below (Sections II.1 – II.8).

1. Allylic substitution in alkenes

The allylic substitution in activated alkenes occurs *via* direct anodic oxidation, and allylic substitution in non-activated or weakly activated alkenes can occur *via* either direct or indirect anodic oxidation, or involve both types of reaction. For representing the full picture of allylic substitution, the direct and indirect routes of anodic oxidation are considered together in Section II. In both cases, cationic intermediates **B**, **C** and **D** are generated at initial stages (see Scheme 1); they enter into solvolysis (Scheme 2, pathway *a*) and deprotonation reactions (Scheme 2, pathways *b*, *c*).[30]

Scheme 2

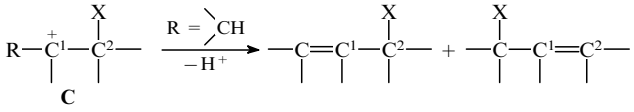
Pathway *a*



B

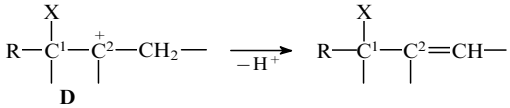
SolvH is protic solvent.

Pathway *b*



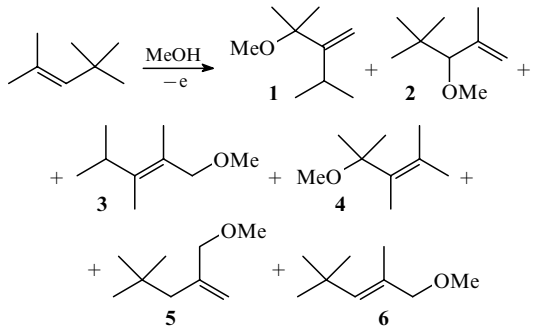
C

Pathway *c*

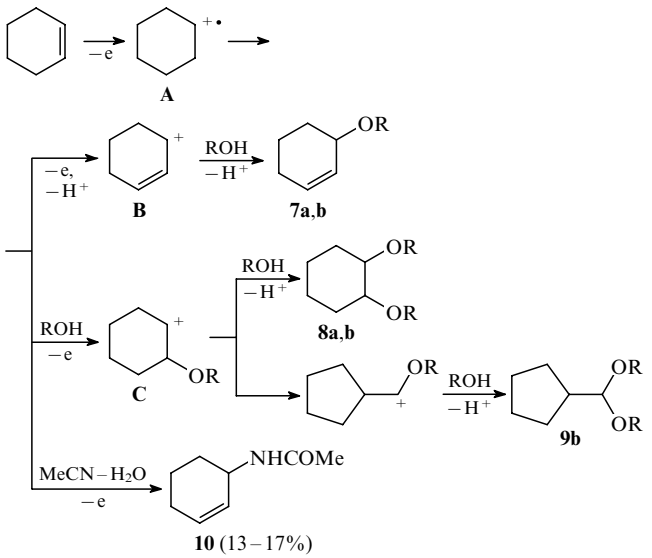


D

Allylic substitution in alkenes has been studied in relation to diisobutene,[40 – 42] cyclohexene,[30, 43 – 48] 1-, 3- and 4-methylcyclohexenes,[30] α- and β-pinenes,[30] allylbenzene,[36, 49] 4-allylanisole and some other allylarenes.[50] The efficiency and the direction of the direct anodic oxidation in undivided cells at a controlled anode potential or in the direct-current mode depends substantially on the nature of the anode material, supporting electrolyte and the solvent. This effect is attributed to different susceptibilities of electrolytes, alkenes and solvents for chemo- and electrosorption on the anode surface. Allylic substitution in non-activated alkenes — diisobutylene and cyclohexene — is most efficient in methanol with tetraalkylammonium toluene-*p*-sulfonate as the supporting electrolyte and with graphite or lead dioxide supported on graphite as the anode material. Diisobutylene is converted into a complex mixture of products mainly consisting of isomeric methoxyoctenes **1** – **6**.[41]

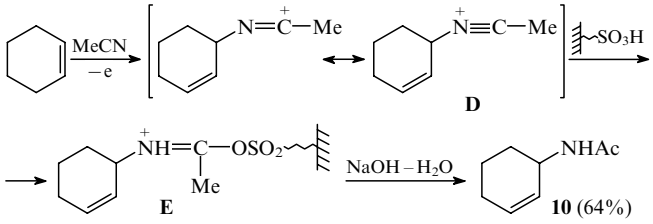


The electrolysis of cyclohexene in acetic acid gave 3-acetoxycyclohexene (**7a**) as the major product; that in methanol yielded 3-methoxycyclohexene (**7b**). In both cases, 1,2-disubstituted cyclohexanes **8a**,**b** are also formed. The composition of reaction products depends on the solvent nucleophilicity: when the electrolysis is carried out in acetic acid, radical cations **A** are converted predominantly into cations **B** and then into the product **7a**, whereas in more nucleophilic methanol, they mainly react with the solvent to give intermediates **C** and then the products **8b** and **9b**.[30] In wet acetonitrile, 3-acetamidocyclohexene (**10**) is formed.[30,43,45]



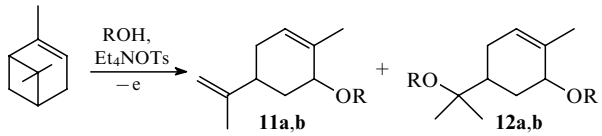
R	Yield (%)		
	7	**8**	**9**
Ac (**a**)	55	1.1	2.6
Me (**b**)	24	2.5	23

To increase the selectivity of electrochemical acetamidation of hydrocarbons, in particular, cyclohexene, the use of an ion exchange resin with sulfonate groups has been proposed.[48] In the presence of an ion exchange resin, the reactive nitrilium ions **D** formed in acetonitrile solutions are transformed into stable imidoyl sufonates **E** attached to the polymeric support. With this approach, the yield of the reaction products markedly increases and the isolation of products is substantially facilitated.



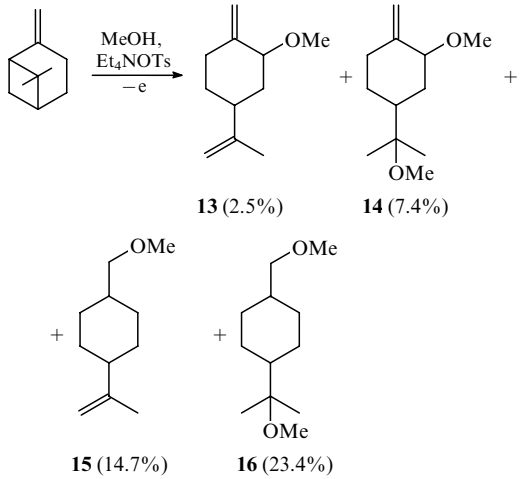
It is worth noting that acetoxylation of 1-, 3- and 4-methylcyclohexenes, oct-1-ene and oct-2-ene, gives the same products both in the electrochemical[30] and standard versions.[50–52] This is evidence in favour of participation of carbenium ions in electrochemical acetoxylation. However, the *cis*- to *trans*-isomer ratios obtained in the electrochemical and chemical acetoxylations are different; the electrochemical process yields mainly *cis*-isomers.

Electrochemical allylic acetoxylation and methoxylation of α-pinene, unlike those of methylcyclohexenes, give predominantly *trans*-isomers of substituted cyclohexenes **11a**,**b** and **12a**,**b**.[30]

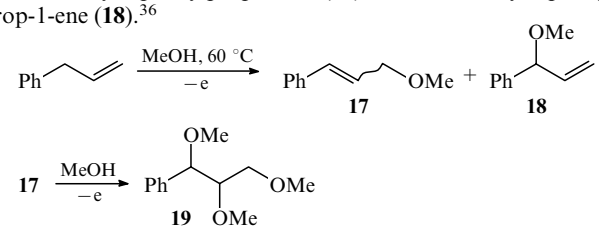


R	Yield (%) (*trans* : *cis* ratio)	
	11	**12**
Ac (**a**)	24 (2.2 : 1)	12 (2.9 : 1)
Me (**b**)	22 (6.2 : 1)	41 (2.6 : 1)

Under similar conditions, allylic methoxylation of β-pinene gives rise to a mixture of mono- and dimethoxy derivatives **13**–**16**.[30]



Electrooxidation of allylbenzene in methanol results initially in 3-methoxy-1-phenylprop-1-ene (**17**) and 3-methoxy-3-phenylprop-1-ene (**18**).[36]



Under conditions of electrolysis, compound **17** is converted almost entirely into 1,2,3-trimethoxypropylbenzene (**19**) because of its lower oxidation potential compared to those of **18** or allylbenzene (1.42, 1.95 and 1.89 V, respectively, see Table 1). The degree of conversion and the yields of electrolysis products depend on the supporting electrolyte used (Table 2).

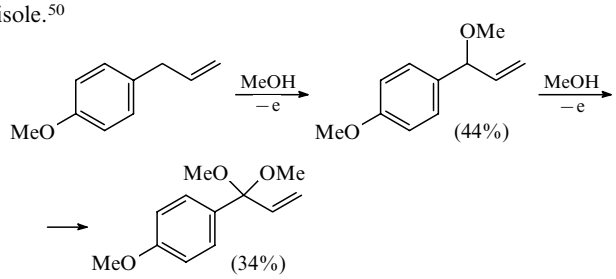
In the presence of acidic electrolytes (TsOH, H_2SO_4), 3-methoxy-3-phenylprop-1-ene (**18**) undergoes fast isomerisation into 3-methoxy-1-phenylprop-1-ene (**17**); as a consequence, the product of allylbenzene trimethoxylation, namely, the compound **19**, is produced predominantly. The major products formed in the presence of basic electrolytes are the allylic methoxylation products **17** and **18**. When neutral salts are used as electrolytes (Bu_4NBF, TsONa), the products of allylic methoxylation and trimethoxylation of allylbenzene are formed in comparable amounts.

Table 2. Effect of the supporting electrolyte on the degree of conversion and the yield of products of allylbenzene electrolysis.[36]

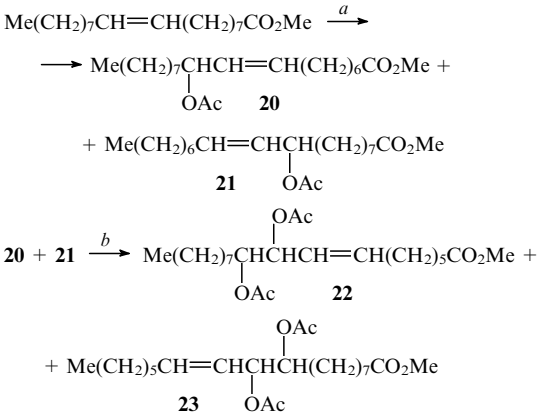
Electrolyte	Conversion (%)	Yield (%)		
		17	**18**	**19**
MeOLi	58	8	59	4
MeONa	24	4	54	9
Bu_4NBF_4	26	5	36	43
TsONa	63	4	32	25
TsOH	62	4	–	55
H_2SO_4	82	2	–	44

Note. Electrolysis under amperostatic conditions in an undivided cell (ACU), Pt anode, Cu cathode, 220 mA cm^{-2}, 6.8 F mol^{-1}, MeOH, 60 °C. Here and below, F is the quantity of electricity equal to one Faraday.

In an initial stage of electrolysis in methanol with a graphite anode and with sodium methoxide as the supporting electrolyte, 4-allylanisole is methoxylated similarly to allylbenzene at the benzylic carbon atom; however, during the subsequent, more extensive electrooxidation, it is converted into 1,1-dimethoxyallylanisole.[50]



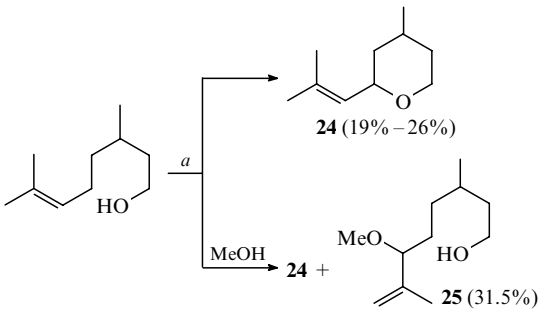
In the anodic oxidation of methyl oleate, allylic substitution also takes place. This yields predominantly unsaturated monoacetates **20** and **21** (yield of up to 60%); further electrooxidation affords unsaturated diacetates **22** and **23** (upon subsequent allylic substitution). The highest yield of the diacetates (85%) was attained when the anode current density was 8 mA cm^{-2} and the consumption of electricity was ~4 F mol^{-1} (see Ref. 53).



(*a*) ACU, Pt anode, 1.3 F mol^{-1}, AcOH, $LiClO_4$;
(*b*) ACU, > 1.3 F mol^{-1}.

Apart from unsaturated mono- and diacetates **20**–**23**, small amounts of the corresponding saturated mono- and diacetates are also formed.

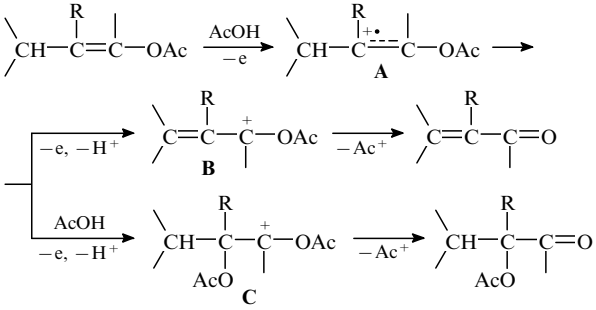
Allylic substitution can follow an intramolecular pathway provided that the electrogenerated cation of type **B** (see Schemes 1 and 2) contains an internal nucleophile. An example of this reaction is anodic oxidation of citronellol in acetonitrile or propylene carbonate giving rise to 2-(2-methylprop-1-enyl)-4-methyltetrahydropyran (**24**), a valuable fragrance compound known as rosenoxid.[54, 55] The use of methanol instead of acetonitrile changes the electrochemical behaviour of citronellol: the yield of the product **24** decreases to 7%, while 3,7-dimethyl-6-methoxyoct-7-en-1-ol (**25**) becomes the major product of electrolysis.



(*a*) ACU, C anode, 40 mA cm^{-2}, 2 F mol^{-1}, MeCN or propylene carbonate, Et_4NOTs.

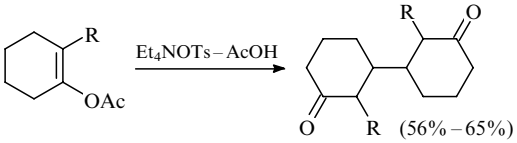
2. Transformation of enol acetates into enols and α-acetoxy ketones

During the electrolysis of enol acetate in acetic acid, radical cations **A**, generated in the first stage, undergo electrooxidation, deprotonation, and solvolysis to give α-acetoxy-substituted allylic cations **B** and α,β-diacetoxy-substituted carbenium ions **C**. Elimination of acetyl cations from these intermediates results in enones and α-acetoxy ketones.[39, 56]



The nature of the supporting electrolyte exerts a crucial influence on the composition of the electrolysis products. Indeed, when a solution of Et_4NOTs in AcOH or in MeOH is used as the electrolyte, amperostatic electrolysis of enol acetates in a divided cell (ACD) with a carbon anode, as a rule, results predominantly (in some cases, solely) in enones;[39] when the anodic oxidation is carried out in potassium acetate or triethylamine, α-acetoxy ketones are produced (Table 3).

It is noteworthy that in an undivided cell, enol acetates are converted almost entirely into 1,6-diketones as a result of cathodic dimerisation of the enones formed. For example, enol acetates derived from cyclohexanones are transformed into bis(3,3′-dioxo)cyclohexyls.[57]



R = H, Me.

In the presence of catalytic amounts (0.4 mol % – 1.0 mol %) of metal salts (iron and copper sulfates, cobalt acetate), the cathodic dimerisation is completely suppressed and cycloalk-2-enones become the major product of electrolysis, as in a divided cell (yield 80% – 86%).[57]

Electrochemical transformation of enol acetates into enones served as the basis for the development of a general method for the synthesis of 2-mono- and 2,3-disubstituted cyclopent-2-enones.[56, 57]

Table 3. Composition of products of anodic oxidation of enol acetates in AcOH.[39, 56, 58]

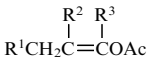
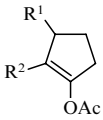
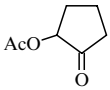
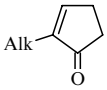
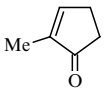
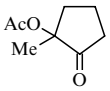
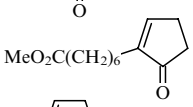
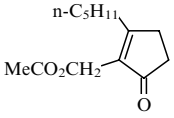
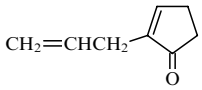
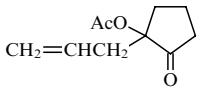
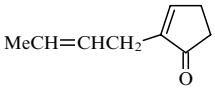
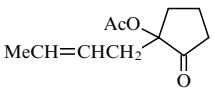
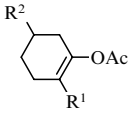
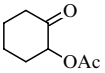
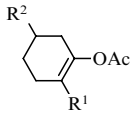
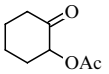
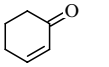
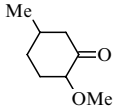
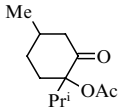
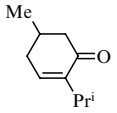
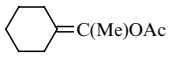
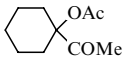
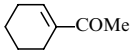
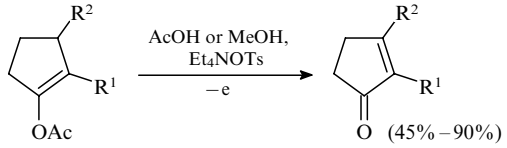
Substrate	R^1	R^2	R^3	Electrolyte	Products	Yield (%)
	n-C_5H_{11}	H	Me	Et_4NOTs	n-$C_6H_{13}CH(OAc)COMe$ n-$C_5H_{11}CH=CHCOMe$	24 6
	Alk(C_1-C_5)	H	Me	AcOK or Et_3N	$AlkCH_2CH(OAc)COMe$	54–78
	H	H	Et	AcOK or Et_3N	AcO(Me)CHCOEt	66
	H	H, Me	Ph	AcOK or Et_3N	AcO(Me)C(R^2)COPh	47–73
	H	Me	Pr^i	AcOK or Et_3N	AcO(Me)C(Me)$COPr^i$	20
	H	H		Et_4NOTs		3
						37
	H	Alk(C_1-C_9)		Et_3NOTs		66–90
	H	Me		AcOK or Et_3N		24
						59
	H	$(CH_2)_6CO_2Me$		Et_4NOTs		84
	H	Bn		Et_4NOTs		45
	n-C_5H_{11}	CH_2CO_2Me		Et_4NOTs		69
	H	$CH_2CH=CH_2$		AcOK or Et_3N		12
						59
	H	$CH_2CH=CHMe$		AcOK or Et_3N		3
						43
	H	H		Et_4NOTs		25
						9

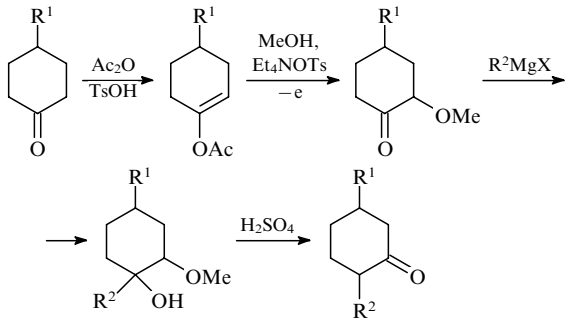
Table 3 (continued).

Substrate	R^1	R^2	R^3	Electrolyte	Products	Yield (%)
	H	H		Et_4NOH		39
						1
	H	Me		Et_4NOTs [a]		55
	Pr^i	Me		AcOK or Et_3N		60
						25
				Et_4NOTs		3
						55

Note. Electrolysis under amperostatic conditions in a divided cell (ACD), carbon anode; [a] electrolysis was carried out in methanol.



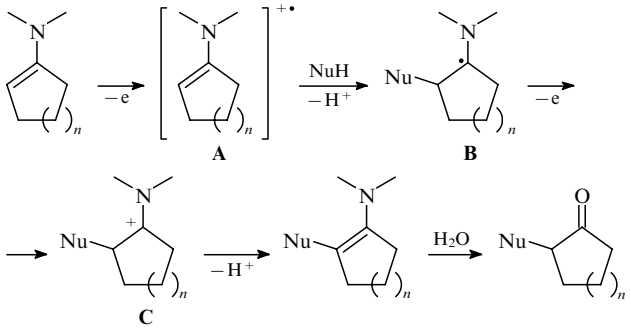
Methoxylation of enol acetates, which occurs similarly to acetoxylation, is used to accomplish 1,2-shift of the carbonyl group in ketones. An example of such transformation for substituted cyclohexanones is given below.[58]



3. Reactions of enamines

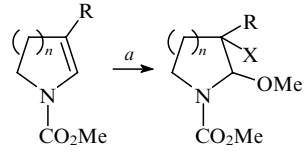
Electrooxidation of enamines affords radical cations **A**, which then add a nucleophile to give radical intermediates **B**. Electrooxidation of these species followed by deprotonation of cationic intermediates **C** gives rise to enamines containing a nucleophilic substituent in the β-position. Hydrolysis of the enamines furnishes the corresponding α-substituted ketones.[59, 60]

This electrochemical process was implemented for cyclopentanone ($n = 1$) and cyclohexanone ($n = 2$) enamines. Methanol and the anions derived from acetylacetone, ethyl acetoacetate and diethyl malonate were used as nucleophiles, and a methanolic solution of sodium methoxide was used as the electrolyte.[59, 60]



$n = 1, 2$.

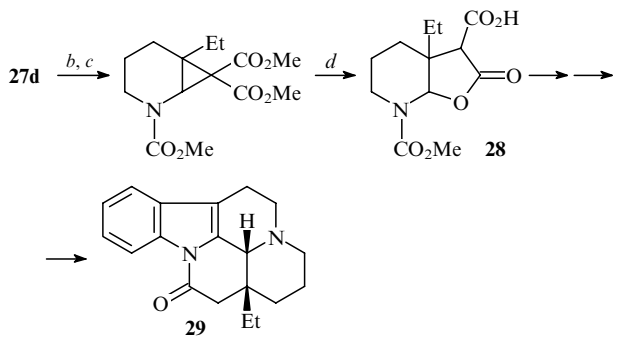
N-Methoxycarbonyl-substituted enamines **26a–d** are converted into halomethoxylation products **27a–d** upon electrolysis in methanol in ammonium bromide or iodide as the supporting electrolyte.



26a–d **27a–d**

Compound **26**	R	*n*	The yield of compounds **27** (%)
a	Me	1	38
b	Me	2	42
c	Et	1	66
d	Et	2	93

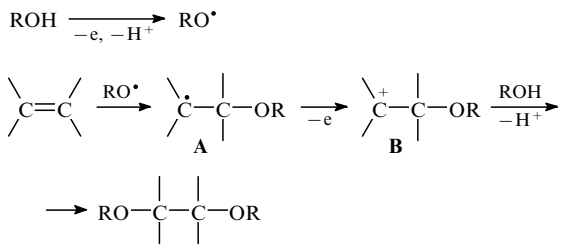
Compound **27d** has been used to synthesise a bicyclic derivative of α-carboxybutyrolactone **28**, which is a key intermediate in the synthesis of the alkaloid eburnamonine (**29**).[61,62]



(*a*) ACU, Pt anode, 75 mA cm^{-1}, 3.5 F mol^{-1}, MeOH, NH_4X (X = Br, I); (*b*) $CH_2(CO_2Me)_2$, Et_3N, $TiCl_4$; (*c*) MeOH, 20 equiv. KOH, Δ; (*d*) DMF, Δ.

