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Electrochemically induced chain reactions in organic synthesis

A I Ilovaisky, V M Merkulova, M N Elinson, G I Nikishin

Contents

I.	Introduction	381
II.	Electrochemically induced chain reactions in a divided cell	381
III.	Electrochemically induced chain reactions in an undivided cell	390
IV.	Conclusion	394

Abstract. Data on the use of electrochemically induced chain reactions in organic synthesis are considered systematically and generalized. These processes are of particular practical interest in view of the energy saving. Examples are given of the use of electrochemically induced chain reactions for the synthesis of different classes of organic compounds under electrolysis conditions. The bibliography includes 123 references.

I. Introduction

Electrochemically induced chain reactions comprise a new promising area of research, which has attracted ever increasing interest of researchers in the fields of electrochemistry and organic chemistry. The distinguishing feature of electrochemically induced chain reactions is that the electrochemical initiation (step $\mathbf{A} \pm e^- \rightarrow \mathbf{B}$, where **B** is a charged particle) is excluded from the subsequent chain reaction both in reduction and oxidation processes. Thus, the generated active particle **B** is then involved in the repeating cycle to form the target product. Evidently, under these conditions, the current yield of the product will be much higher than 100%, up to hundreds or thousand percent (the quantity of electricity passed $Q \ll 1\,F$).†

Taking into account that the amount of electricity consumed during the synthesis of the target product is the main parameter of electrochemical reactions, this type of transformations is of the most practical interest primarily in view of the energy saving.

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The present review summarizes the data on the use of electrochemically induced chain reactions in organic synthesis published mainly in the last 15 years. Reviews completely focused on electrochemically induced chain reactions are lacking. In the existing reviews and monographs on electrocatalytic reactions,[1–5] electrochemically induced chain reactions are considered only briefly and reactions in an undivided cell remain beyond their scope. The aim of the present review is to close this gap and to show the modern trends of the use of electrochemically induced chain reactions in organic synthesis. In a divided cell, the processes occur in the cathode compartment, unless otherwise stated.

II. Electrochemically induced chain reactions in a divided cell

1. Substitution

a. Radical nucleophilic substitution $S_{RN}1$

The electrochemically induced radical nucleophilic aromatic substitution ($S_{RN}1$) can be represented by the following general scheme:[6]

Initiation:

$$ArX + e^- \rightleftharpoons ArX^{-\bullet}$$

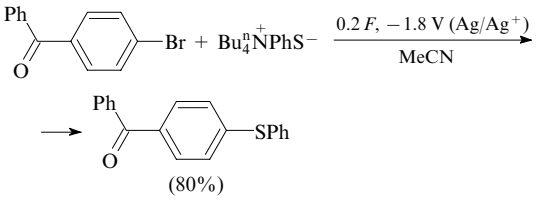
Chain propagation:

$$ArX^{-\bullet} \longrightarrow Ar^{\bullet} + X^-$$
$$Ar^{\bullet} + Nu^- \rightleftharpoons ArNu^{-\bullet}$$
$$ArNu^{-\bullet} + ArX \rightleftharpoons ArNu + ArX^{-\bullet}$$

$$ArX + Nu^- \longrightarrow ArNu + X^-$$

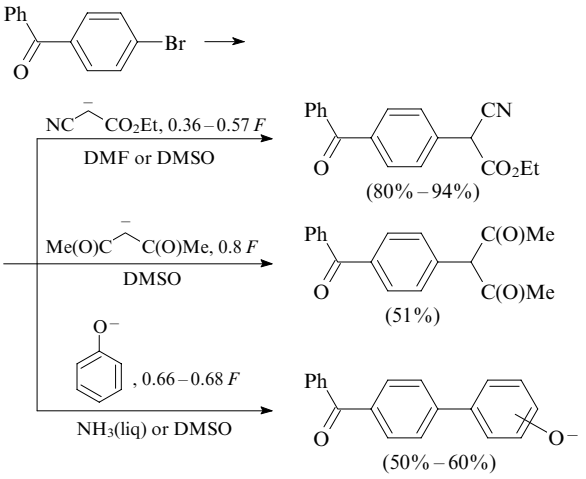
The replacement of the bromine atom in 4-bromobenzophenone (ArX) by the thiophenolate anion (Nu^-) at the reduction potential of the substrate is the first example of this type of reactions.[7]

† The theoretical quantity of electricity in chain reactions is taken equal to $1\,F$, where F is the Faraday number, *i.e.*, 96484.56 C mol^{-1}.