4. Dimethoxylation and diacetoxylation of alkenes

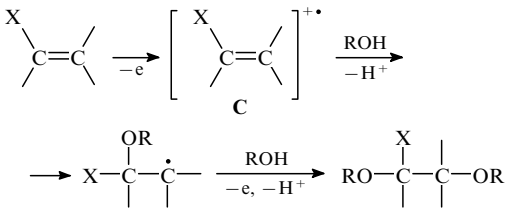
The scheme of electrochemical dimethoxylation and diacetoxylation of non-activated alkenes includes the formation of radical intermediate **A**, its electrooxidation and the reaction of the carbenium ion **B** with MeOH or AcOH.



R = Me, Ac.

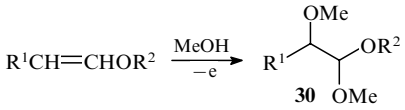
Electrochemical dimethoxylation of alkenes, for example, of conjugated arylalkenes and enol ethers (or esters) occurs with high selectivity and results in the formation of products in high yields. The most interesting examples are listed in Table 4.

Electrochemical dimethoxylation of weakly activated double bonds in arylalkenes (styrene, 2-phenylpropene and so on) takes place as an irreversible two-electron process (one two-electron oxidation wave is observed).[26,75] Highly activated double bonds in vinylanisole, 4-propenylanisole, α,α′-dimethoxystilbene and so on are dimethoxylated in two steps (two single-electron waves are observed), the first being reversible and the second being irreversible.[24,25,75,76]

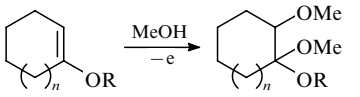


X = Ar, Bn, AlkO; R = Me, Ac.

The transfer of the first electron from the substrate molecule adsorbed on the anode, which occurs on the anode, is the rate-limiting step of this reaction. In the radical cations **C** thus formed, the highest spin density and the positive charge density are located on the β-carbon atom.[75] The process selectivity is markedly affected by the arylalkene concentration both in the solution and on the anode surface, by the current density at the anode, the anode material and the nature of the electrolyte anion.[26,40,75,77] The rate of oxidation of *trans*-alkenes is about an order of magnitude higher than that for the *cis*-isomers.[78] The yield of dimethoxylation products increases with a decrease in the substrate concentration in the solution and on the anode surface and with an increase in the current density up to values close to limiting ones; the yield sharply increases when a platinum, lead dioxide, or magnetite anode is used instead of the graphite anode[75] and sodium toluene-*p*-sulfonate is used as the electrolyte.[77] Unlike $NaClO_4$, sodium toluene-*p*-sulfonate exhibits desorption-replacing properties with respect to arylalkenes and other organic substrates; as a consequence, the substrate concentration on the anode surface during the electrolysis with TsONa is 50 times lower than that in the presence of $NaClO_4$. The same effect, although less pronounced, can be traced for tetrabutylammonium tetrafluoroborate. The highest yields (substance yield 60% – 80% and current yield 66% – 71%) of the products of dimethoxylation of arylalkenes are attained with a Pt anode, Bu_4NOTs or Bu_4NBF_4 as the supporting electrolyte and when the substrate concentration is close to 1 mol $litre^{-1}$ (see Ref. 64). Under similar conditions of electrolysis in the presence of potassium hydroxide as the electrolyte, enol ethers are converted predominantly into acetals and ketals of α-methoxy-substituted aldehydes and ketones. For example, alkyl vinyl ethers give rise to α-methoxyaldehyde acetals **30**, 1-alkoxycycloalkenes are converted into α-methoxycycloalkanone ketals **31**,[39,59,72,79] while bicyclic enol ethers yield dimethoxy-substituted oxabicycloalkanes **32**.[73,74]

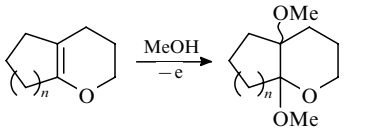


R^1	R^2	Yield of **30** (%)
H	Me	60
H	Et	68
H	Bu^n	75
n-C_6H_{13}	Me	60



31 (45% – 60%)

n = 0, 1; R = Me, Et.



32 (64% – 68%)

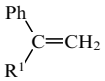
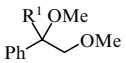
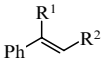
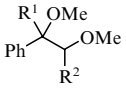
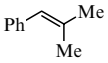
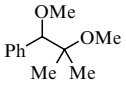
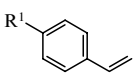
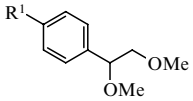
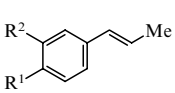
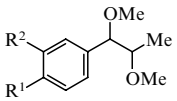
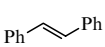
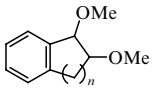
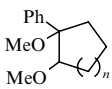
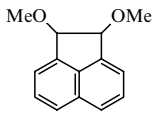
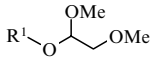
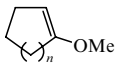
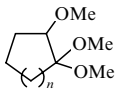
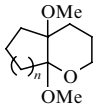
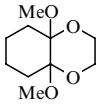
n = 2, 8.

The selectivity of dimethoxylation of arylalkenes and enol ethers is substantially affected by the competing electrooxidative dimerisation and oligomerisation reactions, which will be considered in Section II.5. These side reactions are effectively suppressed by tris(4-bromophenyl)amine. In the presence of this compound, the yield of the reaction product in the dimethoxylation of propenylbenzene increases to 93%.[80]

Electrochemical diacetoxylation of alkenes at the double bond is usually accompanied by allyllic substitution; this diminishes the synthetic value of this process.

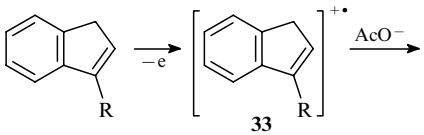
This reaction carried out in acetic acid with potassium or sodium acetate as the supporting electrolyte occurs with moderate selectivity but only for alkenes the structure of which rules out the possibility of allylic substitution, for example, stilbenes, 1,1-diphenylethylene,[81] indene and 1-alkylindenes.[82–85] In these cases, the yields of diacetoxylation products do not exceed 40%. An example is provided by 1-alkylindenes, which are converted into 1-alkyl-2,3-diacetoxyindans in 55% – 75% yields; small amounts of 2-acetoxy-1-alkyl-3-hydroxyindans (yields 6% – 20%) are formed simultaneously.[84] A mechanism for the anodic acetoxylation of indenes involving the intermediate for-

Table 4. Electrochemical dimethoxylation of arylalkenes and enol ethers under conditions of diaphragmless anodic oxidation in methanol.

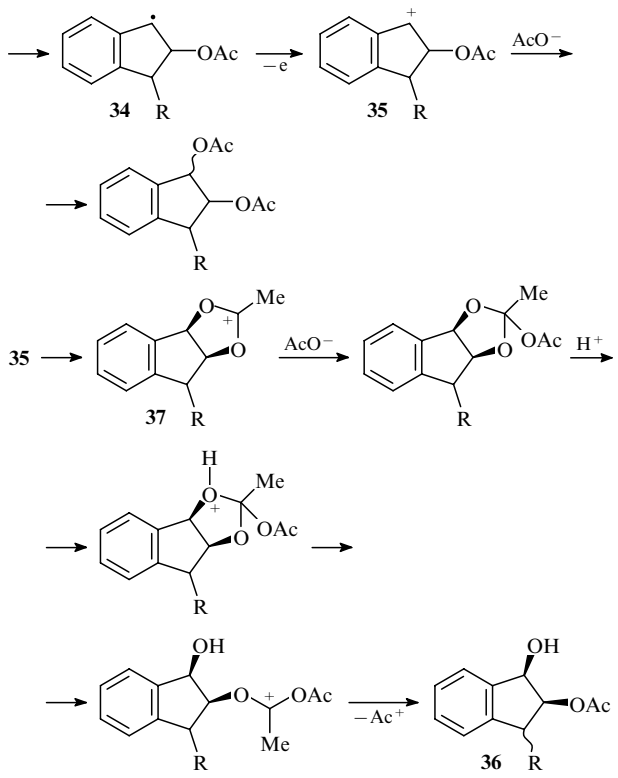
Substrate	R^1	R^2	Electrolyte	Method	Product	Yield (%) [a]	Ref.
	H		Bu_4NBF_4	A		63–80	63, 64
	H		KF	A		80	64
	Me		KF	A		70	65
	Ph		Et_4NClO_4	B		69	33
	Ph		KF	A		86	65
	H	Me	KF	A		76	65
	Me	Et	KF	A		73	65
			Bu_4NBF_4	A		75 (63)	63
	Me		KF	A		88	65
	Me		MeONa	B		36	33
	Me		Bu_4NBF_4	A		65 (52)	63
	Cl		MeONa	B		31	33
	MeO	H	Bu_4NBF_4	A		76	65
	MeO	H	KF	A		76	65
	MeO	MeO	$NaClO_4$, NaOH	B		70 (70)	66
	OCH_2O		KF	A		58	65
			KF	A	Ph(OMe)CHCH(OMe)Ph	41	67
			MeONa	B		64	68
 $n = 1, 2$			Bu_4NBF_4	A		87 (72) [b]	63
			Bu_4NBF_4	C		88 [b]	69
			Bu_4NBF_4	C		90 [c]	69
 $n = 1–3$			Bu_4NBF_4	C		81 [b]	69
			Bu_4NBF_4	A		71 (71) [c]	63
			Bu_4NBF_4	C		76 [c]	69
			Bu_4NBF_4	C		90 [d]	69
			Bu_4NBF_4	A		80	70
			MeONa	B, D		–	71
	Me		KOH	B		68	72
	Et		KOH	B		60	72
	Bu		KOH	B		75	72
 $n = 1, 2$			MeONa	D		45 [b]	59
			KOH	B		60 [c]	72
 $n = 1, 2$			KOH	B		68 [b]	73, 74
			KOH	B		80 [c]	73, 74
			Bu_4NBF_4	C		70	73, 74

Note. Method A: ACU, Pt anode, 100–220 mA cm^{-2}, 1.9–2.5 F mol^{-1}, 60 °C; method B: ACU, Pt anode, 8–80 mA cm^{-2}, 2.0–6.2 F mol^{-1}, −5–20 °C; method C: ACU, C anode, 100 mA cm^{-2}, 2.0 F mol^{-1}, 60 °C; method D: ACU, C anode, 8 mA cm^{-2}, 2.0–3.5 F mol^{-1}, ~20 °C.
[a] The substance yield (or the current yield, in parentheses) is given relative to the converted substrate; [b] $n = 1$; [c] $n = 2$; [d] $n = 3$.

mation of radical cation **33**, radical **34** and carbenium ion **35** has been proposed.[85] The side products, namely, acetoxy-3-hydroxy-derivatives **36**, are produced from cation **37**, which results from an intramolecular attack of the OAc group on the electron-deficient centre of the carbenium ion **35**.



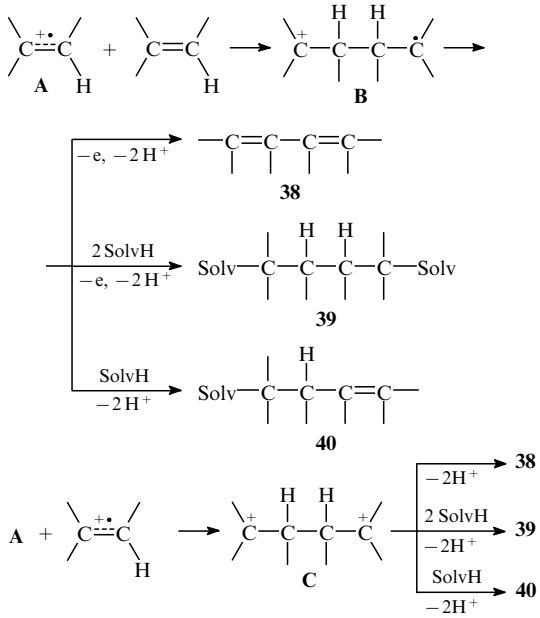
33



R = H, Me, Et, Pr^n, Pr^i, Bu^n, Bu^t.

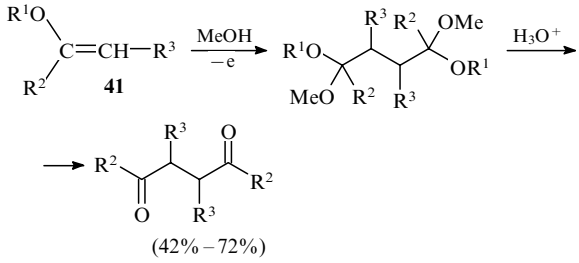
5. Dimerisation of alkenes

The electrochemical transformation of alkenes into dimerised products of type **38**–**40** takes place *via* several consecutive steps. Radical cations **A** generated in the first step undergo recombination and add to the initial alkene molecules. The radical-cation and dication intermediates **B** and **C** undergo solvolysis, electrooxidation and deprotonation giving rise to unsubstituted and substituted (saturated and unsaturated) dimeric compounds.

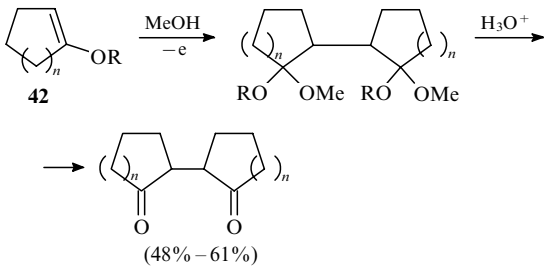


SolvH is a protic solvent.

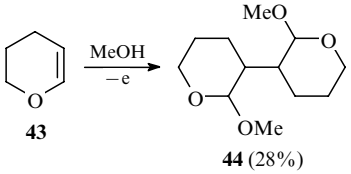
The optimal conditions for these reactions are as follows: the initial concentration of alkene >1 mol litre^{-1}, methanol as the solvent, $NaClO_4$ as the supporting electrolyte, and a graphite anode.[33, 35, 38, 72] Under these conditions, the aliphatic and alicyclic vinyl ethers **41**, **42** are converted into ketals of 1,4-dicarbonyl compounds, which are hydrolysed to give the corresponding diketones; 5,6-dihydro-4-pyran (**43**) is converted into dimethoxy derivative **44**.[38, 72]



R^1 = Me, Et; R^2 = H, Et, Ph; R^3 = H, Me, Bu^n.

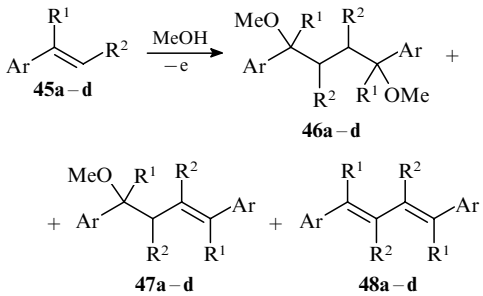


R = Me, Et; *n* = 2, 4.



Dimerisation of vinyl ethers **41**–**43** is accompanied by side addition of methanol to the double bond, which is catalysed by the protons resulting from anodic oxidation of the solvent and solvolysis of electrogenerated radical cations. To suppress this reaction, electrolysis of vinyl ethers is usually carried out in the presence of bases, for example, pyridine or 2,6-lutidine.[38]

Unlike vinyl ethers, arylalkenes are unable to add methanol under conditions of electrooxidative dimerisation; therefore, the reaction can be carried out without a base. The composition, the structure and the yield of dimerisation products of arylalkenes depend on the type of substitution at the double bond, the nature of the supporting electrolyte and the anode potential.[33, 34] Thus electrolysis of arylalkenes **45a**,**c** in the presence of sodium perchlorate yields 1,4-dimethoxy-1,4-diarylbutanes **46a**,**c** as the only or major products, while in the presence of sodium camphorsulfonate, 1,4-diaryl-1-methoxybut-1-ene **47a** and 1,4-diarylbuta-1,3-diene **48a** are formed (Table 5). Electrolysis of 2-phenylpropene (**45b**) with the $NaClO_4$ electrolyte at an anode potential of 1.6–1.7 V yields dimer **48b**; at lower potentials (1.1–1.2 V), a mixture of dimers **46b**, **47b** and **48b** in 4.2 : 2.5 : 1 ratio is formed. In the case of 4-methoxystyrene (**45c**), an increase in the potential from 0.8 to 1.2–1.3 V increases the yield of the dimer **46c** from



Ar = Ph, 4-$MeOC_6H_4$; R^1 = H, Me; R^2 = H; R^1–R^2 = $(CH_2)_3$.

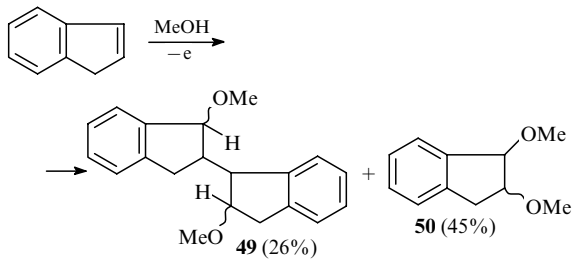
Table 5. Electrooxidative dimerisation of arylalkenes **45** in methanol.[33, 34]

Compound **45**	Ar	R^1	R^2	Electrolyte	Potential /V	Reaction product (yield) (%)
a	Ph	H	H	$NaClO_4$–MeONa (10 : 1)	1.1	**46a** (64)
	Ph	H	H	Sodium camphorsulfonate	1.6–1.7	**47a** (28) + **48a** (36)
b	Ph	Me	H	$NaClO_4$–MeONa (10 : 1)	1.6–1.7	**48b** (67)
	Ph	Me	H	$NaClO_4$–MeONa (10 : 1)	1.1–1.2	**46b** (42) + **47b** (17) + **48b** (10)
c	4-$MeOC_6H_4$	H	H	$NaClO_4$, MeOH, CH_2Cl_2	1.2–1.3	**46c** (79)
	4-$MeOC_6H_4$	H	H	$NaClO_4$, MeOH, CH_2Cl_2	0.8	**46c** (66)
d	Ph	$(CH_2)_4$		$NaClO_4$, MeOH, CH_2Cl_2	0.9	**46d** (3.4)

Note. Electrolysis was carried out under potentiostatic conditions in an undivided cell (PCU) with a graphite anode; the current yield was determined relative to the isolated products; the initial concentration of the substrate was 5.8–6.0 mol litre^{-1}.

66% to 79%. Alkenes with a greater extent of substitution at the double bonds, for example, 1-phenylcyclohexene **45d** give the corresponding dimer **46d** in a yield of only 3.4%.

Apart from dimer **49**, the electrooxidative dimerisation of indene gives dimethoxylation product **50**.[33, 34]

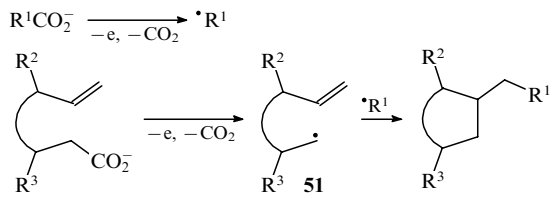


6. Intramolecular electrooxidative cyclisation

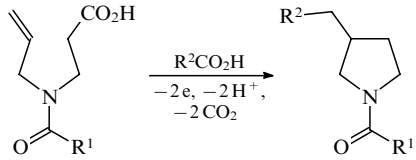
Intramolecular electrooxidative cyclisation is possible for alkenes the molecules of which contain, in addition to the C=C bond, a group capable of electrooxidative transformation into a radical-cation or a radical centre and the chain separating them consists of three to five atoms. The radical cations and radical intermediates electrogenerated from alkenes of this type, for example, from unsaturated carboxylic acids, unsaturated ethers and carbamates, activated α-stannyl or α-silyl groups, aryl(hetaryl)alkenes and non-conjugated α-alkoxy- and α-acetoxydienes, are converted into cyclic products upon intramolecular addition at the double bond followed by solvolysis or other secondary reactions. These processes are considered in more detail below, in Sections II.6.a–e.

a. Cyclisation of unsaturated carboxylic acids

In the cyclisation of unsaturated carboxylic acids, the reaction products result from intramolecular cyclisation of alkenyl radicals **51** generated by the anodic oxidation of the anions of unsaturated acids under conditions of the Kolbe reaction.

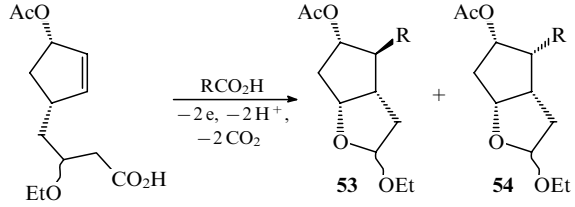


The recent comprehensive reviews devoted to this known reaction [1–4, 86] describe, along with other aspects, the results of application of anodic oxidation to the generation of radicals from carboxylic acids and investigation of the electrochemical cyclisation of unsaturated acids. Further progress along this line [87–90] resulted in the elaboration of new methods for the synthesis of natural and related cyclic products, for example, pyrrolidines **52**,[88, 89] precursors of prostaglandins **53** and **54**[90] and angular triquinanes **55**.[91]

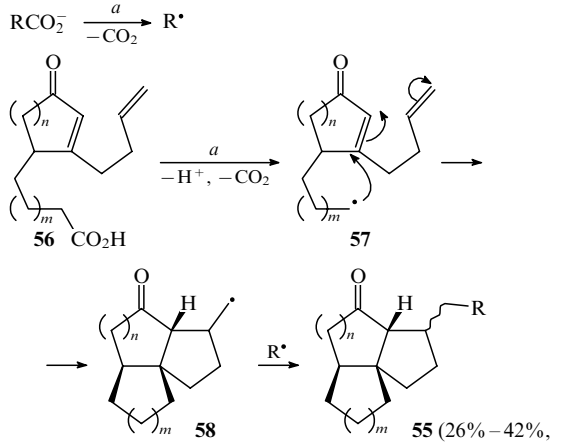


52 (46%–58%)

R^1 = H, Me; R^2 = Me, n-C_5H_{11}, $(CH_2)_4CO_2Me$.



R	Yield (%)	
	53	**54**
Me	50	18
n-C_8H_{17}	40	14
$(CH_2)_2CO_2Me$	42	14
$CH_2SiMe_2CH_2$	30	8
Me_3SiCH_2	29	10
n-$C_5H_{11}COCH_2CH(SiMe_3)$	4–5	–



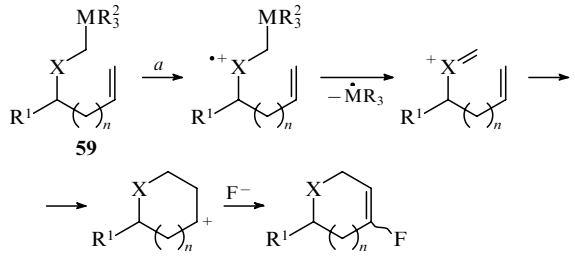
R = Me, n-C_5H_{11}, $(CH_2)_2CO_2Me$; n = 1–3, m = 1, 2; (*a*) ACU, Pt anode, steel cathode, 25 mA cm^{-2}, 1.2 F mol^{-1}, MeOH, 4 equiv. of RCO_2H neutralised by KOH to 5%, 40–45 °C.

The formation of the compounds **55** from acids **56** takes place *via* regio- and stereoselective radical tandem cyclisation initiated by anodic oxidation and giving rise to three new C–C bonds. Two

bonds are formed at the stage of cyclisation of radical **57**, and the third one, upon recombination of tricyclic radical **58** with the R$^{\bullet}$ radical generated from the saturated acid, which is used as the second reactant. This distinguishes electrochemical cyclisation from tandem cyclisations initiated by chemical methods: in this case, C–H or C–I bonds are formed at the final stage.[92–94] An advantage of the electrochemical tandem cyclisation is that it does not use organotin reagents, normally employed in the chemical version, and the combination of the initial unsaturated and saturated acids makes it possible to change the side chain of the product **55**.

b. Cyclisation of unsaturated ethers and carbamates activated by α-stannyl and α-silyl groups

Silyl, stannyl or thioaryl groups in the α-position markedly decrease the oxidative potentials of ethers or carbamates **59**; this facilitates the electrochemical transformation in oxonium (X = O) or *N*-acyliminium (X = NCO_2Me) ions.[95–101] Intramolecular cyclisation of substrates **59** yields products containing an endocyclic fluorine atom, indicating a cationic mechanism of the reaction (in the case of a radical mechanism, an exocyclic product would be formed at $n = 1$). The supporting electrolyte, namely, tetrabutylammonium tetrafluoroborate or hexafluorophosphate, serves as the source of the fluorine anion at the final stage of the process.[98]



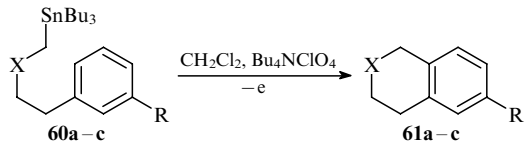
59

(50%–98%, *cis* : *trans* = 1.2 : 3)

M = Sn, Si; R^1 = H, Me; R^2 = Alk; X = O, NCO_2Me; n = 1, 2; (*a*) ACU, graphite anode, CH_2Cl_2, Bu_4NBF_4.

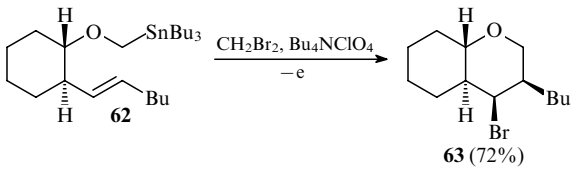
Trialkylstannyl groups exert a more pronounced activating effect than trialkylsilyl groups; as a consequence, cyclic products are formed in higher yields from stannyl derivatives.

This method has been used to convert α-stannyl-substituted arylaliphatic ethers **60a–c** into isochroman (**61a**), 6-fluoroisochroman (**61b**) and *N*-methoxycarbonyl-1,2,3,4-tetrahydroisoquinoline (**61c**). The transformation of *trans*-1-(tributylstannylmethoxy)-2-(hex-1-enyl)cyclohexane (**62**) gave rise to *trans*-3-butyl-4-bromo-1-oxadecalin (**63**).[99, 101]



60a–c **61a–c**

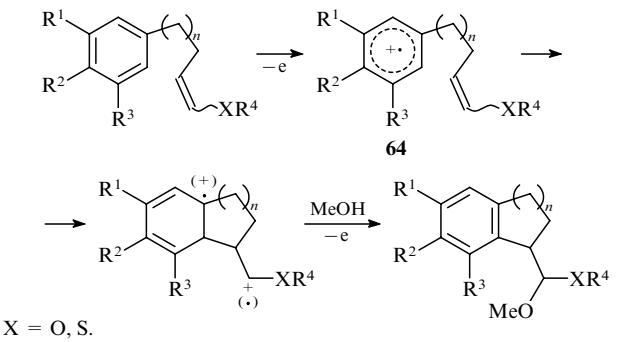
X = O: R = H (**a**, 55%), F (**b**, 80%); X = NCO_2Me, R = H (**c**, 54%).



62 **63** (72%)

c. Cyclisation of aryl and hetarylalkenes

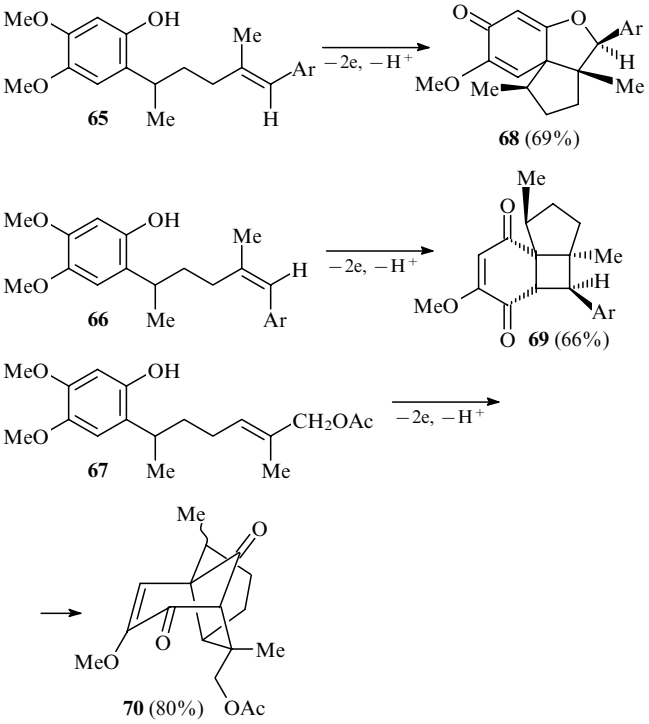
Intramolecular cyclisation of aryl- and hetarylalkenes is a result of transformations of radical cations **64** electrogenerated from these substrates. This cyclisation is one of the most useful reactions induced by direct anodic oxidation.[102–118]



64

X = O, S.

The structure of the bi- and polycyclic compounds thus obtained depends on the nature and the stereochemistry of substituents at the double bond. For example, cyclisation of substrates **65–67** having related structures but differing in the nature and the positions of substituents at the double bond affords absolutely different tricyclic compounds **68–70**, precursors of natural products.[102–111]



65 **68** (69%)

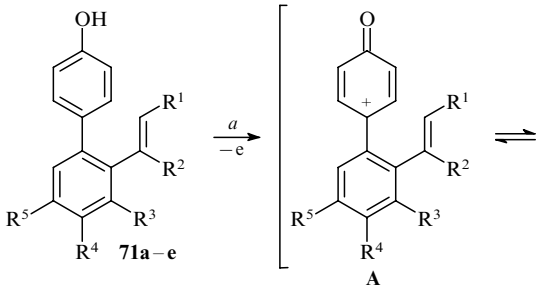
66 **69** (66%)

67

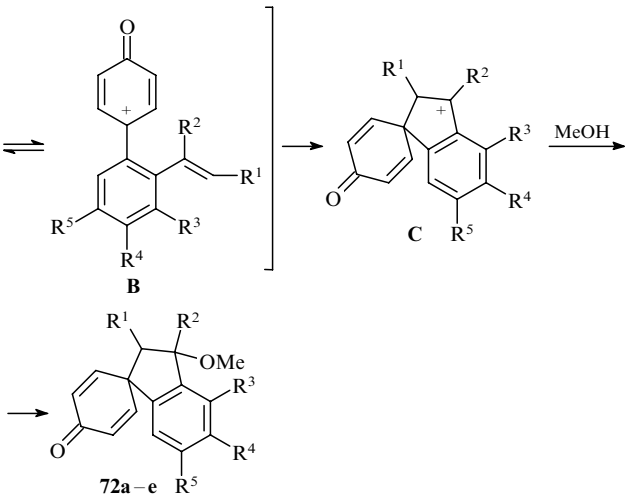
70 (80%)

Mild experimental conditions and high product yields are important advantages of this method for the preparation of this type of polycyclic polyfunctionalised compound.

4-Hydroxy-2′-alkenylbiphenyls **71a–e** have been used as examples to study the influence of the structure of the initial substrates, electrolysis conditions and some other factors on the cyclisation. Presumably,[112, 113] the initial step represents generation of cationic intermediates **A** and **B** induced by anodic oxidation; this is followed by their cyclisation and the reaction of cations **C** with methanol giving rise to compounds **72a–e**.[112, 113]



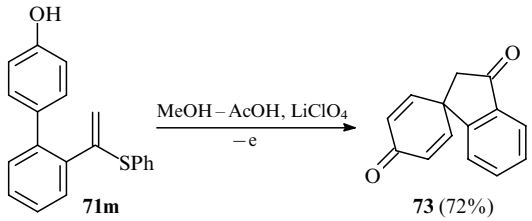
71a–e **A**



(*a*) ACD, platinum wire or glass carbon anode, 1.6–2.0 F mol^{-1}, MeOH or MeOH–AcOH (CH_2Cl_2, MeCN), $LiClO_4$, 0–20 °C.

Compound **71**	R^1	R^2	R^3	R^4	R^5	The yield of compounds **72** (%)	Ref.
a	H	H	H	H	H	16	112, 113
b	H	Me	H	H	H	85	112, 113
c	H	Ph	H	H	H	65	112, 113
d	Me	H	H	H	H	35	112, 113
e	$(CH_2)_3$		H	H	H	69	112, 113
f	H	H	Me	H	H	70	114
g	H	H	H	H	OMe	47	115
h	H	Me	H	H	OMe	84	115
i	H	Me	H	OMe	H	80	115
j	H	H	H	OMe	OMe	70	115
k	H	Me	H	OMe	OMe	92	115
l	H	Me	H	OCH_2O		70	115

The cyclisation of 4-(2′-alkenylphenyl)phenols **71b**,**c**,**e**, containing α-substituents in the alkenyl group, occurs with high yields (65%–85%). In the case of the compounds **71** in which R^2 = H the yields are much lower. The compound **71m**, containing a phenylthio group at the double bond, is converted into diketone **73**.

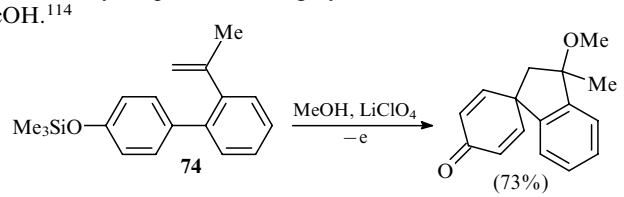


The yields of reaction products also depend on the solvent, current density, anode material and addition of mild acids, for example, acetic acid. The highest yields are attained when the reaction is carried out in a mixture of acetonitrile with methanol (4 : 1) containing 5–10 equiv. of AcOH, using lithium perchlorate as the supporting electrolyte and a current density of 0.84 mA cm^{-2} on a platinum electrode.[113]

The increase in the yields of the compounds **72** following the replacement of hydrogen at the α-carbon atom in the olefinic group by a methyl group is presumably [115] due to the fact that in this case, the cationic intermediate exists preferably in conformation **A**, in which the double bond is close to the reaction centre. For the substrates **71** in which R^2 = H, conformation **B** is preferred. A similar effect is exerted by the methyl group in the *ortho*-position to the alkenyl substituent. For example, the transformation of 4-hydroxy-2′-vinyl-3′-methylbiphenyl (**71f**) gives the cyclisation product — spirodienone **72f** — in 70% yield.[114]

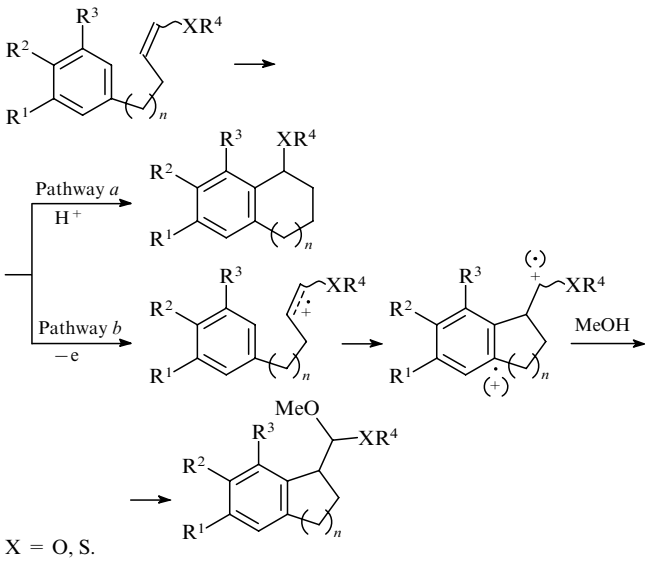
Cyclisation of 4-hydroxyarylalkenes with R^2 = H containing methoxy groups in the *para*-position or both in the *para*- and *meta*-positions relative to the vinyl group (the compounds **71g**,**j**) is more efficient. Similar *meta*-methoxy-derivatives do not cyclise. Cyclisation of *para*- and *meta*-methoxy-substituted **71h**,**i**,**k**,**e** in which R^2 = Me gives products in high yields.[115]

The trimethylsilyl ethers of 4-hydroxyarylalkenes, for example, compound **74**, unlike the corresponding phenols, are converted into cyclic products in high yields even in the absence of AcOH.[114]



Silyl ethers can cyclise in the presence of bases. Thus, depending on the nature of the functional groups present in the substrate, this process can be carried out both in a neutral medium and in the presence of acids or bases.

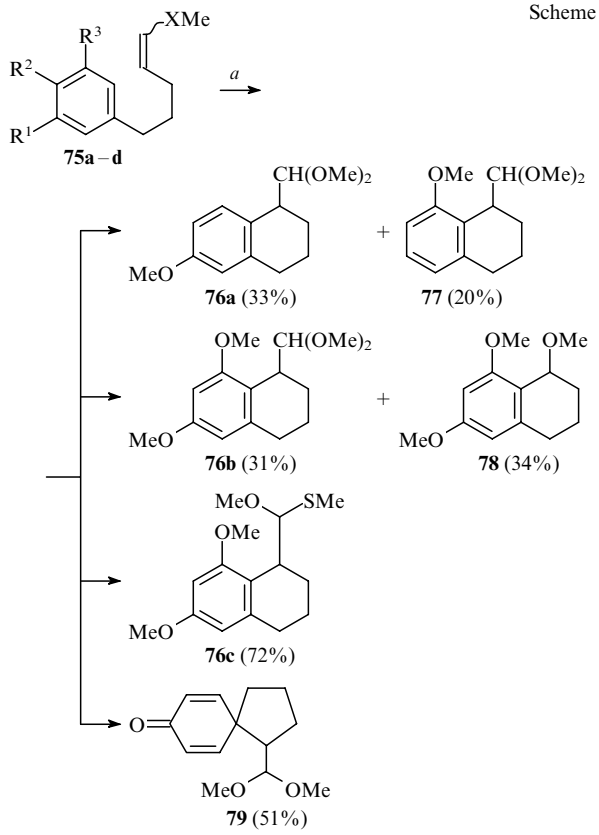
Within the framework of investigation of cyclisation, anodic oxidation of aryl- and hetarylalkenes with electron-enriched double bonds has been vigorously developing in recent years.[116–118] The interest in these reactions is determined by the possibility of performing the cyclisation of arylalkenes with a regioselectivity (pathway *b*) differing from that observed in the case of the Friedel–Crafts cyclisation (pathway *a*). The cyclisation process during the anodic oxidation is based on the inversion of polarity of enol ethers. This reaction makes it possible to prepare cyclic products of various structures from the same initial substrate, depending on the method used to initiate cyclisation.



Thus by anodic oxidation of enol ethers and enol thioethers **75a**–**c**, cyclisation products, namely, substituted tetralins **76a**–**c**, **77**, and **78** have been prepared in high yields. Under the same conditions, the enol ether **75d** is converted into spiro derivative **79** (Scheme 3).[116, 118]

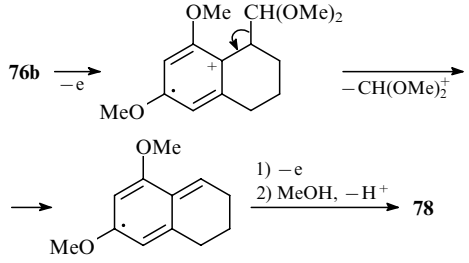
It should be noted that cyclisation of the enol ether **75a** to give the tetralins **76a** and **77** is accompanied by the formation of 1,6- and 1,8-dimethoxytetralins, resulting from further electrooxidation. The tetralin **76b**, formed from the enol ether **75b**, is converted into 1,6,8-trimethoxytetralin **78**.[118]

Scheme 3

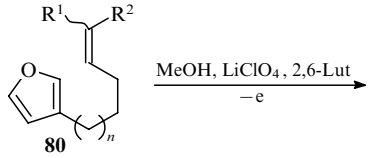


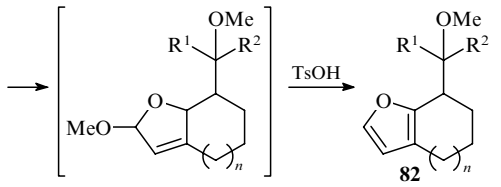
75: R^1 = OMe, R^2 = R^3 = H, X = O (**a**); R^1 = R^3 = OMe, R^2 = H, X = O (**b**), S (**c**); R^1 = R^3 = H, R^2 = OMe, X = O (**d**); (*a*) ACD, glass carbon anode, 1.6–2.0 F mol^{-1}, MeOH–CH_2Cl_2 (1 : 4), $LiClO_4$, 5 equiv. of 2,6-lutidine (2,6-Lut), ~20 °C.

These side reactions do not take place if electrolysis is carried out with a controlled potential (1.1 V). Unlike cyclisation of the enol ethers **75a**,**b**, cyclisation of the enol thioether **75c** under similar conditions occurs without further oxidation of the reaction product **76c**.

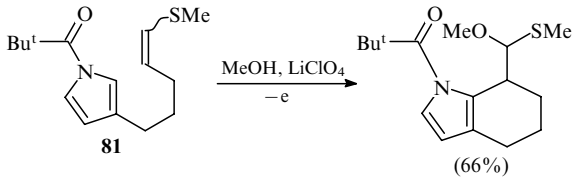


The cyclisation of furyl- (**80**) and pyrrolyl-substituted alkenes **81** containing electron-enriched double bonds induced by anodic oxidation has opened a new way for assembling bicyclic structures incorporating five-membered heterocycles.[116,117] A compound of type **82** can be used in the synthesis of furan-containing bi- and polycyclic natural products.[119–126]



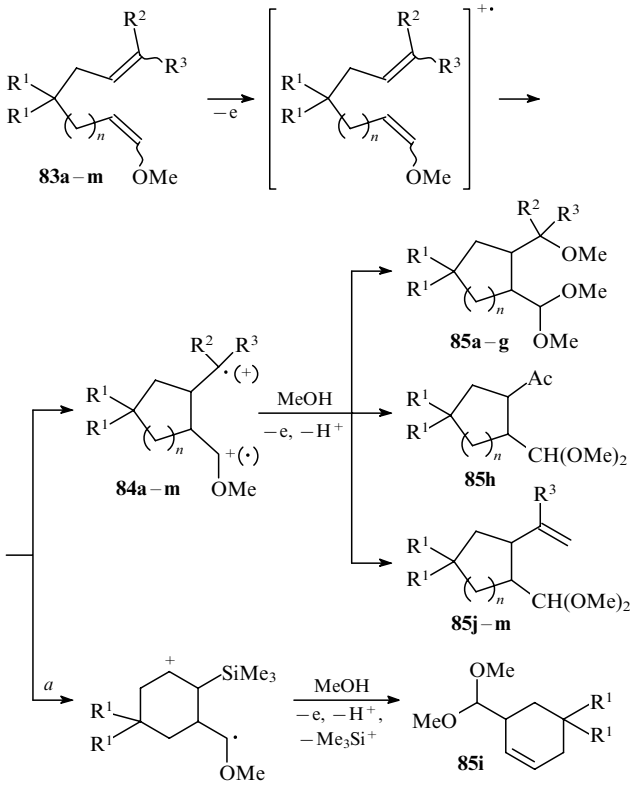


R^1 = SMe, OMe, Ph, Me, CH_2SiMe_3; R^2 = H, Me, *n* = 1, 2.



d. Cyclisation of non-conjugated 1-alkoxy-dienes

Cyclisation of non-conjugated 1-alkoxy-dienes has not yet been adequately studied. This electrochemical process, which has much in common with cyclisation of aryl- and hetarylalkenes, has found application for the synthesis of carbocyclic compounds. The value of this method is dictated by the possibility of reverting the polarity of the β-carbon atom in the initial 1-alkoxy-dienes **83a**–**m** from nucleophilic to electrophilic due to the fact that an initial stage of the process is transformation of the substrates into radical cations **84a**–**m**.[127–134] The electrolysis conditions and the yields of the reaction products **85a**–**m** are listed in Table 6.



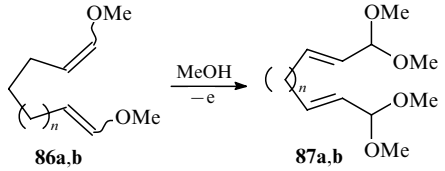
(*a*) R^1 = Me, R^2 = $SiMe_3$, R^3 = H.

The 1-methoxy-dienes **83** (*n* = 1–3), which contain substituents R^2 and R^3 activating the double bond, ensure the most selective formation of cyclic compounds (see Table 6).[127–134] Cyclisation of 1-methoxy-dienes **86a**,**b** does not proceed under similar conditions: these compounds are converted into unsaturated dialdehyde diacetals **87a**,**b**.

Table 6. Anodic oxidation of 1-methoxy dienes **83a**–**m**.

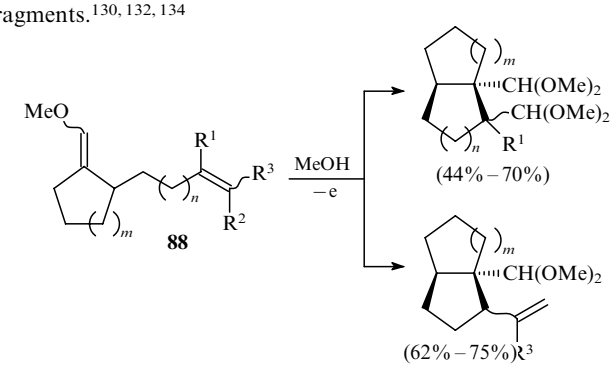
Compound **83**	n	R^1	R^2	R^3	Reaction product	Yield (%)	Ref.
a	1	Me	OMe	H	**85a**	68	128
b	1	H	OMe	H	**85b**	70	128
c	2	H	OMe	H	**85c**	65	128
d	3	H	OMe	H	**85d**	50	128
e	1	H	Ph	H	**85e** [a]	65–73	127, 128
f	2	H	Ph	H	**85f**	65	128
g	1	H	Me	Me	**85g**	60	128
h	1	Me	OMe	Me	**85h**	62	132
i	1	Me	$SiMe_3$	H	**85i**	29	129
j	1	Me	CH_2SiMe_3	H	**85j** [a]	84	132
k	1	Me	CH_2SiMe_3	Me	**85k**	89	128
m	2	H	CH_2SiMe_3	H	**85m**	59	128

Note. Conditions of electrolysis: ACU, Pt or wire glass carbon anode, 15 mA cm^{-2}, 2 F mol^{-1}, methanol–THF (1 : 1) or MeOH–CH_2Cl_2 (1 : 4), $LiClO_4$, 2,6-Lut. [a] A mixture of *trans*- and *cis*-isomers.



n = 4 (**a**), 12 (**b**).