The yield of substitution products depends on the electrophilicity of the radicals Ar$^\bullet$, the concentration of the nucleophile and pK_a of the solvent.[7] The side reactions are common to substitution reactions and include the competitive reduction of radicals at the cathode and proton abstraction from the solvent. Hence, the control of the potential, the low proton-donating ability of the solvent and an anhydrous medium are required for these reactions to proceed; therefore, most of analytical experiments on the study of the substitution reaction mechanism were performed in liquid ammonia.

Preparation experiments were carried out in liquid ammonia, MeCN and DMSO. Apart from 4-bromobenzophenone,[8,9] 4-bromo- and 4-iodobenzonitriles,[9] 4-bromonaphthalene,[9] 4-bromoacetophenone[10] and 2-chloroquinoline[11,12] were used as substrates; PhS^-, Bu^tS^-, CN^- and $(EtO)_2PO^-$ served as electrophiles. The quantity of electricity passed was 0.01–0.5 *F*, and the yield of substitution products was 40%–100% (200%–10 000% current yield). Examples of the use of anions of CH-acids[13] and phenoxide anions as nucleophiles are of interest. In the latter case, C- rather than O-coupling products are formed in the *ortho* to *para* isomer ratio of 2 : 1.[14,15]

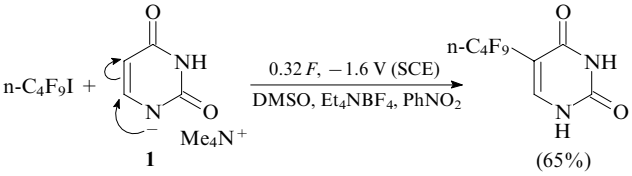


Noteworthy also is the use of the nucleophiles $PhSe^-$ and $PhTe^-$ in the synthesis of (phenylseleno)benzonitriles (0.26–0.8 *F*, 36%–78% yield),[16] as well as of (phenylseleno)- and (phenyltelluro)benzophenones.[17] In the latter case, the addition of an electron transfer mediator (azobenzene) and a proton donor (fluorene) suppresses the side reaction with the solvent (MeCN), resulting in an increase in the yield of the products from 17%–30% to 40%–80% and an increase in the current yield to 200%–450% with a simultaneous decrease in the amount of electricity passed from 0.3–0.5 to 0.1–0.2 *F*.[17]

In the case of aliphatic substrates, the radical nucleophilic substitution occurs only with strong electrophilic perfluoroalkyl radicals (R_F). The reaction is initiated by the dissociative electron transfer and does not give the radical anions, which are formed in the reactions with aromatic halides, but gives directly perfluoroalkyl radicals, which then react with a nucleophile to give a radical-anion product.[18]

$$R_FX + e^- \longrightarrow R_F^\bullet + X^-$$
$$R_F^\bullet + Nu^- \longrightarrow R_FNu^{-\bullet}$$
$$R_FNu^{-\bullet} + R_FX \longrightarrow R_FNu + R_F^\bullet + X^-$$
$$R_FX + Nu^- \longrightarrow R_FNu + X^-$$

In these reactions, n-C_4F_9I and n-$C_6F_{13}I$ were used as substrates; anions of substituted imidazoles, uracil (**1**), xanthine, hypoxanthine and 2-mercaptothiazole were used as nucleophiles; DMSO or MeCN served as the solvent; the quantity of electricity passed was 0.1–0.8 *F*; the yield of substitution products was up to 70% (the current yield was up to 570%). Mediators (nitrobenzene, 4-nitropyridine *N*-oxide, terephthalonitrile) were employed to reduce the passivation of electrodes.[18–20]

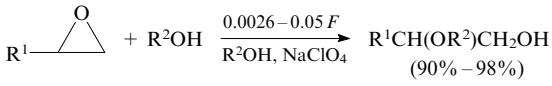


The substitution reactions involving radical ions play an important role in investigations of the mechanisms of organic reactions, the elucidation of the nature and reactivity of intermediates and the determination of structure–properties relationships. However, the synthetic potential of these reactions is fairly limited, because they require a complex apparatus and absolutely anhydrous medium.