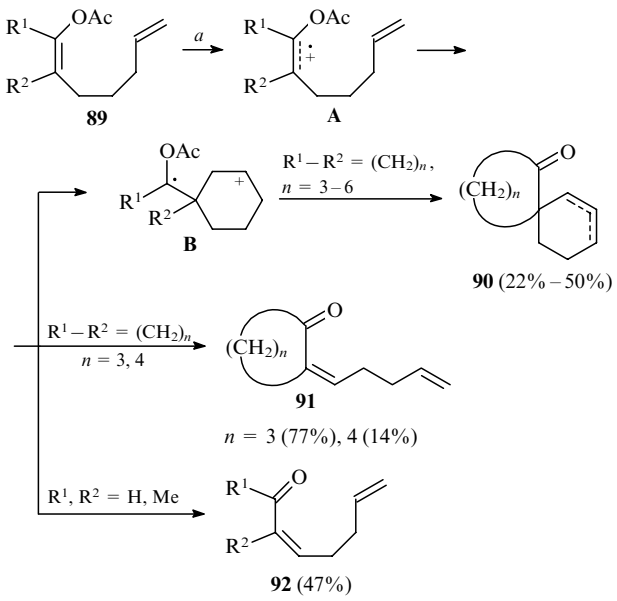
The principle of electrochemical cyclisation of linear 1-methoxy-dienes has been extended successfully to compounds **88**, containing cyclopentane (m = 1) and cyclohexane (m = 2) fragments.[130, 132, 134]



R^1, R^2 = H, Me; R^3 = OMe, $SiMe_3$; m, n = 1, 2.

e. Cyclisation of non-conjugated 1-acetoxy-dienes

Cyclisation of non-conjugated 1-acetoxy-dienes **89** has many common features with the transformation of enol acetates into enones and α-acetoxy ketones (see Section II.2). A fundamental distinction between these electrochemical processes is that radical cations **A** electrogenerated from the 1-acetoxy-dienes **89** can react with a second C=C bond acting as an internal nucleophile. The intramolecular electrophilic attack on the double bond by the cationic centre of the radical cation gives rise to cyclic radical cation **B**. The subsequent deprotonation and electrooxidation of intermediate **B** are accompanied by elimination of the acetyl cation, resulting in the formation of cyclisation product **90** and competitive formation of conjugated enones **91** or **92**.[135]

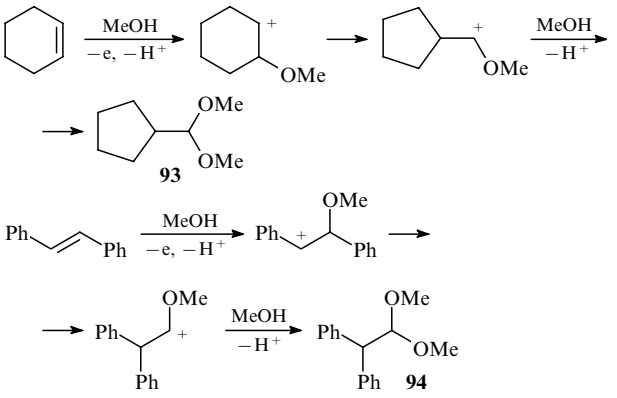


(*a*) ACU, graphite electrodes, 4–10 F mol^{-1}, AcOH, Et_4NOTs (1 mol $litre^{-1}$), ~20 °C.

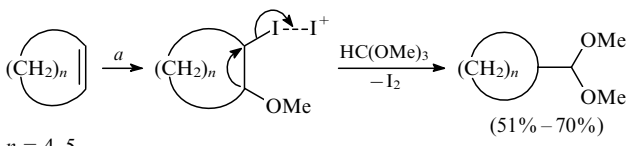
Cyclisation of radical cations **A** by a radical mechanism does not occur under these conditions.

7. Transformations of alkenes with skeletal rearrangement

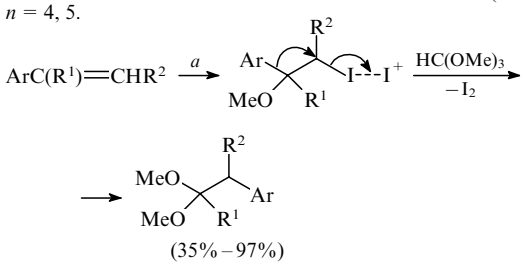
The transformations of alkenes with skeletal reconstruction take place as a result of rearrangement of carbenium ions, which are intermediates in the anodic oxidation of alkenes. For example, cyclohexene is converted into cyclopentanecarbaldehyde dimethyl acetal (**93**),[136] while *trans*-stilbene yields diphenylacetaldehyde dimethyl acetal (**94**).[67]



Since carbenium ions react competitively with MeOH, the dimethyl acetals **93** and **94** are formed as mixtures with 1,2-dimethoxycyclohexane and 1,2-dimethoxy-1,2-diphenylethane. When anodic oxidation of cyclohexene, *trans*-stilbene and related alkenes is carried out in trimethyl orthoformate in the presence of iodine, this side process is suppressed and acetals are produced as the only electrolysis products.[136] The promotory effect of iodine is related presumably [136] to the formation of iodonium salts, which efficiently assist the rearrangement.



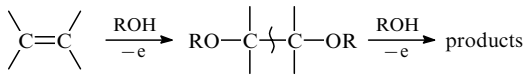
n = 4, 5.



Ar = Ph, 4-MeC_6H_4, 4-$MeO_2CC_6H_4$, 4-ClC_6H_4; R^1 = H, Me; R^2 = H, Me, Ph, CH_2OMe; (*a*) ACU, graphite anode, 0.1 mA cm^{-2}, 3–17 F mol^{-1}, $HC(OMe)_3$, $LiClO_4 \cdot 3H_2O$, 0.25–1.2 equiv. I_2, 20–100 °C.

8. Cleavage of the double bond in alkenes

Electrochemical cleavage of the double bond in alkenes takes place in an aqueous or alcoholic solution. This is a two-stage process consisting of vicinal dioxygenation of the alkene double bond at the initial stage and cleavage of the C–C σ-bond in the resulting species at the subsequent stage.

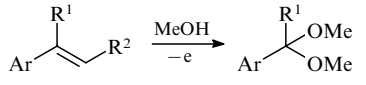


ROH is water or alcohol.

For conjugated arylalkenes, aryl(areno)cycloalkenes and enol acetates, the two stages can proceed successively as a one-pot reaction because the same electrolytes are effective for both processes. The attempts to cleave the double bond in enol ethers in the same way failed (see Section II.8.b).

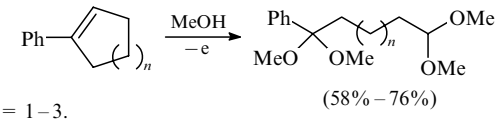
a. Direct cleavage of the C=C bond in arylalkenes, aryl(areno)cycloalkenes and enol acetates

Stepwise investigation of styrene electrooxidation in methanol in an undivided cell showed that the initial and the subsequent stages of this process are affected in different ways by the nature of the electrolyte, anode material and temperature. The highest selectivity (76%–80%) of the first stage (degree of substrate conversion 90%–93%) is attained in potassium fluoride or tetrabutylammonium tetrafluoroborate as the supporting electrolyte with a platinum anode, while for the second stage a selectivity of 70%–83% (degree of conversion 85%–98%) is observed in the presence of sodium toluene-*p*-sulfonate and tetrabutylammonium tetrafluoroborate with a graphite anode.[64, 65] Operation of the overall process under conditions favourable for the second stage permits preparation of the target products in higher yields. Under these conditions, conjugated arylalkenes were converted into benzaldehyde acetals and arylketone ketals (the consumption of electricity is 4–8 F per mole of alkene).[64, 137–139]



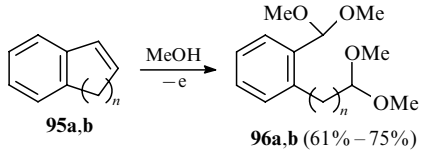
Ar = Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$; R^1 = H, Me, Ph; R^2 = H, Me, Et.

1-Phenylcycloalkenes give acetal and ketal derivatives of ω-benzoylalkanals.[64, 140]



n = 1–3.

Indene (**95a**) and 1,2-dihydonaphthalene (**95b**) form the bis(acetals) **96a**,**b**.[64, 140]

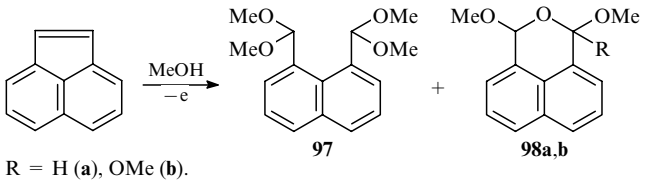


95a,**b**

96a,**b** (61%–75%)

n = 1 (**a**), 2 (**b**).

Acyclic (**97**) and cyclic (**98a**,**b**) acetals of naphthalene-1,8-dicarboxaldehyde were prepared from acenaphthene.[70] The **97** to **98a**,**b** ratio depends substantially on the electrolyte used: in the presence of potassium fluoride, these products are formed in 30% and 34% yields, respectively; in the presence of tetrabutylammonium tetrafluoroborate, the ratio is ~1 : 25 (overall yield 57%).



97 **98a**,**b**

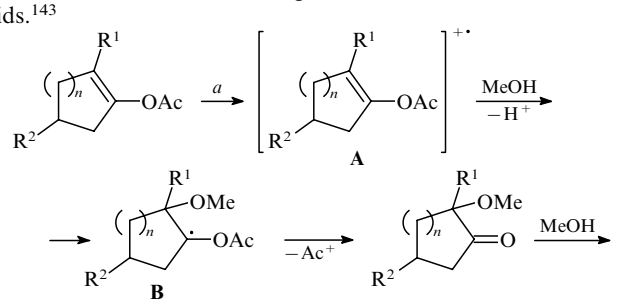
R = H (**a**), OMe (**b**).

The process selectivity sharply decreases when the initial alkene concentration is higher than 1.0 mol $litre^{-1}$ because of the increase in the relative amount of the alkene involved in the side dimerisation, oligomerisation and polymerisation reactions (see Section II.5). The decrease in the alkene concentration in the reaction mixture by using its gradual addition to the electrolyte during electrolysis makes it possible to increase the product yield to 15%–20%.[65]

The predominant formation of the cyclic acetals **98** from acenaphthene is, apparently, caused by the fact that, during the electrolysis in the presence of Bu_4NBF_4, the space near the anode surface gets acidified by the electrogenerated HBF_4, which catalyses the transformation of the acetals **97** into **98a**,**b**.

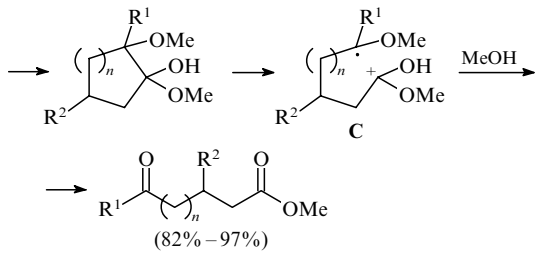
The rupture of the C–C bond in glycols formed upon the electrooxidation of the double bond in conjugated arylalkenes in aqueous and water-organic media proceeds at a substantially higher rate than that in their alkyl ethers. In this case, the process cannot be stopped at the stage of formation of glycols due to the fast rupture of the C–C bond in the HO–C–C–OH fragment. Direct anodic oxidation of propenylbenzene, anethole and isosafrole has been studied in most detail.[138–142] Anisaldehyde was prepared from anethole in high substance yield (81%–85%) but a low current yield (~20%).[141, 142] The cleavage of double bond in isosafrole has not resulted in the synthesis of 3,4-methylenedioxybenzaldehyde (piperonal) in a yield higher than 34%.

Electrochemical rupture of the C=C bond in enol acetates proceeds *via* consecutive transformation into radical-cation and radical intermediates **A** and **B**, α-methoxy ketones, their semiketals, and radical cations **C** and gives rise to esters of oxoalkanoic acids.[143]



A

B

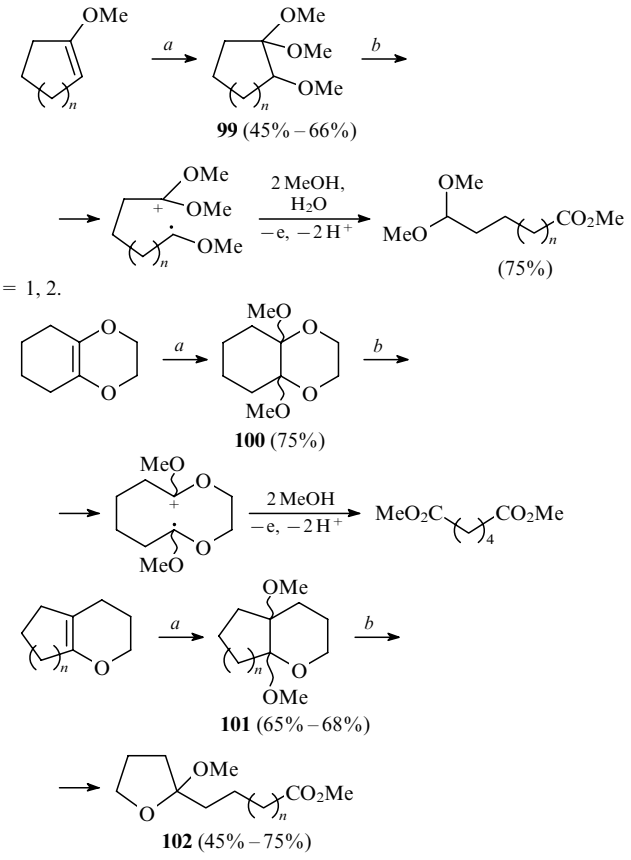


n = 1, 2; R^1, R^2 = H, Me, Pr^i; (*a*) ACU, Pt anode, 4 F mol^{-1}, MeOH – AcOH (10 : 1), $LiClO_4$, 2 – 8 °C.

Starting from (+)-menthone enol acetate, methyl (+)-3,7-dimethyl-6-oxooctanoate was prepared by this method in 74% yield.[143]

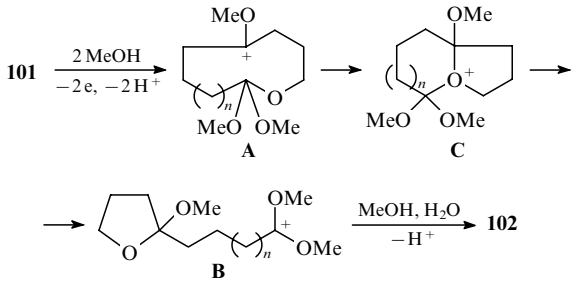
b. Direct cleavage of the double bond in cyclic enol ethers

It has been noted above that cleavage of the double bond in enol ethers cannot be carried out as a one-pot reaction with the same selectivity as for conjugated arylalkenes, aryl- and benzocycloalkenes. This is due to the fact that the electrochemical vicinal dialkoxylation of enol ethers proceeds with a satisfactory selectivity only with basic electrolytes, which are inefficient at the stage of electrooxidative cleavage of dialkoxylation products. Therefore, the process is carried out as two separate electrochemical stages with isolation of the products of dialkoxylation of enol ethers **99** – **101** after the first stage.[59, 144 – 146]



n = 2, 8; (*a*) ACU, Pt anode, 3.5 – 6.2 F mol^{-1}, MeOH, MeONa or KOH, – 5 – 20 °C; (*b*) ACU, graphite anode, 6 – 8 F mol^{-1}, MeOH, Et_4NOTs or Bu_4NBF_4, 20 °C.

The electrochemical processes at the second stage result in ring opening in the dialkoxylation products **99** – **101**. In the case of the compounds **101**, the reaction is accompanied by their electrooxidative rearrangement into methyl ω-(2-methoxytetrahydrofuryl)alkanoates **102**. The rearrangement takes place due to isomerisation of intermediates **A** into carbocations **B** *via* oxonium ions **C**. The subsequent alcoholysis of cations **B** results in the reaction product **102**.[145, 146]



III. Reactions induced by indirect anodic oxidation

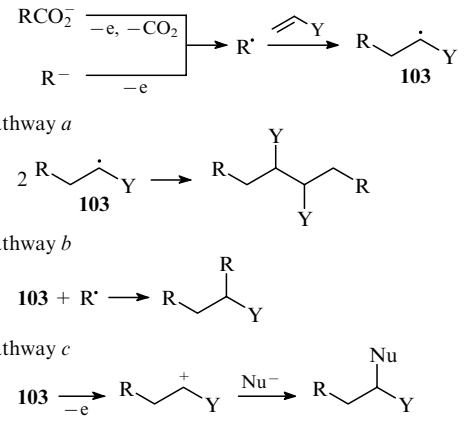
In the reactions induced by indirect anodic oxidation, unlike reactions induced by direct anodic oxidation, no direct electron transfer from the alkene molecule takes place at the anode. In this case, alkenes are involved in the electrochemical process through interaction with electrogenerated inorganic or organic radicals, ions or reagents (see Scheme 1). These intermediates arise from their precursors at potentials lower than the potentials of alkene oxidation. The process of alkene transformation into products takes place partly or entirely in the bulk solution rather than on the anode surface and is markedly facilitated and accelerated. This strategy allows one to perform electrochemical transformations of alkenes impossible in the case of direct anodic oxidation and thus extends the scope of applicability of anodic processes in organic synthesis.

The most typical precursors for the generation of oxidants and reagents in the alkene transformations induced by indirect anodic oxidation are anions of organic and inorganic acids, variable-valence metal compounds and triarylamines.

1. The reactions of alkenes with radicals electrogenerated from carboxylate anions and 1,3-dicarbonyl and related compounds

In the anodic oxidation of carboxylate, acetoacetate, malonate and cyanoacetate anions, carbon-centred radicals are generated;[1 – 4, 86] in the presence of alkenes, they add to the double bond. The resulting radical adducts **103** are converted along two routes: they either undergo pairwise or cross recombination (Scheme 4, pathways *a*, *b*) or are oxidised to give carbocations (pathway *c*). Subsequently the carbocations react with internal or external nucleophiles.[1 – 4]

Scheme 4

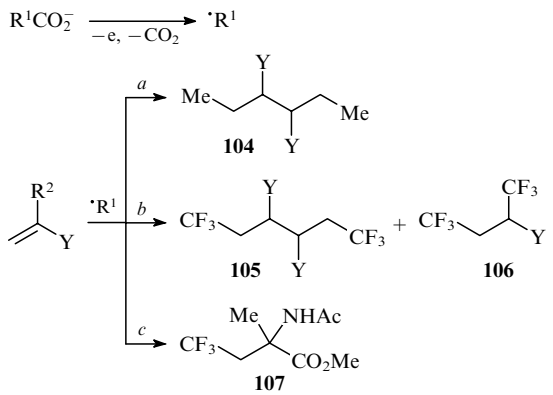


a. Reactions of alkenes with alkanoic acids

The reactions of alkenes with radicals generated from saturated acids and 1,3-dicarbonyl and related compounds have been generalised in a review,[5, 6] which covers the data published up to 1981. In this review, we consider later publications.

The main difference between alkene reactions with radicals generated by the anodic oxidation of alkanoic acids and their reactions with similar radicals generated by chemical methods is that the electrochemical method makes it possible to vary the radical concentration on the electrode surface over a broad range by varying the current density and thus to control the process. An increase in the current density favours recombination of radicals, while a decrease facilitates the oxidation of radicals. The electrochemical and chemical processes also differ in the way in which electron-withdrawing substituents Y in the alkene molecule influence the reaction route. The formyl, acetyl and alkoxycarbonyl groups direct the electrochemical reaction exceptionally to pathway *a* [147] and the chemical reaction, to pathway *a* or *b*. The alkenes $CH_2=CHY$ with electron-donating substituents Y, such as alkyl, aryl, vinyl and alkoxyl groups are converted along each of the three pathways: *a*, *b* and *c* (see Scheme 4).[5,6]

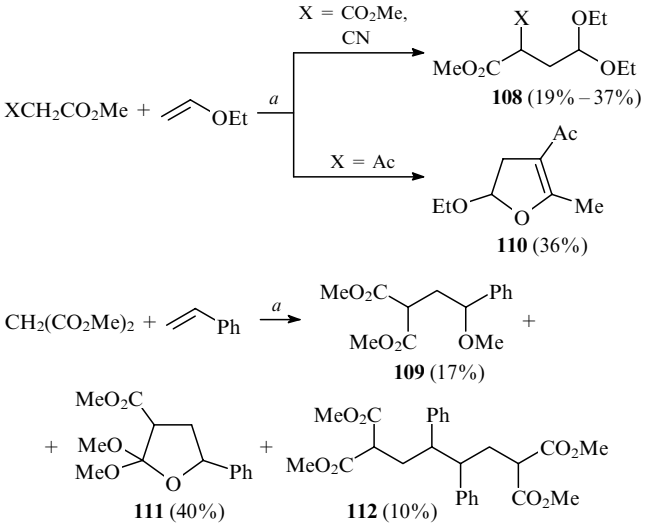
The electrochemical reactions under consideration have been studied in relation to the methylation [147] and trifluoromethylation [148–162] of acrylates,[147–159] methacrolein, vinyl ketones,[147] acrylo- and fumaronitrile,[149,160] esters of fumaric, maleic [151,152] and but-3-enoic acids,[150] alkenes,[148,149,153,154] vinyl acetate,[151,152] isopropenyl acetate, allyl chloride,[153,154] but-3-en-1-ol [161] and undec-10-enoic acid.[162] These reactions are normally carried out in an aqueous solution of a mixture of acetonitrile with partially (to 10%) neutralised acetic or trifluoroacetic acid in a cell with platinum electrodes at an anodic current density of 50–100 mA cm^{-2} and with passage of 1.1–1.5 F of electricity per mole of the acid.[147,159] Methylation and trifluoromethylation of methacrolein, vinyl ketones and acrylates results under these conditions in pairwise and cross coupling of the arising radicals to give 2:2 (**104**, **105**) and 2:1 (**106**) adducts in 40%–80% yields.[147–149,156,157] The decrease in the anodic current density to 1 mA cm^{-2} and a decrease in the temperature from 20 to 0–5 °C directs the reaction of trifluoroacetic acid with methyl methacrylate almost entirely along pathway *c* giving rise to methyl 2-acetamido-2-methyl-4,4,4-trifluorobutanoate (**107**). The compound **107** is formed upon oxidation of the initial radical adducts and the reaction of the resulting carbocations with the solvent (MeCN).[156] This change in the direction of the process is due to the fact that electrooxidation of radical adducts occurs much faster than their dimerisation.[159]



Y = CHO, Ac, CO_2H, CO_2Me, CN; (*a*) R^1 = Me, R^2 = H, 50 mA cm^{-2}; (*b*) R^1 = CF_3, R^2 = H, 50–100 üA·cü$^{-2}$; (*c*) R^1 = CF_3, R^2 = Me, Y = CO_2Me, 1 mA cm^{-2}, 0–5 °C.

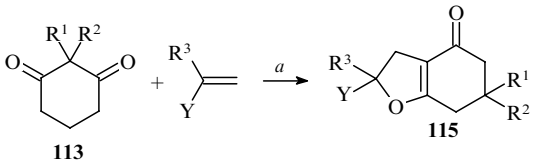
b. Reactions of alkenes with 1,3-dicarbonyl and related compounds

Radical adducts formed by ethyl acetoacetate, diethyl malonate or malononitrile with vinyl ethyl ether or styrene are oxidised at the anode to cationic intermediates, which react with external or internal nucleophiles being thus converted into linear (**108**, **109**) and/or cyclic products (**110**, **111**). The adducts formed with styrene also give dimers **112**.[163]



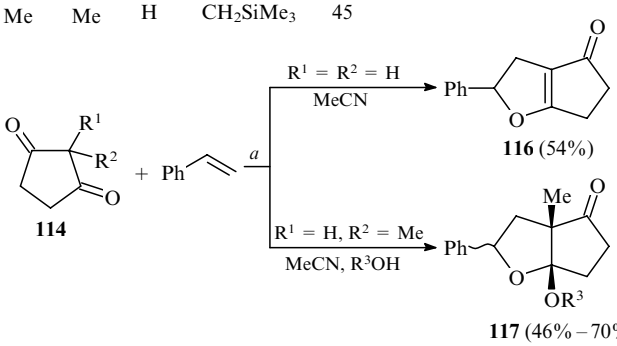
(*a*) ACU, 14 mA cm^{-2}, 1.5 F mol^{-1}, EtOH or MeOH, EtONa or MeONa.

Joint electrolysis of cycloalkane-1,3-diones **113**, **114** with alkenes affords the products of formal [3+2]-cycloaddition, dihydrofuran (**115**, **116**) and tetrahydrofuran (**117**) derivatives.[164–167]



(*a*) ACU, 14 mA cm^{-2}, 1.5 F mol^{-1}, MeCN.

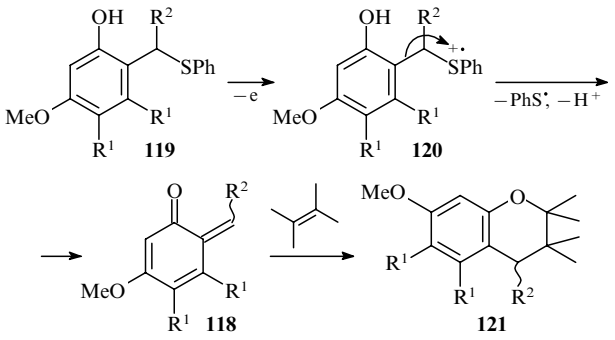
R^1	R^2	R^3	Y	Yield of **115** (%)
H	H	H	Ph	85
H	H	Me	$CH=CH_2$	62
H	H	H	OEt	57
Me	Me	H	Ph	97
Me	Me	H	CH_2SiMe_3	45



R^3 = H, Me; (*a*) ACU, 14 mA cm^{-2}, 1.5 F mol^{-1}.

2. Reactions with electrochemically generated *o*-quinonemethides

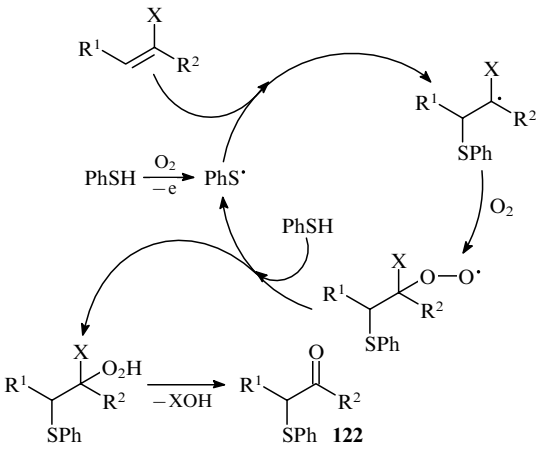
o-Quinonemethides **118** are generated upon the anodic oxidation of *o*-[1-(phenylthio)alkyl]phenols **119** in nitroethane followed by fragmentation of the radical cations **120** thus formed with elimination of the phenylthiol radicals. In the presence of alkenes, which are active acceptors of *o*-quinonemethides, cycloaddition to give chromans **121** takes place.[168,169]



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

3. Arylthiocarbonylation

Electrochemically initiated arylthiocarbonylation is typical of alkenyl sulfides and alkenylsilanes. In this reaction, they are converted into α-phenylthio ketones **122**.[170–172]

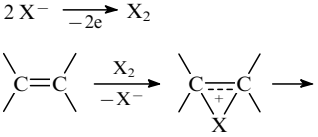


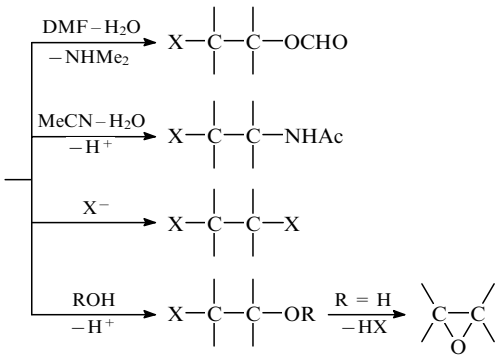
X = SPh, $SiMe_3$; R^1, R^2 = H, Alk.

The reaction is carried out in an undivided cell (at ~20 °C) in acetic acid with Et_4NOTs as the supporting electrolyte in the presence of 2–4 equiv. of benzenethiol with passage of 20 mA current for 1-min periods at 30-min intervals (0.16–1.19 F mol^{-1}) and with bubbling oxygen.

4. Halogenation, halooxygenation, haloacetamidation, epoxidation and other related reactions

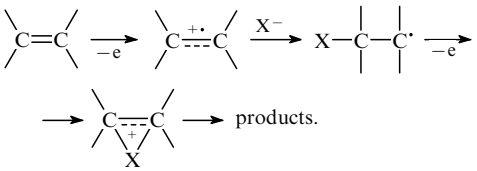
Anodic oxidation initiates halogenation, halooxygenation and related reactions in aqueous MeCN or DMF or in water-alcoholic media, in the presence of chloride, bromide or iodide anions. The halide anions are readily oxidised due to the low oxidation potentials (0.8, 0.4 and 0.2 V *vs.* Ag/Ag^+, respectively), being converted into molecular chlorine, bromine and iodine; these reagents are responsible for alkene halogenation, halooxygenation and haloacetamidation [173–184] and, under certain conditions of electrolysis, epoxidation [184–193] and other related reactions (for example, azidoalkoxylation,[194] oxyselenenation, acetamidoselenenation,[195–198] acetamidosufenation,[199] intramolecular arylthio- and arylseleno-esterification and lactonisation,[200–203] and nitroacetamidation [203,204]).





X = Cl, Br, I.

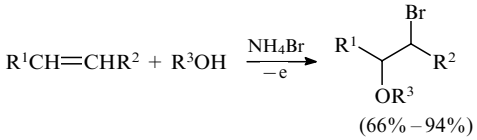
In the case of alkenes activated by electron-donating substituents, competitive formation of these products *via* radical cations is also possible.



Due to the high discharge potential of fluoride anions (2.5 V), fluorination, fluorooxygenation and fluoroacetamidation of alkenes occurs exclusively with participation of radical cations.[205–207]

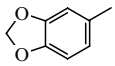
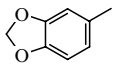
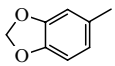
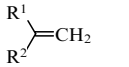
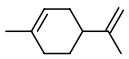
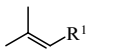
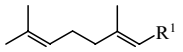
The composition of oxidation products in the presence of hydrogen halide salts depends considerably on the substrate type, the nature of the solvent and electrolysis conditions (Table 7, 8). A highly selective transformation of alkenes into halohydrins and epoxides takes place in water and aqueous acetonitrile or dimethylformamide with participation of bromides; sodium and tetraalkylammonium bromides as well as readily regenerable poly(4-vinylpyridine) hydrobromide are the most effective among them.[192] The selectivity of epoxidation is greatly affected by the medium pH and the anode current density. In a solution of sodium bromide in aqueous acetonitrile, the reaction medium becomes alkaline at the final stage of electrolysis in an undivided cell; this induces the transformation of the bromohydrin formed into the epoxide. Oxidation of an alkene under similar conditions with a small amount of an acid added (normally, sulfuric and hydrochloric acid) permits bromohydrin to be produced in a nearly quantitative yield. In the case of α-arylalkenes (for example, isosafrole), glycols are formed under these conditions due to hydrolysis of α-bromo-β-hydroxyalkylarenes.[184] The selectivity of transformation of alkenes into bromohydrins and epoxides sharply decreases for an anode current density of > 20 mA cm^{-2} and an anode potential of > 1.5 V. For alkenes reactive towards halogen molecules, the optimal values are 1–2 mA cm^{-2} and 0.8 V.[179,180]

Alkene bromoalkoxylation is highly selective in anhydrous alcohols at an anode current density of 100–200 mA cm^{-2} under conditions that ensure complete cathodic reduction of the dihalides formed in a competing reaction to give the initial alkene (graphite anode, nickel cathode, 30 °C, 5.6 F mol^{-1} of electricity) (see Table 8).[182]



R^1 = Alk, Ar; R^2 = H, Alk; R^3 = Me, Et, Pr^i, Bu^t.

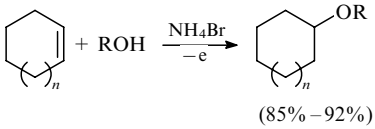
Table 7. Influence of electrolysis conditions on the composition of products of anodic oxidation of acyclic alkenes in the presence of halogen-containing mediators (20–45 °C).

Alkene	R^1	R^2	Mediator	Solvent	Method	Yield of the reaction product (%) [a]			Ref.
						mono-halide	dihalide	epoxide	
$R^1CH=CHR^2$	Alk	H	HCl	H_2O	A	(85–90)	(10)	–	173
	CH_2Cl	H	HCl	H_2O	A	(85–90)	(10)	–	173
	Alk	H	NaBr	H_2O	B	60 (90)	–	–	174
	Alk	Alk	NaX (X = Cl, Br)	H_2O	B	–	–	65–88	186–189
	Bn	Me	Et_4NBr, $NaClO_4$	MeOH	B	(50)	(35)	–	177
	Bn	Me	Et_4NI, $LiClO_4$	MeCN–H_2O	B	(51)	–	–	177
	Ph	Me	Et_4NCl, $LiClO_4$	MeCN–H_2O	C	65	–	–	178
	Ph	Me	Et_4NCl, $LiClO_4$	DMF–H_2O	C	85	–	–	178
	(*E*)-Ph	Ph	Et_4NCl, $LiClO_4$	MeCN–H_2O	C	–	65	–	178
	(*E*)-Ph	Ph	Et_4NCl, $LiClO_4$	DMF–H_2O	C	47	23	–	178
	(*E*)-Ph	Ph	$Et_4NF\cdot 3HF$	MeCN	B	34	–	–	205–207
	Ph	H	$Et_4NF\cdot 3HF$	MeCN	B	40	traces	–	206
	Ph	H	Et_4NCl, $LiClO_4$	DMF–H_2O	C	75	–	–	178
	Ph	H	NH_4Cl	MeOH–MeCN	D	95 (35)	–	–	182
	Ph	H	NH_4Br	ROH	D	65–78	–	–	182
		Me	NaBr	MeCN–H_2O	E	23 [c]	–	71	184
		Me	NaBr, H_2SO_4	MeCN–H_2O	E	~100	–	–	184
		Me	NaX (X = Cl, I)	MeCN–H_2O	E	39–43 [c]	–	–	184
	Me	Me	HCl	H_2O	A	(85–90)	10	–	173
	Alk	H	see [b]	DMF–PhH–H_2O	E	–	–	80	192
	$Cl(CH_2)_{10}$	H	see [b]	DMF–PhH–H_2O	E	–	–	62	192
	Ph	Ph	$Et_4NF\cdot 3HF$	MeCN	B	0–21	48–63	–	205–207
	Bn	H	NH_4Br	MeOH	D	93	–	–	182
	Bn	H	NH_4Br	EtOH	D	63	–	–	182
	Bn	Me	NH_4Br	MeOH	D	94	–	–	182
	H	OMe	NH_4X (X = Cl, Br)	$MeO(CH_2)_2OH$	E	87–92	–	–	180
	H	OMe	NH_4I	$MeO(CH_2)_2OH$	E	60	–	–	180
	H	OBu^n	NaN_3–NH_4OTs	MeOH	G	66–81 [d]	–	–	194
	Me	OMe	NaN_3–NH_4OTs	MeOH	G	82 [d]	–	–	194
			Et_4NBr, $LiClO_4$	MeOH	C	50	–	–	176
	CH_2OAc		NaCl, HCl	$Cl(CH_2)_2Cl$–H_2O (2:1)	E	85	–	–	179
	CO_2H		NaCl, HCl	CH_2Cl_2–H_2O	E	55	–	–	179
	CO_2Me, CH_2OAc, CH_2SO_2Ph		MBr (Na, K, Li)	MeCN–H_2O (5:1)	E	–	–	75–91	190, 191
			Et_4NBr	MeCN–H_2O (5:1)	E	–	–	82	190, 191

Note. Method A: ACU, PbO_2 anode, 50–200 mA cm^{-2}; method B: PCU, Pt anode, 0.4–1.5 V; method C: ACU, Pt anode, 20 mA cm^{-2}, 2.0 F mol^{-1}; method D: ACU, graphite anode, 110 mA cm^{-2}, 5.6–9.5 F mol^{-1}; method E: ACU, Pt anode, 6–13 mA cm^{-2}, 4–10 F mol^{-1}; method F: ACU, Pt anode, 0.3–6.0 mA cm^{-2}, 2.1–3.5 F mol^{-1}; method G: ACD, graphite anode, 25 mA cm^{-2}, 3.0 F mol^{-1}.

[a] Substance yield (in parentheses, current yield); [b] poly(4-vinylpyridine) hydrobromide; [c] 1-[3,4-(methylenedioxy)phenyl]propane-1,2-diol; [d] α-azido ketone ketal.

When the quantity of electricity increases to 10–14 F mol^{-1} and the nickel cathode is replaced by a brass one, or by a nickel cathode coated with powdered Raney nickel, not only dibromide but also the bromo ether formed is reduced. The reaction yields ethers and thus it can formally be regarded as a very facile and effective method for the addition of alcohols to alkenes.[63, 208]



(85%–92%)

n = 1, 2, 7; R = Me, Et, CH_2CH_2OMe.

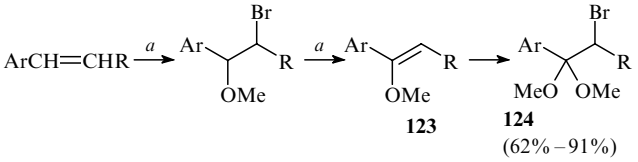
Table 8. Influence of electrolysis conditions on the composition of products of anodic oxidation of cyclic alkenes in the presence of halogen-containing mediators (20–45 °C).

Alkene	R^1	R^2	Mediator	Solvent	Method	Yield of the reaction product (%) (see [a])		Ref.
						mono-halide	dihalide	
	1	H	NH_4Br	MeOH	A	75	–	63, 182
	1	H	Et_4NBr	MeOH	B	54	14	175
	1	H	Et_4NCl	$MeCN-H_2O$	B	40	–	175
	1	H	Et_4NBr	$MeCN-H_2O$	B	–	68	175
	1	H	I_2, $LiClO_4$	$MeCN-H_2O$	C	(85)	–	177
	1	H	Et_4NCl	$DMF-H_2O$	B	58	22	175
	1	H	Et_4NBr	$DMF-H_2O$	B	16	64	175
	1	H	$Et_4NBr-(PhSe)_2$	$MeOH-H_2SO_4$	D	95–98	–	196
	1	H	$Et_4NBF_4-(PhSe)_2$	MeCN	C	77	–	197
	1, 2, 7	OMe	NH_4X (X = Cl, Br, I)	MeOH	E	85–94 [b]	–	180
	1, 2, 7	OAc	NH_4X (X = Cl, Br)	$MeCN-H_2O$	E	55–95 [c]	–	180
	1, 2, 3, 7	OAc	NaN_3-NH_4OTs	MeOH	F	67–83 [d]	–	194
	7	$OSiMe_3$	NH_4I	$MeCN-H_2O$ (3 : 1)	E	97 [c]	–	180
			MBr (M = Li, K, Na)	MeOH	E	69–74	–	180
			NH_4X (X = Br, I)	MeOH	E	93–96	–	180
			NH_4Cl	MeOH	E	60	–	180
			Et_4NBr	MeOH	E	97	–	180
			NaN_3-NH_4OTs	MeOH	F	60 [d]	–	194
			NaBr	MeOH	A	66	–	182

Note. Method A: ACU, graphite anode, 110 mA cm^{-2}, 5.6–9.5 F mol^{-1}; method B: potentiostatic conditions, a divided cell (PCD), Pt anode, 0.8–1.3 mA cm^{-2}; method C: PCU, Pt anode, 0.4–1.5 V; method D: ACU, Pt anode, 6–13 mA cm^{-2}, 4–10 F mol^{-1}; method E: ACU, Pt anode, 0.3–6.0 mA cm^{-2}, 2.1–3.5 F mol^{-1}; method F: ACD, graphite anode, 25 mA cm^{-2}, 3.0 F mol^{-1}.

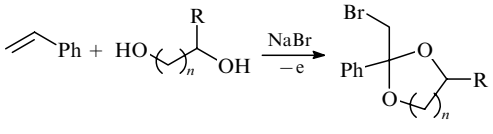
[a] Substance yield (in parentheses, current yield); [b] α-halocycloalkanone dimethyl ketals. [c] α-halocycloalkanones. [d] α-azido ketone ketal.

In more profound electrooxidation of arylalkenes in the sodium bromide electrolyte, the bromo ethers formed are dehydrobrominated and the resulting enol ethers **123** are converted into α-bromoalkyl aryl ketone dimethyl ketals **124** under the action of methanol and bromine.[63, 209]



R = H, Alk; (*a*) ACU, Pt anode, brass cathode, 220 mA cm^{-2}, 9 F mol^{-1}, MeOH, NaBr, 60 °C.

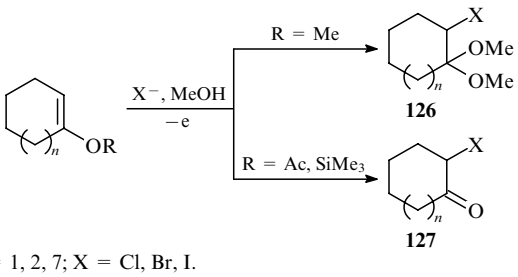
Electrolysis of styrene in ethylene-, 1,3-propylene- or 1,3-butylene glycol gives rise to cyclic ketals of bromomethyl phenyl ketones **125**.[63]



125 (66%–80%)

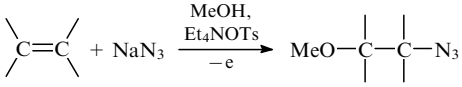
n = 1, 2; R = H, Me.

Anodic oxidation of enol ethers in the presence of ammonium bromide yields ketals of α-halo ketones **126**. When lithium, sodium, or potassium bromide is used, the yield of the ketals decreases by 20%–30%. α-Halo ketones **127** are formed in 55%–97% yields from enol acetates and trimethylsilyl ethers under similar conditions (see Table 8).[180]



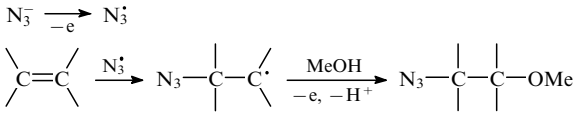
n = 1, 2, 7; X = Cl, Br, I.

Other reactions induced by anodic oxidation proceed similarly to electrochemical halooxygenation and haloacetamidation of alkenes. For example, azidomethoxylation of alkenes is documented.[194]

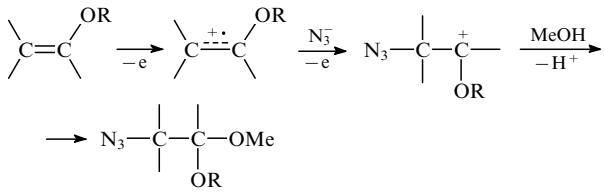


Two mechanisms have been proposed for this reaction, namely, pathway *a* for non-activated alkenes and pathway *b* for activated alkenes.[194]

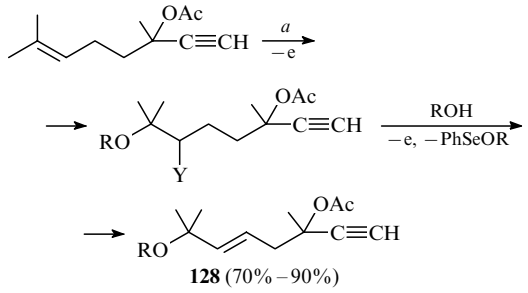
Pathway *a*



Pathway *b*



Alkene oxyselenenation – deselenenation results in allyl ethers such as **128**.[195, 196]

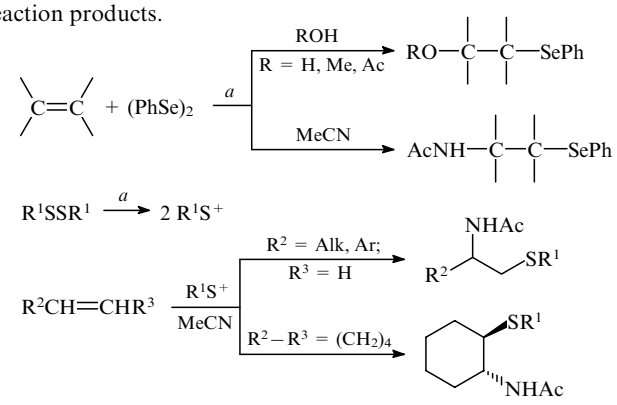


128 (70% – 90%)

R = H, Me; Y = SePh, Se(O)Ph; (*a*) ACU, Pt anode, 10 – 20 mA cm^{-2}, ROH or MeCN – H_2O, 0.1 equiv. $(PhSe)_2$, 1.5 equiv. $MgSO_4$, 60 – 70 °C.

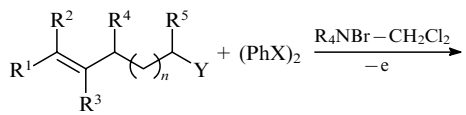
Electrolysis of alkenes in the presence of diselenides and disulfides is accompanied by hydroxy-, alkoxy- and acetamidoselenenation [196 – 198] and acetamidosulfenation.[199]

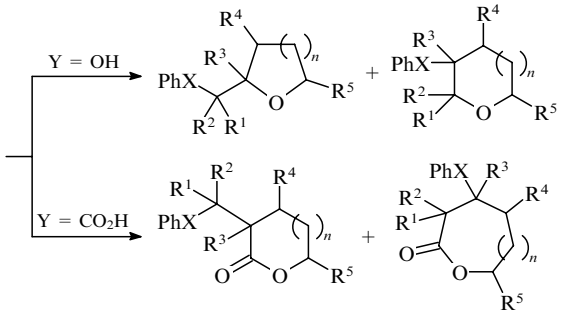
Hydroxy-, alkoxy- and acetamidoselenenation reactions are initiated by electrogenerated halogenonium ions. Under the action of these species, diphenyl diselenide and diphenyl sulfide are converted into phenylselenenyl and phenylsulfenyl halides. These electrophilic intermediates add to alkenes, and the resulting adducts react with external or internal nucleophiles to give reaction products.