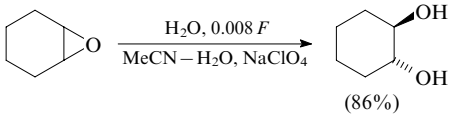
b. Nucleophilic substitution in aliphatic compounds

Epoxides undergo ring opening during the electrolysis both in the anode and cathode compartments of a divided cell.

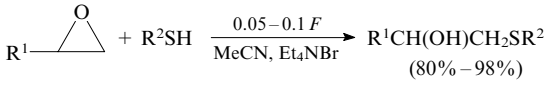
In the anode compartment, the reaction catalyzed by electrogenerated acid ($HClO_4$) gives alkoxy-substituted alcohols or diols depending on the nature of the nucleophile used (alcohol or water, respectively).[21]



R^1 = Ph, Me, $PhOCH_2$, $ClCH_2$, $CH_2{=}CHCH_2OCH_2$;
R^2 = H, Me, Et, Pr^n, Pr^i

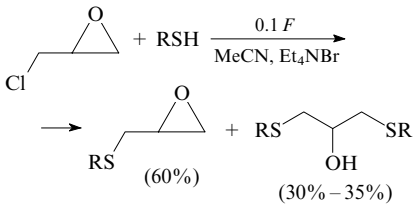


The reactions of epoxides with thiols in the cathode compartment afford thio-substituted alcohols; electrogenerated thiolate anions act as initiators.[22]



R^1 = Ph, Me; R^2 = Bu^n, n-C_8H_{17}, Ph

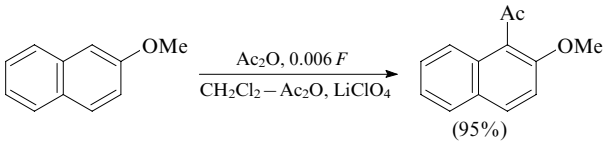
Under these conditions, epichlorohydrin gives a mixture of 2,3-epoxypropyl alkyl sulfides and 1,3-di(alkylthio)propan-2-ols.[22,23]



R = Bu^n, n-C_8H_{17}, n-$C_{10}H_{21}$

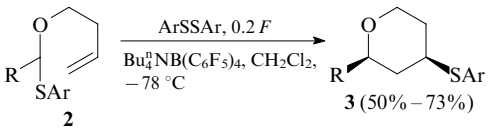
c. Electrophilic aromatic substitution

The acylation of electron-donating aromatic compounds by carboxylic acid anhydrides was performed with the use of electrogenerated acid ($HClO_4$) in the anode compartment of a divided cell.[24] In the presence of electrogenerated acid, anhydride forms the acylium cation $RC{=}O^+$ functioning as a reactive intermediate. Isomeric alkoxynaphthalenes and dimethoxybenzenes, anisole and anthracene were used as substrates; acetic, propionic and pivalic anhydrides served as acylating agents; the quantity of electricity passed was 0.003–0.02 *F*; the yield of the products was 20%–95% (550%–27 000% current yield).



2. Addition to unactivated multiple bonds

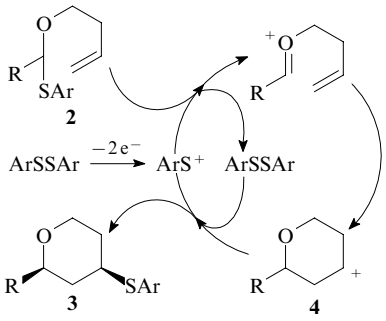
Examples of the electrochemically induced addition to unactivated multiple bonds are rare. The cationic chain cyclization of *O*-homoallyl *S*-aryl thioacetals **2** in the anode compartment of a divided cell[25] induced by electrogenerated arylthio cations is of most interest among these reactions.



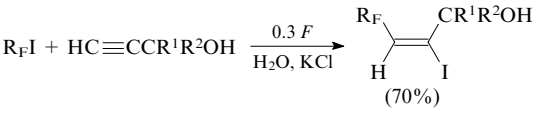
R = H, n-C_7H_{15}, cyclo-C_6H_{11}, Ph, $PhCH_2$, $MeOCH_2CH_2$;
Ar = 4-FC_6H_4

Initially, the electrolysis of ArSSAr generates the ArS^+ cation, which reacts with the substrate to form the alkoxycarbenium ion and ArSSAr followed by cyclization and regeneration of ArS^+ at the final step (Scheme 1). The observed high stereoselectivity (almost exclusively *cis* isomer **3** is formed) was attributed[25] to the fact that the formation of cation **4** and its subsequent reaction with ArSSAr proceed in a concerted mode.