(*a*) ACU, Pt anode, 6.7 – 13 mA cm^{-2}, MeOH, AcOH, MeCN – H_2O, $Et_4NX - H_2SO_4$ (X = Cl, Br, I).

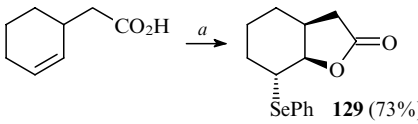
Unsaturated alcohols and acids undergo intramolecular arylthio and arylseleno esterification and lactonisation during electrolysis in the presence of disulfides and diselenides.[200 – 203] The reaction mechanism is similar to the mechanism of electrochemical alkoxyselenenation and acetamidosulfenation.





R^1, R^2, R^3, R^4, R^5 = H, Me; $R^1 - R^2$ ùöù $R^1 - R^3 = (CH_2)_m$ (m = 2, 3); n = 0, 1, 2; Y = OH, CO_2H; X = S, Se.

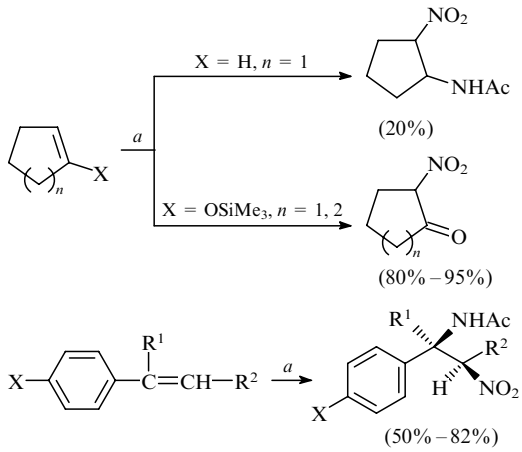
Electrochemical intramolecular phenylthio and phenylseleno esterification and lactonisation of unsaturated alcohols and carboxylic acids proceed with high selectivity (50% – 86%) only in the case where five- and six-membered rings are formed. If the substrate double bond is endocyclic as, for example, in cyclohexen-3-ylacetic acid, stereospecific *trans*-addition of phenylsulfenyl and phenylselenenyl halides takes place to give *cis*-fused bicyclic system **129**.[201, 202]



129 (73%)

(*a*) ACU, graphite anode, Cu cathode, 400 mA cm^{-2}, 6 F mol^{-1}, MeOH, 0.5 equiv. $(PhSe)_2$, NH_4Br, 15 – 20 °C.

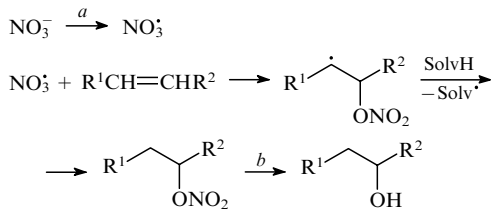
Nitronium tetrafluoroborate resulting from anodic oxidation of N_2O_4 in MeCN adds to alkenes to give nitroacetamidation products.[203, 204]



X = H, Br; R^1 = H, Me; R^2 = H, Me, Ph;
(*a*) $NO_2^+ BF_4^-$ (0.25 mol litre^{-1} in MeCN), – 70 °C.

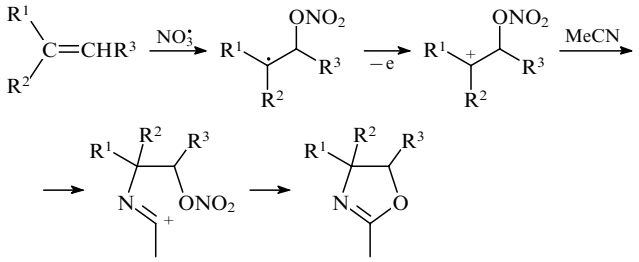
5. *o*-Nitration and diacylation

Electrochemical *o*-nitration and diacylation involve the nitrate radical NO_3 generated by the anodic oxidation of the nitrate anions.[210] In the presence of terminal alkenes and cycloalkenes, the nitrate radicals add to them, and the resulting radical adducts are converted into alkyl nitrates upon detachment of hydrogen atoms from the solvent. The resulting alkyl nitrates are transformed into the corresponding alcohols without isolation.[211]



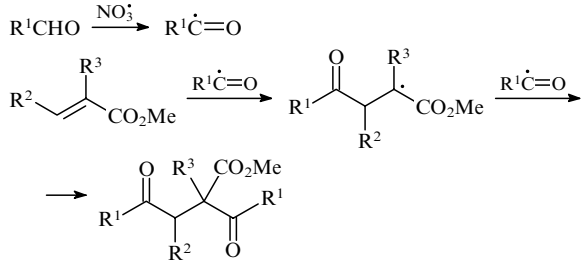
R^1 = Alk, R^2 = H; R^1-R^2 = $(CH_2)_m$ (m = 4, 6); (*a*) ACU, Pt anode, 50 mA cm^{-2}, 8 F mol^{-1}, $MeCN-H_2O-Et_2O$ (10 : 2 : 1), $LiNO_3$, 10 °C; (*b*) NaSH.

Under similar conditions of electrolysis, 1,1-di- and 1,1,2-trisubstituted alkenes furnish oxazoline derivatives.[211]



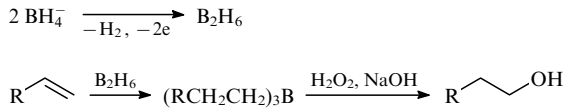
R^1 = Me, Et, n-C_9H_{19}; R^2 = Me, Et; R^3 = H, Me.

In the case where the reaction mixture contains, apart from nitrate (usually, lithium, ammonium, sodium, or potassium nitrate) and alkene, an aldehyde in a concentration sufficient for trapping nitrate radicals, diacylation of the alkene takes place.[212]



6. Hydroboration

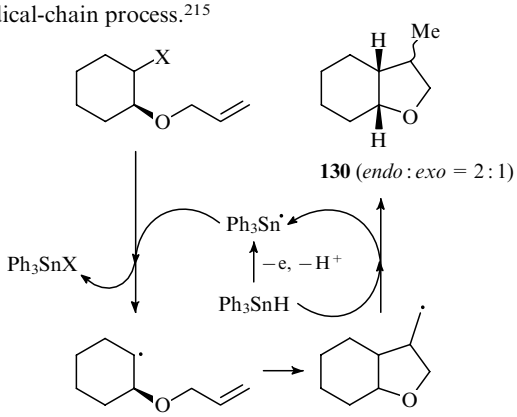
Electrochemical hydroboration of alkenes includes two stages, namely, electrogeneration of diborane from borohydride anions and addition of the diborane formed *in situ* to alkenes to give trialkylboranes; treatment of these products with hydrogen hydroperoxide in an alkaline medium results in alkanols.[213,214]



Hydroboration is carried out with the sodium iodide electrolyte under galvanostatic conditions in an undivided cell with a platinum anode and a steel cathode by passing 2 F of electricity per mole of alkene. The reaction is regio- and stereoselective and gives products in high yields. This procedure has been used to prepare primary alkanols from unsaturated and hydroxy- and acetoxy-substituted terminal alkenes (yields 64%–81%), cycloalkanols from cycloalkenes (70%–72%), (−)-*cis*-myrtanol from (−)-β-pinene (82%), *exo*-borneol from norbornene (72%), *etc*. The method is promising for organic synthesis. The electrogenerated diborane can also reduce carboxylic acids to the corresponding alcohols.[214]

7. Electrochemical cyclisation assisted by tin hydrides

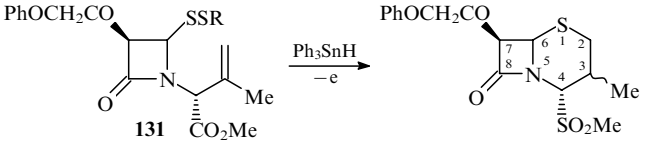
The electrochemical cyclisation assisted by tin hydrides is illustrated by transformation of 2-halocyclohexyl allyl ethers into octahydro-3-methylbenzofuran **130** (yield 65%). Tin hydrides act in this reaction as precursors of tin-centred radicals and as hydrogen atom donors, while the electric current initiates this radical-chain process.[215]



130 (*endo* : *exo* = 2 : 1)

X = Br, I; (*a*) ACD, Pt electrodes, 10 mA cm^{-2}, 0.2–0.5 F mol^{-1}, THF, Bu_4NBF_4, 1.2 equiv. Ph_3SnH, ~20 °C.

Similarly, octahydro-3-methylidenebenzofuran was prepared from 2-halocyclohexyl propargyl ethers (65%–69%), β-lactam derivative **131** was converted into dihydrocephalosporin **132**.



132 (80%, 3α : 3β = 1 : 2)

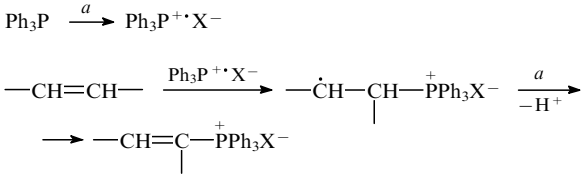
R is 2-benzothiazolyl.

These reactions can also be carried out in undivided cells. However, complete conversion of the substrate in an undivided cell required a four times greater quantity of electricity.

An advantage of the electrochemical method over the chemical methods in which azoisobutyronitrile, benzoyl peroxide, trialkylboranes, *etc*., serve as initiators[216,217] is higher stereoselectivity.

8. Phosphorylation

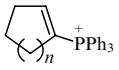
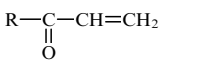
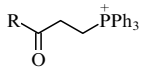
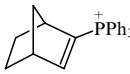
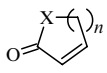
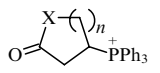
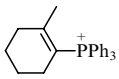
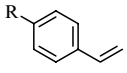
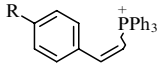
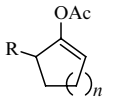
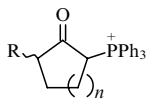
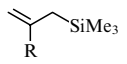
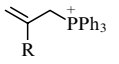
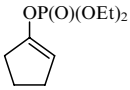
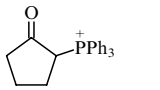
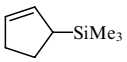
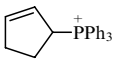
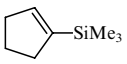
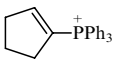
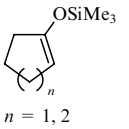
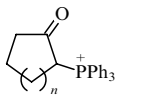
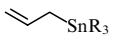
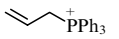
Indirect electrochemical phosphorylation of alkenes and cycloalkenes occurs upon the electrophilic addition of triphenylphosphinium radical cations generated by anodic oxidation of triphenylphosphine followed by electrooxidative deprotonation of the adduct thus formed. The reaction yields 1-alkenyl- and 1-cycloalkenyl-substituted triphenylphosphonium salts.[18,218–220]



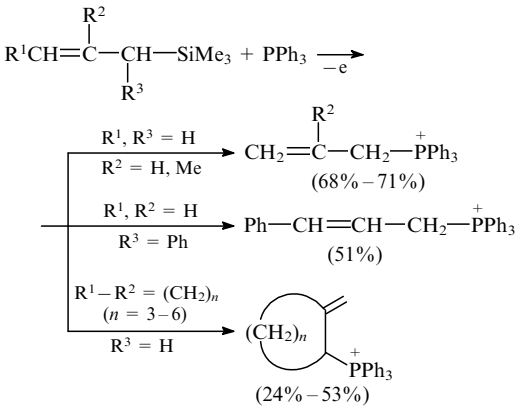
X = ClO_4, BF_4; (*a*) X^-, ACU, graphite anode, Fe cathode, 1.07 mA cm^{-2}, 2 F mol^{-1}, CH_2Cl_2, 0.2 equiv. Ph_3P, 0.5 equiv. 2,6-LutHClO$_4^-$ or 1.33 equiv. K_2CO_3, N_2 atmosphere, ~20 °C.

This reaction has been used to prepare phosphonium salts from ethylene, C_5-C_8 cycloalkenes, norbornene, substituted styrenes, vinyl and allylsilanes, α,β-unsaturated compounds, *etc*. (Table 9).[218–225] When vinyl- and allylsilanes are used, desilylation of the adducts formed initially takes place, and phosphorylated alkenes are formed as the reaction products.[220–222]

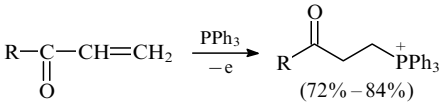
Table 9. Electrochemical triphenylphosphorylation of alkenes.

Alkene	Method	Reaction product	Yield (%)	Ref.	Alkene	Method	Reaction product	Yield (%)	Ref.
 $n = 1-4$	A		50–60	219–221	 R = H, Me, Et, NH_2, OEt	B		55–84	221, 224
	A		65	219–221	 X = CH_2, n = 1, 2; X = O, n = 2	B		61–67	221, 224
	A		40	220, 221					
 R = H, Me	A		80–100	220, 221	 R = H, Me; n = 1–3	C		47–96	221, 225
 R = H, Me	B		68–71	220, 221		C		23–51	221, 224
	B		21	221–223					
	B		24	221–223	 n = 1, 2	C		11–30	221, 224
	B		61	221–223					

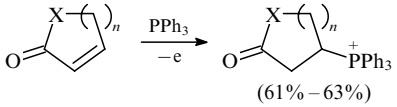
Note. Method A: ACU, graphite anode, stainless-steel cathode, 1.07 mA cm^{-2}, 2 F mol^{-1}, CH_2Cl_2, 0.2–1 equiv. of Ph_3P, 0.5 equiv. of 2,6-$LutHClO_4$ or 2,6-$LutHBF_4$, ~20 °C; method B: ACU, glass carbon anode, Pb cathode, 1.1 mA cm^{-2}, 1.8 F mol^{-1}, CH_2Cl_2, 2 equiv. of Ph_3P, 0.5 equiv. of 2,6-$LutHClO_4$ or 2,6-$LutHBF_4$, K_2CO_3, ~20 °C; method C: ACU, glass carbon anode, Pb cathode, 1 mA cm^{-2}, 2 F mol^{-1}, MeCN, 1–3 equiv. of Ph_3P, 0.5 equiv. of $LiBF_4$, N_2 atmosphere, ~20 °C.



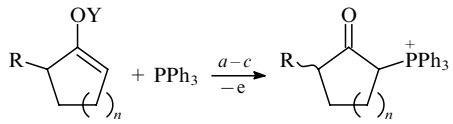
Electrochemical reactions of triphenylphosphine with vinyl ketones, acrolein, cycloalk-2-enones, ethyl acrylate, acrylamide [220, 223] and cycloalkenol ethers [220, 224] give rise to phosphorylated ketones.



R = H, Me, Et, EtO.



X = CH_2O, n = 1, 2.



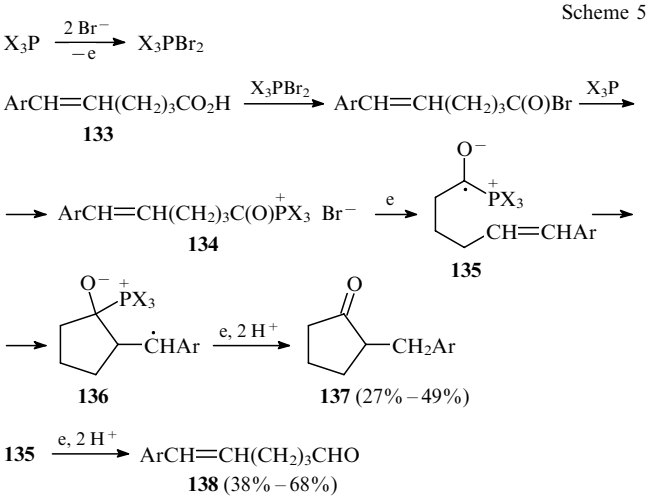
R = H, Me; n = 1–3; (*a*) Y = Ac (47%–96%); (*b*) Y = $P(O)(OEt)_2$ (23%–51%); (*c*) Y = $SiMe_3$ (11%).

Electrochemical phosphorylation of carboxy-substituted alkenes **133** by phosphines with Bu_4NBr as the supporting electrolyte results in acylphosphonium salts **134**, which are readily reduced at the cathode under the conditions of diaphragmless electrolysis to give intermediates **135**. These undergo radical cyclisation, electroreduction and protonation and are thus converted first into cyclic intermediates **136** with separated anionic, cationic and radical centres and then into cyclopentanones **137**. The reaction is carried out in an undivided cell (graphite electrodes, 2.4 mA cm^{-2}, 4 F mol^{-1}, CH_2Cl_2, 3 equiv. of X_3P (X = Ph, Bu^n), 1 equiv. of Bu^n_4NBr, 2 equiv. of $MeSO_3H$). Together with cyclopentanones **137**, aryl-substituted alkenals **138** are produced (Scheme 5).[225]

This electrochemical reaction is an example of successful use in organic synthesis of paired electrolysis in which the processes occurring at both the cathode and the anode are involved in the assembling of the final product.

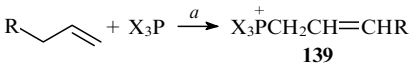
By phosphorylation of alk-1-enes with the phosphines X_3P in the presence of thiols RSH (R = Pr^n, Bu^n) under conditions of electrolysis differing substantially from those used in the studies cited above,[218–225] alk-2-enylphosphonium salts **139** have been

Scheme 5



X = Ph, Bu^n; Ar = 4-YC_6H_4, Y = H, Me, MeO, Cl, Br.

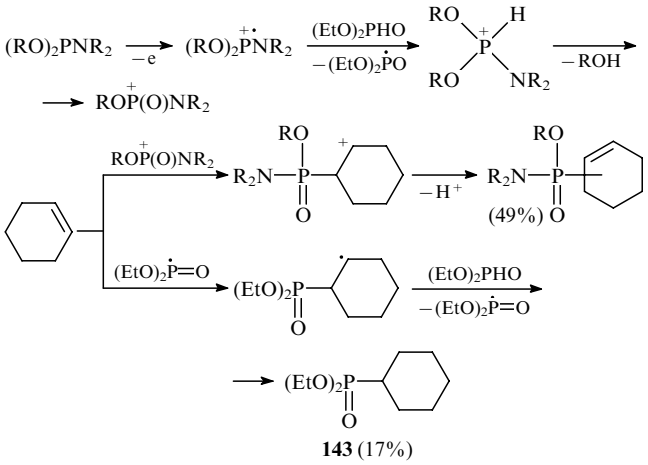
prepared (yields 46%–85%). The products of alkene thioalkylation are formed as side products.[226]



R = n-C_5H_{11}, n-C_6H_{13}; X = Mes, Bu^n; (*a*) ACD, Pt anode, Ni cathode, 4 mA cm^{-2}, 2.2–4.8 F mol^{-1}, MeCN, 0.05 equiv. X_3P, 0.75 equiv. RSH, 0.5 equiv. $NaClO_4$, 0.6 equiv. Na_3PO_4.

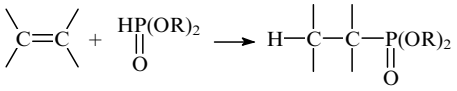
The processes of regiospecific phosphorylation of alkenes presented in Table 9 take place only with triphenylphosphine. If it is replaced by trialkylphosphines, trialkyl phosphites, dialkyl trimethylsilyl phosphites or phosphorous amides, the reactions yield mixtures of phosphorylation products with different positions of the C=C bond in the alkenyl or cycloalkenyl fragment. For example, electrolysis of Et_3P, Pr^n_3P or Bu^n_3P in the presence of cycloalkenes gives rise to regioisomeric cycloalkenyl phosphonium salts with the double bond in positions 1, 2 or 3.[227] This difference between the behaviours of triphenylphosphine and other phosphines in this reaction is related, in the researchers' opinion, to higher thermodynamic stability of alk-1- and cycloalk-1-enyltriphenylphosphonium salts compared to the corresponding trialkylphosphonium salts caused by the effective stabilisation of the positive charge with participation of the π-systems of the phenyl groups. Phosphorylation of hex-1-ene and cyclohexene with trialkyl and dialkyl trimethylsilyl phosphites gives rise to three types of isomeric products, while the reactions involving phosphorous mono- and diamides, yield two types of isomers.[228,229] Phosphorous amides are more basic than alkyl phosphites; thus, they can bind more efficiently the protons generated during the electrolysis, and the prototropic isomerisation of the intermediates is suppressed (Scheme 6).[229]

The yields of alk(cycloalk)-2-enylphosphonates of type **140**, **141** are 2–4 times as high as the yields of other regioisomers. In some cases, they are formed as the only products.[228,229] In the presence of diethyl phosphite or *O*,*O*-dibutyl phosphorothioite as a mediator which changes the nature of the phosphorus-containing active intermediates, the regiodirectivity of phosphorylation of alkenes by phosphorous mono- and diamides changes towards the predominant formation of alk(cycloalk)-1-enyl-substituted phosphonamidates of type **142**. For example, cyclohexenyl phosphonamidates **141** and **142** (1:2 ratio) were prepared in the presence of diethyl phosphite, together with the side product diethyl cyclohexylphosphonate (**143**).[229]



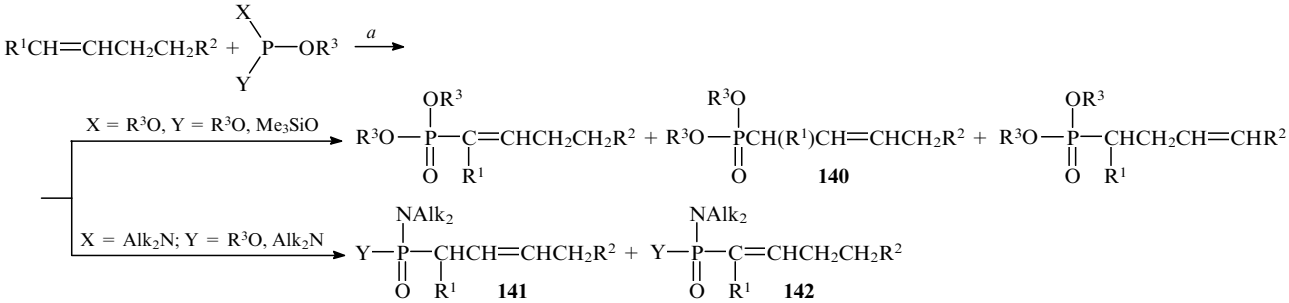
9. Hydrophosphonylation and hydrothiophosphonylation

Indirect electrochemical hydrophosphonylation of alkenes with dialkyl phosphites takes place in the presence of trialkylphosphines, trialkyl and dialkyl trimethylsilyl phosphites [Bu^n_3P, $(Pr^iO)_3P$, $(EtO)_2POSiMe_3$].[230]



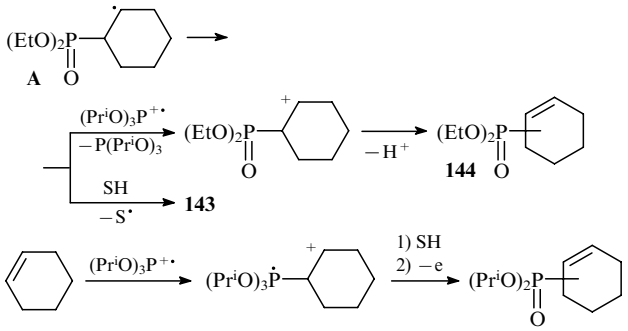
The promotory effect of these compounds is based on electric generation of the radical cations $X_3P^{+\bullet}$ at potentials at which dialkyl phosphites and alkenes are electrochemically inactive (0.8–1.6 V). The products of hydrophosphonylation are formed upon the detachment of hydrogen atoms from dialkyl phosphites by the $X_3P^{+\bullet}$ radical cations and subsequent addition of the generated $(RO)_2P(O)^{\bullet}$ radicals to alkenes. A chain transfer takes place in the reaction between the radical adducts and dialkyl phosphites.[230] The products of hydrophosphonylation of alkenes, for example, cyclohexene,[230] are formed selectively only with the assistance by trialkylphosphines.

Scheme 6

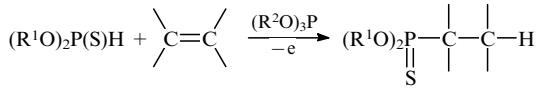


R^1, R^2 = H, Bu^n; R^1-R^2 = $(CH_2)_2$; R^3 = Alk; (*a*) ACD, Pt anode, 0.1–8 mA cm^{-2}, 1.1–1.7 F mol^{-1}, MeCN, 5–6 equiv. of alkene, 0.25 equiv. $NaClO_4$, 8 equiv. Na_3PO_4.

Trialkyl and dialkyl trimethylsilyl phosphite-initiated reactions give rise to saturated and unsaturated phosphonates derived from the mediator and the dialkyl phosphite. The triisopropyl phosphite-assisted reaction of cyclohexene with diethyl phosphite yields eight products including diethyl and diisopropyl cyclohexyl-, cyclohex-1-enyl-, cyclohex-2-enyl- and cyclohex-3-enylphosphonates. Presumably,[230] this is due to active oxidation of the intermediate radical adducts **A** by the radical cations generated from triisopropyl phosphite and to addition of the latter species to cyclohexene.

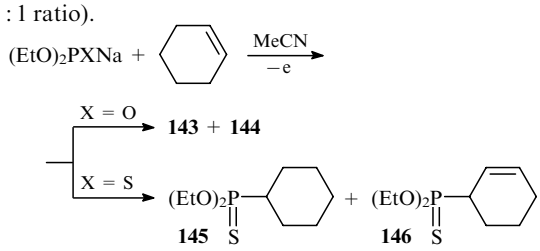


Similarly, the radical cations electrogenerated from trialkyl phosphites initiate hydrothiophosphonylation of alkenes with *O*,*O*-dialkyl phosphorothioites.[231,232]



R^1 = Et, Pr^i, Bu; R^2 = Alk.

Joint electrolysis of alkenes with dialkyl phosphites or *O*,*O*-dialkyl phosphorothioites or with their sodium or lithium salts affords mixtures of alkene hydrophosphonylation (hydrothiophosphonylation) products and the products of substitution of the diethoxyphosphoryl or -thiophosphoryl group for the allylic hydrogen atom.[231–235] Thus the reaction of cyclohexene with sodium diethyl phosphite yields diethyl cyclohexyl- and cyclohexenylphosphonates **143** and **144** (overall yield 52%, 2 : 1 ratio).[232,233] A similar reaction with sodium *O*,*O*-diethyl phosphorothioite gives compounds **145** and **146** in a total yield of 87% (11 : 1 ratio).



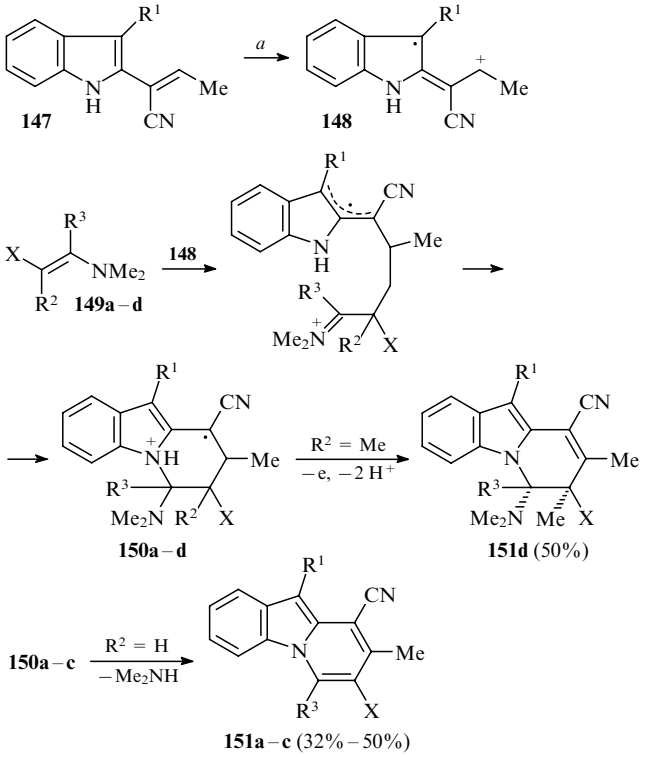
X = O, S.

In the reactions of alkenes with dialkyl phosphorothioites, the formation of phosphorylation products is completely suppressed when a 1 : 1 acetonitrile – THF mixture is used as the solvent.[232]

10. Radical-cation [4 + 2]-cycloaddition of styrenes and enamines to vinylindoles and -pyrroles induced by anodic oxidation

The radical-cation [4 + 2]-cycloaddition reactions have been vigorously studied during the last two decades. Owing to the very low activation barriers, they proceed tens or hundreds times as fast as the ordinary Diels – Alder reactions; hence, they can be performed under milder conditions. The radical-cation [2 + 4]-cycloaddition is highly regio- and chemoselective. Moreover, they can be carried out for dienophiles with electron-donating substituents at the double bond, which do not enter into conventional Diels – Alder reaction. There are strong grounds for believing that they will find extensive application in organic synthesis.[236]

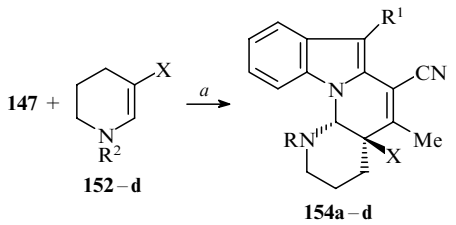
The [4 + 2]-cycloaddition of enamines to 2-vinylindoles or -pyrroles acting as dienes induced by anodic oxidation[237–240] proceeds efficiently only in the case where the difference between the oxidation potentials of dienophiles and dienes does not exceed 500 mV.[241] To avoid polymerisation, there should not be hydrogen atoms at the 3-position of the pyrrole or indole ring. The radical-cation cycloaddition of enamines to 2-vinylindoles **147** includes generation of radical cations **148** at the anode, their addition to enamines **149a–d** and subsequent cyclisation, electrooxidation and deprotonation of the radical-cation cycloadducts **150a–d** to give cycloaddition products **151a–d**.[239,240] The structure and the yield of the reaction product depend most of all on the structure of the initial substrates. Electrolysis of 2-vinylindoles **147** together with methyl β-(*N*,*N*-dimethylamino)acrylate (**149a**) or substituted β-(*N*,*N*-dimethylamino)acrylonitriles **149b–d** affords compounds of the pyrido[1,2-*a*]indole series (**151a–d**), which are of interest as building blocks in the synthesis of indole alkaloids.[237,239]



(*a*) PCU, graphite anode, 0.49 – 0.67 V, CH_2Cl_2 – MeCN (1 : 1) or MeCN, 0.1 equiv. $LiClO_4$.

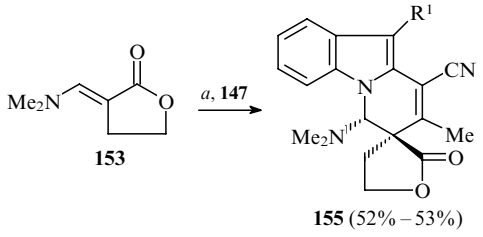
Compounds **149–151**	R^1	R^2	R^3	X	Yield of **151** (%)
a	Me	H	H	CO_2Me	90–91
b	CH_2CH_2OEt	H	H	CO_2Me	62
c	Me	H	Me	CN	68
d	Me	Me	H	CN	53

Cycloaddition of the indoles **147** to 1,4,5,6-tetrahydropyridines **152a–d** or to α-(*N*,*N*-dimethylaminomethylene)butyrolactone (**153**) results in tetracyclic compounds **154a–d**, **155** of the indolo[1,2-*a*]pyridine series incorporating the skeleton of pyrrocoline alkaloids such as goniomitine.[238,239]



152–d **154a–d**

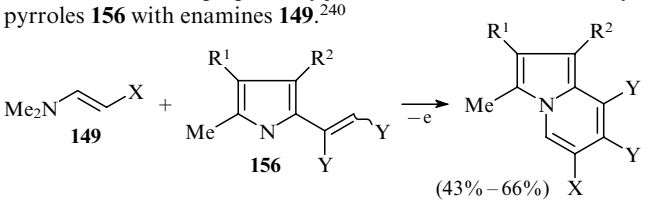
Compound **154**	R^1	R^2	X	Yield (%)
a	H	Me	CO_2Me	91
b	Me	Me	CO_2Me	62
c	H	Me	CN	68
d	H	CH_2CH_2OEt	CN	53



153 **155** (52%–53%)

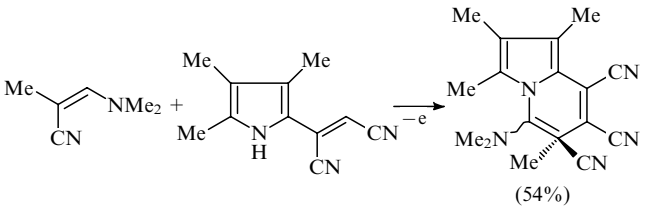
(*a*) PCU, graphite anode, 0.49–0.67 V, CH_2Cl_2–MeCN (1 : 1) or MeCN, 0.1 equiv. $LiClO_4$.

Polysubstituted indolizines, difficult to synthesise by other methods, have been prepared by joint electrooxidation of 2-vinylpyrroles **156** with enamines **149**.[240]

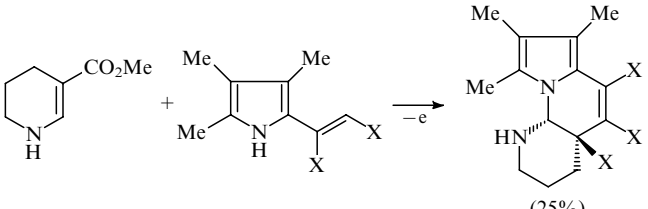


149 **156** (43%–66%)

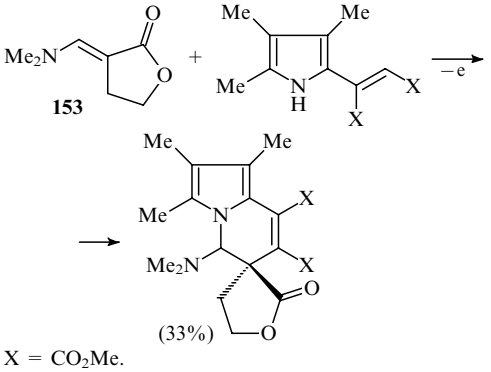
X = CO_2Me, CN, NO_2; Y = CO_2Me, CN; R^1, R^2 = Me, CO_2Me.



(54%)



(25%)



153 (33%)

X = CO_2Me.

The tentative asynchronous mechanism of the radical-cation cycloaddition[241,242] allows the formation of the final product as a mixture of *cis*- and *trans*-isomers because rotation around the C–C bond in the initial radical-cation adduct is possible. The formation of only *trans*-isomers indicates that cyclisation occurs much faster than the rotation around the C–C bond. Stabilisation of the radical intermediates by radical-stabilising substituents such as nitrile or alkoxycarboxyl group is favourable for the reaction.[238,239]

11. Reactions of alkenes induced by electrooxidation of variable-valence metal compounds

Compounds of variable-valence metals (manganese, copper, palladium, ruthenium, nickel, cobalt, cerium, and thallium) act in electrochemical processes as mediators (Med) and participate in the electron transfer at the anode and in the reaction of the oxidised form of the mediator (Med_{ox}) with the substrate (RH). The reaction between RH and Med_{ox} can follow two pathways, one giving rise to a radical cation (pathway *a*) and one giving rise to a radical (pathway *b*).

Pathway *a*

$$RH \xrightarrow[-Med]{Med_{ox}} RH^{+\bullet} + Med \xrightarrow[-H^+]{} R^{\bullet} \longrightarrow \text{products}$$

Pathway *b*

$$RH \xrightarrow{Med_{ox}} R^{\bullet} + MedH^+ \xrightarrow{B} Med + BH^+$$

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

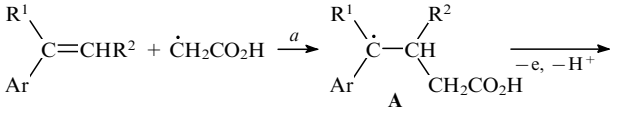
B is proton acceptor.

In many cases, compounds and complexes of variable-valence metals are used in these processes as binary mediator systems in combination with other mediators including organic compounds (CH acids, benzoquinone or triarylamines).

a. Reactions induced by electrooxidation of manganese compounds

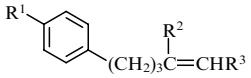
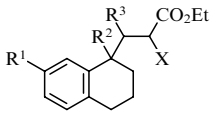
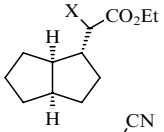
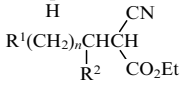
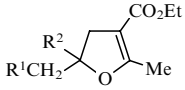
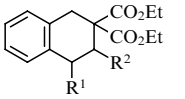
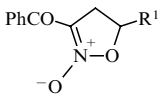
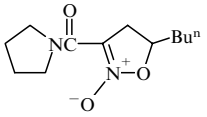
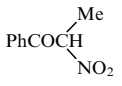
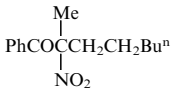
Despite the fact that the addition of carboxylic acids, aldehydes, ketones and amines to alkenes initiated by manganese triacetate or oxidative systems based on it have been comprehensively studied,[243,244] their extensive use is held up, most of all, by the need to introduce relatively large amounts of initiators and by problems associated with their regeneration. In the last decade, a strategy has been developed according to which this type of electrochemical reaction is carried out in the presence of a catalytic amount (0.03–0.2 equiv.) of $Mn(OAc)_2$, acting as a mediator and the source of electrogenerated manganese triacetate. Examples of the addition of CH acids to alkenes initiated by $Mn(OAc)_2$-based oxidative systems are listed in Table 10.

Using the $Mn(OAc)_2$–$Cu(OAc)_2$ mediator system, γ-lactones have been obtained in acceptable yields from acetic acid and styrenes,[246,250] and alk-2-enyl- and cycloalk-2-enyl-substituted cyanoacetic esters were synthesised from ethyl cyanoacetate, alkenes and cycloalkenes.[246,247] In these reactions the carboxymethyl and (ethoxycarbonyl)cyanomethyl radicals together with their adducts with alkenes are formed as intermediates; the former species result from single-electron oxidation of acetic acid and ethyl cyanoacetate by electrogenerated $Mn(OAc)_3$ and the latter arise upon the addition of the primary radicals to alkenes. These secondary intermediates (**A** and **B**) are further oxidised by regenerable Cu(II) ions, which react with radical adducts **A** and **B** by different mechanisms, namely, single-electron transfer for **A** and oxidative β-deprotonation for **B**.[246,247]

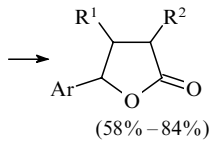


A

Table 10. Electrochemical addition of CH acids to alkenes initiated by manganese diacetate-based oxidative systems.

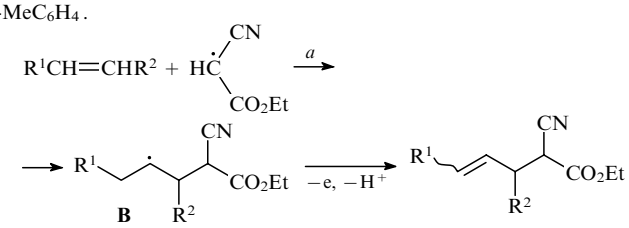
CH acid	Alkene	R^1	R^2	R^3	Method	Reaction product	Yield (%)	Ref.
XCH_2CO_2Et (X = CN, CO_2Et)		H	H	H	A		70–79	245
		Me	H	H	A		58–61	245
		F	H	H	A		53–60	245
		H	Me	H	A		60–73	245
		H	H	Me	A		37–39	245
XCH_2CO_2Et (X = CN, CO_2Et)		–	–	–	A		76–78	246
$NCCH_2CO_2Et$	$R^1CH=CHR^2$	Alk	H	–	A	 n = 2–5, 10	50–64	246, 247
$AcCH_2CO_2Et$		Alk	H, Me	–	A		80–86	246
$PhCH_2CH(CO_2Et)_2$	$R^1CH=CHR^2$	Alk	H	–	A		86	249
		CO_2Et	H	–	A		40	249
		Ph	Ph	–	A		75	249
		AcO	H	–	A		24	249
		see [a]	H	–	A		55	249
$PhCOCH_2NO_2$	$R^1CH=CH_2$	Bu^n	–	–	B		59	248
		$AcOCH_2$	–	–	B		37	248
	$Bu^nCH=CH_2$	–	–	–	B		48	248
	$Bu^nCH=CH_2$	–	–	–	B		54	248

Note. Method A: ACD, graphite anode, 20–30 mA cm^{-2}, 2 F mol^{-1}, AcOH–AcOEt (13:3), 0.03–0.25 equiv. of AcONa, $Mn(OAc)_2 \cdot 4H_2O$, 60–70 °C; method B: ACD, graphite anode, 0.2–0.5 mA cm^{-2}, 2 F mol^{-1}, 0.1 equiv. of AcOH, Bu_4NBF_4, $Mn(OAc)_2 \cdot 4H_2O$, 60 °C. [a] Succinimido.



(58%–84%)

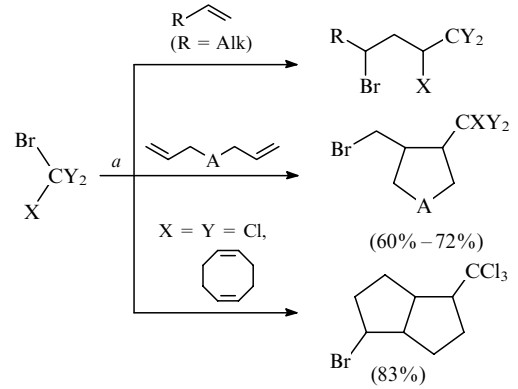
R^1 = H, Me; R^2 = H, Ph, CO_2Et, CH_2OH; Ar = Ph, 4-ClC_6H_4, 4-MeC_6H_4.



(44%–58%)

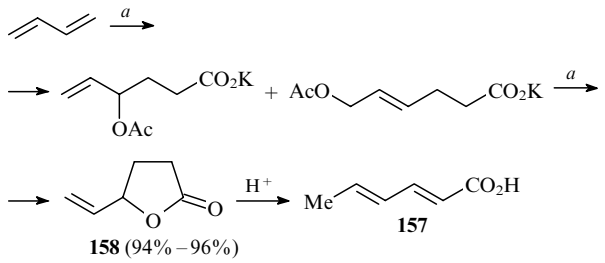
R^1 = $Me(CH_2)_n$ (n = 2, 4, 6), R^2 = H; R^1-R^2 = $(CH_2)_n$ (n = 2–5, 9); (*a*) ACD, graphite anode, 10 mA cm^{-2}, 2 F mol^{-1}, AcOH–Ac_2O (2:1), AcONa, 0.065 equiv. $Mn(OAc)_2 \cdot 4H_2O$, 0.025 equiv. $Cu(OAc)_2 \cdot H_2O$, 95–97 °C.

The binary mediator system, $Mn(OAc)_2$–$NCCH_2CO_2Et$, proved to be a good initiator of free-radical chain addition of polyhalomethanes[251] (bromomalonic esters and methyl bromoacetate) to alkenes.[251,252]



X = Y = Br, Cl; X = Br, Y = F; A = O, NAc; (*a*) ACU, graphite anode, 0.06–0.6 F mol^{-1}, AcOH, AcOK, 0.05 equiv. $Mn(OAc)_2$, 0.1 equiv. $NCCH_2CO_2Me$, 40 °C.

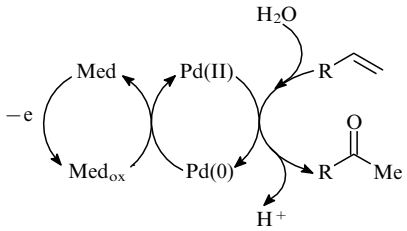
Certain progress has taken shape in the field of practical implementation of indirect electrooxidation with manganese diacetate as a mediator. For instance, electrosynthesis of a precursor of sorbic acid (**157**), namely, γ-vinyl-γ-butyrolactone (**158**), from butadiene and acetic acid, which allows preparation of kilograms of this compound, has been developed.[253]



(*a*) ACU, AcOH – Ac_2O (1 : 1), AcONa, 0.1 equiv. $Mn(OAc)_2 \cdot 4H_2O$, 0.037 equiv. $Cu(OAc)_2 \cdot H_2O$, 95 – 125 °C.

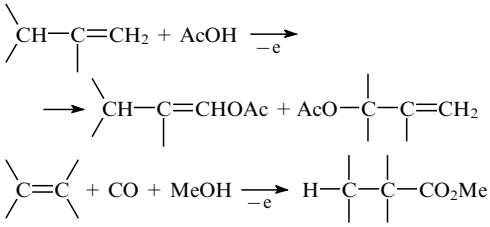
b. Reactions induced by electrooxidation of palladium, ruthenium, osmium and silver compounds

The chemical prototypes of these reactions such as the Wacker process of oxidation of α-alkenes to methyl ketones,[254–256] ethylene to vinyl acetate,[257] hydroalkoxycarbonylation[258–260] and epoxidation of alkenes,[261] suffer from a number of drawbacks including the low rate of oxidation of alkenes with internal double bonds, the explosive risk from the gaseous mixtures of alkenes with oxygen, fast corrosion of the equipment induced by corrosive reaction media, *etc*. Numerous publications have been devoted to the search for new procedures for performing the above-listed reactions.[262–277] Methods of indirect anodic oxidation of alkenes using redox systems consisting of $Pd(OAc)_2$ and an organic mediator (hydroquinone, benzoquinone, their analogues or triarylamines) have been developed to date.[263–269] The mediator acts as an electrogenerated oxidant with respect to Pd(0), which results from the reaction of alkene with Pd(II).



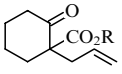
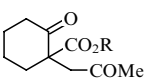
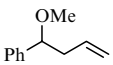
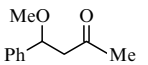
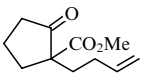
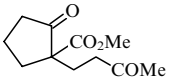
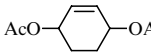
Med is hydroquinone or $(4\text{-}BrC_6H_4)_3N$; Med_{Ox} is benzoquinone or $(4\text{-}BrC_6H_4)_3N^{+\cdot}$.