Scheme 1



The addition of perfluoroalkyl iodides to alkynes in the cathode compartment of a divided cell (a carbon-fibre cathode) was documented.[26] This reaction was proposed to proceed by a free-radical mechanism. Although the reaction affords both isomers, only the *trans* product was isolated in the pure form.

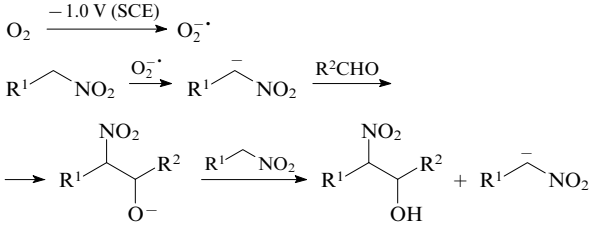


R_F = n-C_4F_9, n-C_6F_{13}; R^1 = R^2 = H, Me; R^1 = Me: R^2 = H, Et

3. Addition to the carbonyl group and its heteroanalogues

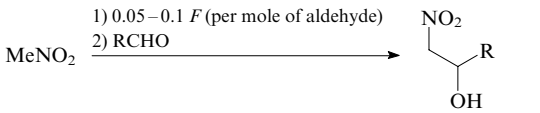
This section concerns a wide range of reactions with CH-acids with different pK_a values, including nitroalkanes,[27–32] malononitrile,[33] chloroform,[34–35] malonic ester,[35] derivatives of phenylacetic acid,[35–36] indene, fluorene,[37–42] *etc*.

Most of studies were devoted to the electrochemically induced addition of nitroalkanes to aldehydes (the nitroaldol reaction, the Henry reaction). The approach to this type of reactions, which has been initially developed by Evans and co-workers,[27–30] involves the activation of nitroalkanes by electrogenerated superoxide.



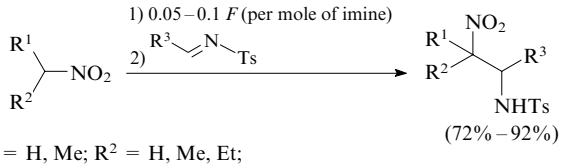
R^1 = H, Me; R^2 = Ph, 2-thienyl, 2-furyl

The reaction was performed in a nitroalkane medium exposed to air by passing 0.02–0.3 *F* of electricity. Generally, the yield of nitro alcohols does not exceed 60% due to the tendency of these compounds to undergo dehydration followed by the Michael addition of nitroalkane to the activated double bond that is formed under the reaction conditions.[28] By performing the pre-electrolysis of nitroalkane (1.1–9-fold excess) under an inert atmosphere at 0 °C followed by the addition of a carbonyl compound to the catholyte, the yield of nitro alcohols was increased to 90% (630%–1300% current yield) even in the case of aliphatic aldehydes.[31,32]



R = Ph, 2-furyl, n-C_7H_{15}, cyclo-C_6H_{11}

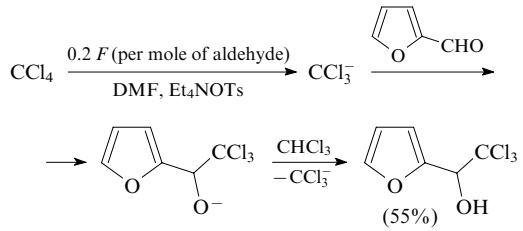
The aza-Henry reaction was performed under similar conditions.[33]



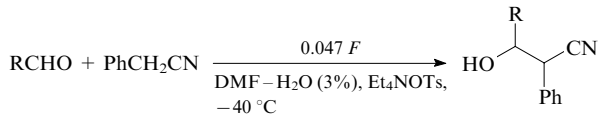
R^1 = H, Me; R^2 = H, Me, Et;
R^3 = Ph, 4-XC_6H_4 (X = Cl, OMe, NO_2, CF_3), 2-furyl, 2-naphthyl

The reaction of malononitrile, whose acidity is comparable with that of nitroalkanes, with aldehydes and ketones affords only Knoevenagel condensation products in 93% – 100% yield (3200% – 33 000% current yield).[34] Benzaldehyde and its derivatives, furan-2-carbaldehyde, linear and cyclic ketones were used as carbonyl compounds. The reaction was performed under solvent-free conditions without the use of a supporting electrolyte at elevated temperature (40 °C) to achieve the homogeneity of the reaction mixture.