This procedure has been used to perform electrooxidative transformation of alkenes into ketones[263–266] or into vinyl or allyl acetates.[267,269] Electrooxidation of alkenes in alcohols in the presence of CO yields esters of alkanoic acids (Table 11).[268]

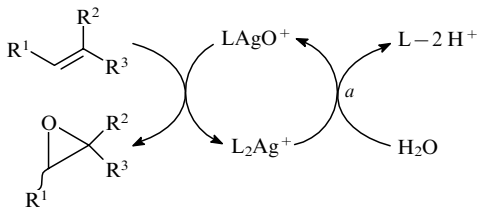


Ruthenium and silver polypyridyl complexes, the ruthenium heteropolyanion $[SiRu(H_2O)W_{11}O_{39}]^{5-}$ and potassium osmate have also shown themselves as effective mediators in indirect anodic oxidation of alkenes. Thus the complex $[Ag(bipy)_2]^+$ (bipy is 2,2′-bipyridine) catalyses epoxidation of alkenes.[270]

Table 11. Indirect anodic oxidation of alkenes with mediator systems containing catalytic amounts (0.01 – 0.1 equiv.) of $Pd(OAc)_2$ or $PdCl_2$.

Alkene	Co-mediator (equiv.)	Electrolyte	Reaction product (isomer ratio)	Yield (%)	Ref.
Dec-1-ene	BQ (0.2)	$Bu_4NBF_4 - HClO_4$	decan-2-one	92	264
	CDA (0.1)	$NaClO_4 - AcONa$	2- and 3-acetoxydec-1-enes (2 : 3)	91	269
	see [a]	LiCl	methyl undecanoates (1 : 3)[b]	73	268
(*E*)-Oct-2-ene	BQ (0.2)	$Bu_4NBF_4 - HClO_4$	octan-2,3,4-ones (6 : 3 : 1)	96	264
(*Z*)-Hept-2-ene	BQ (0.2)[a]	LiCl	methyl octanoates (1 : 3)[b]	50	268
$PhCH=CH_2$	BQ (0.2)	$Bu_4NBF_4 - HClO_4$	acetophenone	79	264
	CDA (0.1)	$NaClO_4 - AcONa$	α-acetoxystyrene	35	269
	see [a]	LiCl	methyl phenylpropionates (1 : 3)[b]	75	268
Cyclohexene	BQ (0.2)	$Bu_4NBF_4 - HClO_4$	cyclohexanone	100	264
	CDA (0.1)	$NaClO_4 - AcONa$	2- and 3-acetoxycyclohexenes (1 : 1)	29	269
	see [a]	LiCl	methyl cyclohexanecarboxylate	50	268
Cycloheptene	CDA (0.1)	$NaClO_4 - AcONa$	2- and 3-acetoxycycloheptenes (1 : 13)	72	269
Cyclohexylethylene	CDA (0.1)	$NaClO_4 - AcONa$	1-acetoxy-1-cyclohexylethylene	33	269
 R = Me, Et	BQ (1.1)	$NaClO_4 - AcONa$		87	265
	TBA (0.05)	Et_4NOTs		89	266
	TBA (0.05)	Et_4NOTs		60	266
Dec-1-en-3-ol	TBA (0.05)	Et_4NOTs	3-hydroxydecan-2-one	41	266
	HQ	$LiClO_4 - AcOLi$		–	267

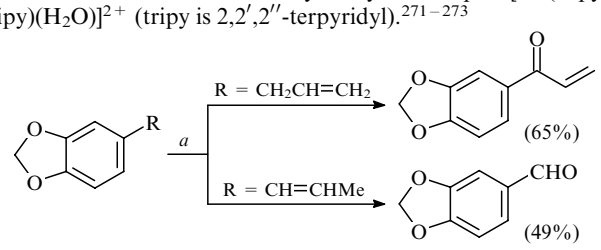
Note. PCD with alternation of electrode polarity (graphite, Pt, Ti – MnO_2), MeCN – H_2O, DMF – H_2O, MeOH or AcOH; BQ is benzoquinone, CDA is copper diacetate, TBA is tri(4-bromophenyl)amine, HQ is hydroquinone. [a] Bubbling of CO during the electrolysis; [b] ratio of esters of linear and branched acids.



R^1	R^2	R^3	Oxirane yield (Current yield) (%)
H	H	Bu^n	– (30)
H	Me	CO_2Bu^i	87 (21)
n-C_5H_{11}	H	CO_2Me	80 (20)
MeO_2CCH_2	H	CO_2Me	90 (20)

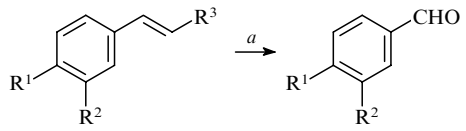
L = bipy; (*a*) ACU, Pt or graphite anode, MeCN – H_2O (19 : 1), $LiClO_4$, 0.0125 – 0.05 equiv. AgOAc, 0.025 – 0.1 equiv. L.

Oxidation of allylic and benzylic C—H bonds and rupture of double bonds in alkenes are catalysed by the complex $[Ru(tripy)(bipy)(H_2O)]^{2+}$ (tripy is 2,2′,2″-terpyridyl).[271 – 273]



(*a*) PCD, Pt anode, 0.8 V, 3.9 F mol^{-1}, $Bu^tOH - H_2O$ (1 : 1), 0.065 equiv. $[Ru(tripy)(bipy)(H_2O)]^{2+}$, pH 6.8 (phosphate buffer), 30 °C.

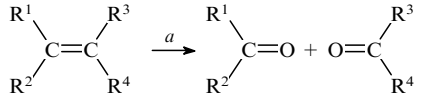
Rupture of double bonds in alkenes also takes place in the presence of $SiRu(H_2O)\cdot W_{11}O_{39}^{5-} - NaIO_3$ [274] and $K_2OsO_2(OH)_4 - HIO_4$ [275] mediator systems.



R^1	R^2	R^3	The yield of aldehyde (%)
H	H	Ph	79
MeO	H	Me	59
MeO	H	4-$MeOC_6H_4$	38
OCH_2O		Me	70

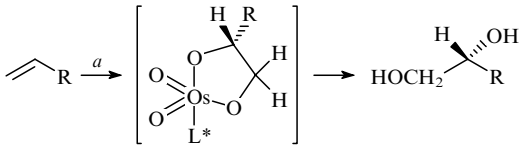
(*a*) ACD, PbO_2 anode, 8 mA cm^{-2}, 3.5 – 5.5 F mol^{-1}, $CH_2Cl_2 - H_2O$, 0.0034 – 0.006 equiv. $SiRu(H_2O)W_{11}O_{39}^{5-}$, 2 equiv. $NaIO_3$, 50 °C.

The $K_2OsO_2(OH)_4 - [K_3Fe(CN)_6]$ system catalyses alkene dihydroxylation and the subsequent cleavage of diols giving rise to ketones (total yields 62% – 91%).[276, 277]



R^1, R^3 = H, Me, Ph; R^2 = H, Me; R^4 = Ph, $(CH_2)_2OCOPh$, 3,4-$(OCH_2O)C_6H_3$; (*a*) ACU, PbO_2 anode, Pt cathode, 5.6 mA cm^{-2}, 5 F mol^{-1}, MeCN – H_2O (10 : 3), Et_4NOTs, 0.04 equiv. $K_2OsO_2(OH)_4$, 0.5 equiv. HIO_4.

The electrochemical asymmetric dihydroxylation of alkenes in the presence of the $K_2OsO_2(OH)_4 - [K_3Fe(CN)_6]$ system and the Sharpless ligand is markedly superior to the corresponding chemical process in enantioselectivity and in yields of target products.[278] The main advantage of the electrochemical variant is that it implies the use of catalytic amounts of the osmate (0.002 equiv.) and the electrically regenerable oxidant, $[K_3Fe(CN)_6]$ (0.1 equiv.). In the classical version, at least a stoichiometric amount of the oxidant is required. The electrochemical dihydroxylation of styrene, 2-methyl-1-phenylpropene, *trans*-stilbene and 1,2-dihydronaphthalene results in the corresponding chiral diols; the degree of conversion is 90% – 97% and the enantiomeric yield is 90% – 100%.[276, 277]



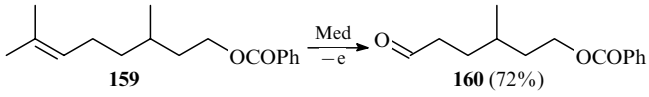
L* is the Sharpless ligand.

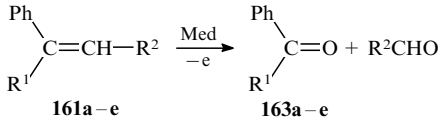
R	The yield of diol (%)	Configuration (*ee*)
Ph	95	*R*(–) (97.3)
Bu^n	71.2	*R*(+) (84.1)
n-C_8H_{17}	69	*R*(+) (91.8)
2-Naphthyl	87	*R*(–) (86.3)

(*a*) ACU, Pt anode, $Bu^tOH - H_2O$ (1 : 1), 0.1 equiv. $[K_3Fe(CN)_6]$, 0.002 equiv. $K_2OsO_2(OH)_4$, 0.01 equiv. L*, 0 – 20 °C.

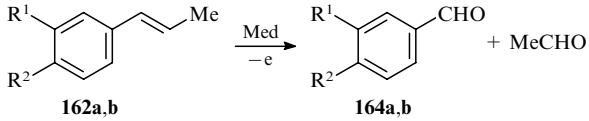
12. Indirect electrochemical rupture of double bonds in alkenes

Indirect electrochemical rupture of double bonds in alkenes takes place with assistance of mediators and mediator systems such as manganese sulfate,[279] methanesulfonate and cerium sulfate,[280, 281] triarylamines,[80] $RuSi(H_2O)W_{11}O_{39}^{5-} - NaIO_3$,[274] $K_2OsO_2(OH)_4 - HIO_4$,[275] PhSSPh – NaBr [80] and $CuCl_2 - O_2$.[282] Two procedures have been developed: a single-stage procedure in which the electric generation of the oxidised form of the mediator (Med_{ox}) and the substrate oxidation by this species take place simultaneously in an electrolytic cell and a two-stage procedure in which the electric generation of Med_{ox} takes place in the cell, while the alkene oxidation by Med_{ox} occurs in a separate reaction vessel. These methods have been used to cleave the double bonds in 3,7-dimethyloct-6-enyl benzoate (**159**) in order to prepare 4-methyl-6-benzoyloxyhexanal (**160**);[275] and in styrenes (**161a – d**),[276, 280, 282] *trans*-stilbene (**161e**),[274, 275] anethole (**162a**)[275] and isosafrole (**162b**)[80, 271, 275, 276, 279] in order to prepare aromatic carbonyl compounds (**163a – d** and **164a,b**). The conditions of synthesis and the product yields are summarised in Table 12.





$R^1 = R^2 = H$ (**a**); R^1 = Me, R^2 = H (**b**); R^1 = Ph, R^2 = H (**c**); R^1 = H, R^2 = Me (**d**); R^1 = H, R^2 = Ph (**e**).



R^1 = H, R^2 = MeO (**a**); $R^1 - R^2 = OCH_2O$ (**b**).

Electrooxidative cleavage of the double bonds in alkenes solves the same problems as chemical methods such as ozonolysis,[283 – 289] oxidation with chromic [290, 291] or cerium reagents,[292]

Table 12. Indirect electrooxidative cleavage of the C=C bond in alkenes.

Alkene	Mediator or mediator system (equiv.)	Method	Product	Yield (%) [a]	Ref.
159	$K_2OsO_2(OH)_4-HIO_4$ (0.04 : 0.5)	A	**160**	72 (29)	275
161b	$K_2OsO_2(OH)_4-HIO_4$ (0.04 : 0.5)	A	**163b**	71 (40)	275
161c	$K_2OsO_2(OH)_4-HIO_4$ (0.04 : 0.5)	A	**163c**	94 (42)	275
161e	$K_2OsO_2(OH)_4-HIO_4$ (0.04 : 0.5)	A	**163e**	66 (33)	275
162b	$K_2OsO_2(OH)_4-HIO_4$ (0.04 : 0.5)	A	**164b**	62 (99)	275
161a	$(MeSO_3)_2Ce(OH)_2(H_2O)$	see [b]	**163a**	89	280
161e	$SiRu(H_2O)W_{11}O_{39}^{5-}-NaIO_3$ [(0.003–0.006) : 0.5]	B	**163e**	79 (57)	274
161a	$SiRu(H_2O)W_{11}O_{39}^{5-}-NaIO_3$ [(0.003–0.006) : 0.5]	B	**164a**	59 (23)	274
162b	$SiRu(H_2O)W_{11}O_{39}^{5-}-NaIO_3$ [(0.003–0.006) : 0.5)]	B	**164b**	70 (44)	274
162b	MnO_2	see [b]	**164b**	54	279
	$Ce(SO_4)_2$	see [b]	**164b**	83	281
	$[Ru(tripy)(bipy)(H_2O)]^{2+}$ (0.065)	C	**164b**	49	271
	PhSSPh–NaBr (0.37 : 0.2)	D	**164b**	53 (70)	80
161d	$(4\text{-}BrC_6H_4)_3N$ (0.041)	E	see [c]	35	80
161a	$CuCl_2$ (0.05)–O_2	F	see [d]	(70)	282

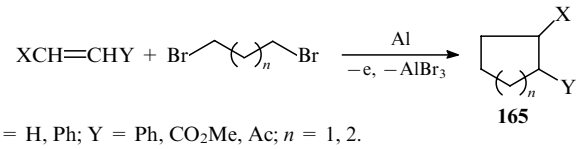
Note. Method A: ACD, PbO_2 anode, 6.7 mA cm^{-2}, 2.5–10 F mol^{-1}, MeCN–H_2O (10 : 3), Et_4NOTs, 20 °C; method B: ACD, PbO_2 anode, 8 mA cm^{-2}, 3.5–5.5 F mol^{-1}, dichloroethane–H_2O (1 : 1), 50 °C; method C: PCD, Pt anode, 0.8 V, Bu^tOH-H_2O (4 : 1), phosphate buffer, 20 °C; method D: ACU, Pt anode, 8 mA cm^{-2}, 6.4 F mol^{-1}, MeCN–H_2O (2 : 1), ~20 °C; method E: ACU, graphite anode, 5 mA cm^{-2}, 3.5 F mol^{-1}, MeOH, $LiClO_4$, 18 °C; method F: PCD, Pt anode, 1.0 V, MeCN, $NaClO_4$, 80 °C.

[a] Substance yield (in parentheses, current yield). [b] Two-step cleavage; conditions of electric generation of Med_{ox} for $(MeSO_3)_2Ce(OH)_2(H_2O)$ and $Ce_2(CO_3)_3$: ACD, Pt anode, 200 mA cm^{-2}, 1.0 F mol^{-1}, $MeSO_3H-H_2O$, 50 °C; for MnO_2 and $MnSO_4\cdot 4H_2O$: ACD, PbO_2 anode, 200 mA cm^{-2}, 2.2 F mol^{-1}, 2 equiv. of H_2SO_4, 20 °C; for $Ce(SO_4)_2$ and $Ce_2(SO_4)_3$: ACD, Pt anode, 200 mA cm^{-2}, 1.2 F mol^{-1}, H_2SO_4, 20 °C. [c] $PhCH(OMe)_2$. [d] PhCHO.

the RuO_4–MeCHO–O_2 system,[293] *etc.*[294,295] The drawbacks peculiar to chemical methods have been largely overcome in the electrochemical method for the cleavage of double bonds in alkenes.

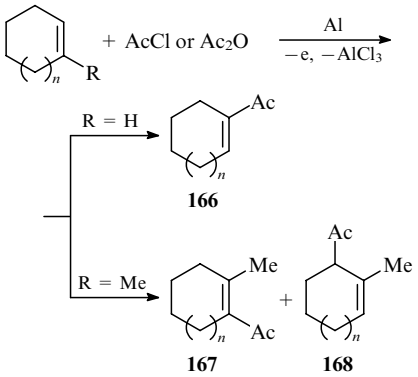
13. Reactions involving sacrificial metallic anodes

Electrochemical alkylation or acylation of alkenes with organic halides and acyl halides giving rise to C–C bonds is carried out using sacrificial metallic (usually, aluminium, zinc and magnesium) anodes. Their role is to suppress the formation of halogen molecules and thus to prevent halogenation of alkenes. The electrochemical formation of a C–C bond is an alternative to the reaction including deprotonation of organic CH acids induced by metals, organometallic compounds or strong bases and subsequent alkylation with the organic halide. In this case, the C–C bond formation is usually accompanied by side reactions, namely, O-alkylation, dialkylation or condensation of the substrate. In the processes with sacrificial anodes, the C–C bond is formed more selectively. For example, the reactions of activated alkenes with organic 1,1-, 1,3- and 1,4-dihalides,[296] non-activated alkenes with acylating reagents,[297,298] and cyclisation of unsaturated bromoacetals [299] afford compounds **165**–**169** in high yields.



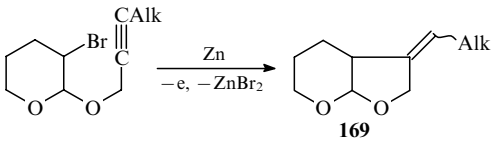
165

X = H, Ph; Y = Ph, CO_2Me, Ac; n = 1, 2.



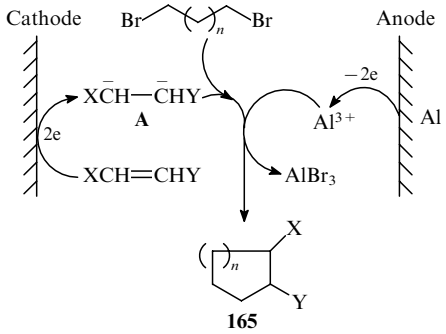
166 **167** **168**

R = H, Me; n = 1, 2.



169

Besides preventing the generation of molecular bromine, a sacrificial aluminium anode participates (through Al^{3+} ions) in stabilisation of the type **A** dianions generated by cathodic reduction of the activated alkene.

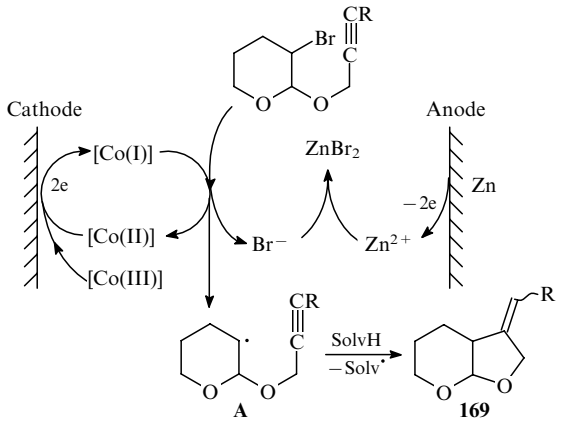


165

The substituted cycloalkanes **165** are formed in reasonable yields (30%–60%) only from activated alkenes, namely, esters of maleic, fumaric, cinnamic and acrylic acid and 4-phenylbut-3-en-2-one, upon reaction with 1,3- and 1,4-dihaloalkanes. The reaction proceeds with high stereoselectivity (isomer ratio *trans* : *cis* > 10 : 1). Cyclobutane derivatives are obtained by this method in very low yields, and only from 1,2-dichlorides. When 1,2-dibromides are used, electrochemical debromination takes place. In the reaction of dimethyl maleate with 1,3-dibromopropane, dimethyl 2-allylbutanedioate (yield 10%) and 1,2-cyclopentadicarboxylate (50%) are formed.[296]

In acylation of cycloalkenes with acetyl chloride, an aluminium anode not merely suppresses the generation of molecular chlorine but also catalyses the reaction, due to the influence of $AlCl_3$ formed during the electrochemical process. The electrochemical acylation occurs more selectively than the classical Friedel–Crafts reaction.[300–304] Joint electrolysis of equimolar amounts of acetyl chloride and cyclohexene or cycloheptene in an undivided cell at −10 to −5 °C (3 F mol^{-1}) results in complete conversion of cycloalkenes into 1-acetylcycloalkenes **166** (yields 60%–80%).[297,298] The transformation of 1-methyl-substituted cycloalkenes gives rise to two isomers, 1-acetyl-2-methylcycloalkenes **167** and 3-acetyl-2-methylcycloalkenes **168**, in a total yield of 65%–85%; the compounds **168** markedly predominate. Elec-

trochemical acetylation of acyclic alk-1-enes involves only the terminal carbon atom but the yields are relatively low (22% – 25%). The side products formed are α,β-dichlorides (1% – 10%), which become the only reaction products when a carbon or platinum anode is used.



The intramolecular electrochemical cyclisation of unsaturated bromoacetals to dioxabicycloalkanes **169** is an example in which the use of sacrificial metallic anodes is combined successfully with the catalysis of the cathodic single-electron reduction of organic halides with cobaloxime. The cathodic generation of Co(I) complexes, single-electron reduction of bromoacetal to radical **A** by these complexes, cyclisation of the radical and subsequent transformation into the final product (yields 70% – 77%) are the key steps of this process.

Electrochemical reactions of alkenes with sacrificial metallic anodes provide good results in many cases where the chemical analogues either do not occur at all or are hardly suitable due to the low yields of the target products. This also eliminates the necessity of performing a labour-consuming and, in some cases, unsafe step of the synthesis of organometallic compounds. By using high current densities (up to 1 A dm^{-2}), one can produce substantial amounts of reaction products.

IV. Conclusion

Although electrochemical reactions are a powerful tool for transforming and assembling organic molecules, they are still used in most cases only by specialists and have not become a routine method of chemical synthesis. We hope that this review would be useful not only as a source of specially selected information but also as a manual for the practical use of electrochemical reactions for solving problems of organic synthesis. From this standpoint, reactions carried out in an electrolytic cell not separated into electrode compartments, which are simple in experimental implementation and require much less electricity, are more advantageous. The review demonstrates the substantial progress achieved in recent years in the investigation of alkene reactions induced by anodic oxidation and in development, on this basis, of theoretical and procedural aspects of modern organic chemistry. First of all, this refers to indirect anodic oxidation of alkenes with assistance by inorganic and organic mediators and mediator systems. Study of electrochemical processes involving these systems made it possible not only to establish the regularities and propose mechanisms of transformation of alkenes into functionally substituted products but also to elaborate simple methods which ensure high degrees of alkene conversion with minimum electricity consumption to give compounds the synthesis of which by chemical methods is either impossible or difficult from the experimental standpoint. Substantial progress has also been achieved in the study of electrochemical cyclisation, [4 + 2]-cycloaddition, phosphorylation, rupture of double bonds, and reactions involving sacrificial anodes. Methods of electrochemical transformation of alkenes and other organic compounds under conditions of diaphragmless electrolysis (in which both anodically and cathodically induced processes are involved in the assembling of the final product) have been developed. Vivid examples of this type of transformation are cyclisation of carboxy-substituted arylalkenes to give 2-benzylcyclopentanones in the presence of a tertiary phosphine (Scheme 5) [225] and indirect electrochemical reduction of carboxylic acids to the corresponding alcohols with assistance by the same reagent.[305] In our opinion, the scope of application of organic electrosynthesis should be extended. This is largely due to the fact that electric current would remain one of the most available, inexpensive and facile oxidants and reductants.

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