An original method for the activation of CH-acids by the addition of the appropriate easily reducible halide was described by Shono *et al*.[35,36] The scheme of the reaction is exemplified below by the addition of $CHCl_3$ to aldehydes. The reaction begins with the direct reduction of the added CCl_4 ($CCl_4 : CHCl_3 = 1 : 10$), but it is maintained by deprotonation of $CHCl_3$ by the anion that is generated *via* the addition of CCl_3^- to aldehyde.

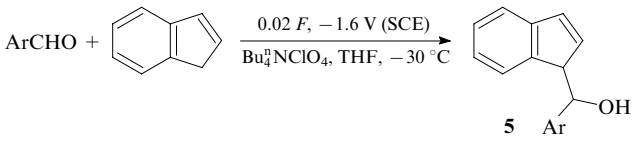


This method was used for the synthesis of numerous addition products of $CHCl_3$, $CHBr_3$ and $CHCl_2CO_2Me$ to various aldehydes in 10% – 60% yields. Dimethyl malonate, $PhCH_2CN$ and $PhCH_2CO_2Me$ were also used as CH-acids. In this case, the corresponding α-brominated CH-acid (5%) was added as the easily reducible halide, and 0.1 *F* of electricity was passed (yield 35% – 80%).[36] More recently, Torii and co-workers [37] developed an efficient procedure for the synthesis of aldol addition products of phenylacetic acid derivatives ($PhCH_2CN$, $PhCH_2CO_2Et$) and $NCCH_2SPh$ to aldehydes in 75% – 90% yield (1500% – 2200% current yield) without the use of an activating additive.



R = Ph, 2-furyl, 2-thienyl, n-C_7H_{15}

The weak CH-acids, indene (pK_a 20.1) and fluorene (pK_a 22.6), add to aromatic aldehydes in THF at the reduction potential of aldehyde.[38–41]



The maximum yield of alcohols **5** (74% – 93%) was achieved in the reaction with 2,6-dichlorobenzaldehyde in the presence of a 10 – 20-fold excess of CH-acid. For benzaldehyde and terephthalic aldehyde, the yield decreases to 12% – 30%. The reaction mechanism involves the reduction of aldehyde to the radical anion, which abstracts a proton from CH-acid. The resulting carbanion adds to the starting aldehyde. The chain propagation is provided by the protonation of the addition product of another CH-acid molecule.

Initiation:

$$ArCHO + e^- \longrightarrow [ArCHO]^{-\cdot}$$

$$[ArCHO]^{-\cdot} + AH_2 \longrightarrow [Ar\dot{C}HOH] + AH^-$$

Chain propagation:

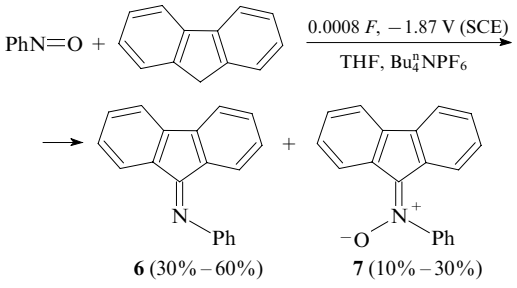
$$ArCHO + AH^- \longrightarrow [ArCH(O^-)AH] \rightleftharpoons [ArCH(OH)A]^-$$

$$[ArCH(OH)A]^- + AH_2 \longrightarrow ArCH(OH)AH + AH^-$$

AH_2 is indene or fluorene

In DMF – $Bu^n_4NPF_6$ alcohols **5** undergo dehydration induced by electrogenerated base to form Knoevenagel condensation products ArCH=A; in some cases, this is followed by the Michael addition of CH-acid to form adducts $ArCH(AH)_2$.[41] Naphthaldehyde, 3-methoxy- and 4-dimethylaminobenzaldehydes and pyrrole-2-carbaldehyde were used as substrates; the quantity of electricity passed was 0.03 – 0.3 *F*, the yields of ArCH=A and $ArCH(AH)_2$ were 3% – 50% and 0% – 70%, respectively.

The corresponding reactions of nitrobenzene, which is a heteroanalogue of benzaldehyde, with indene and fluorene afford a mixture of anil **6** and nitrone **7**;[42,43] at −30 °C, anil **6** was prepared in 97% yield (120 000% current yield).[43]



The electrochemically induced aldol-crotonic condensation at the reduction potential of aldehyde was described.[44]

$$RCH_2CHO \xrightarrow[DMF,\ Et_4NOTs]{e^-,\ 0.0075\ F,\ \text{from } -1.8 \text{ to } -2.1\ V\ (SCE)} [RCH_2CHO]^{-\cdot}$$

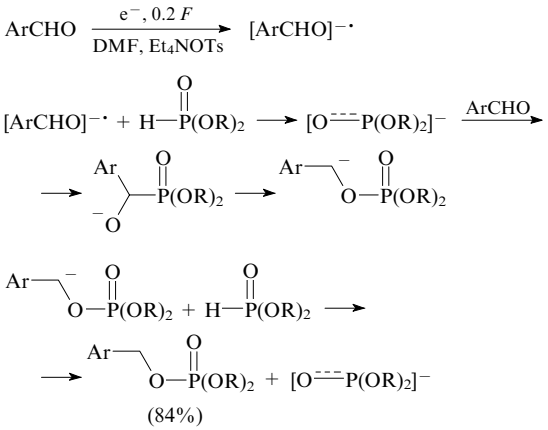
$$[RCH_2CHO]^{-\cdot} + RCH_2CHO \longrightarrow R\bar{C}H{-}CHO \xrightarrow{RCH_2CHO}$$

$$\longrightarrow R{-}CH(O^-){-}CH(R){-}CHO \longrightarrow R{-}CH{=}CH{-}CHO + OH^-$$

R = Et, Pr^n, Pr^i

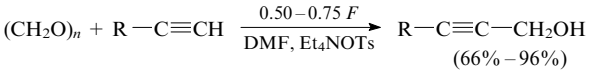
The corresponding α,β-unsaturated aldehydes were synthesized in 72% – 76% yield (10 000% current yield).

The addition of phosphonates (heteroanalogues of CH-acids) to aldehydes proceeds by a similar scheme.[45]

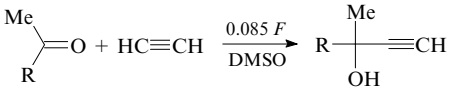


Ar is 1-naphthyl, R = Alk

The addition of terminal alkynes to paraformaldehyde[46] and ketones[47] produces the corresponding propargyl alcohols.

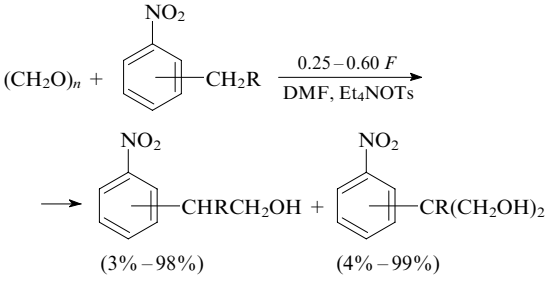


R = Ph, $THPOCH_2$, $Me_2C(OTHP)$, $Me_2C{=}CHCH_2CH_2C(OH)$
(THP is tetrahydropyran-2-yl)



R = Me, Et

Finally, alkylnitroarenes successfully act as CH-acids.[48]



R = H, Me

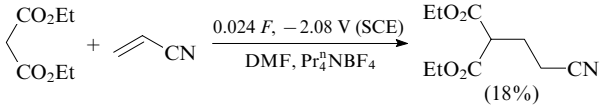
Depending on the nature of the substituent and its position towards nitro group, different amounts of mono- and bis-addition products are formed.

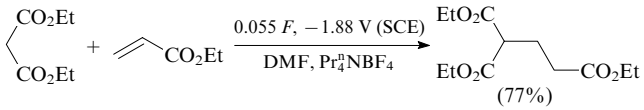
4. Addition to the activated double bond

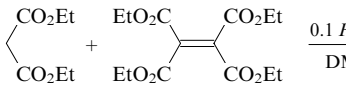
a. Addition of CH-acids and their analogues to the activated double bond (Michael reaction)

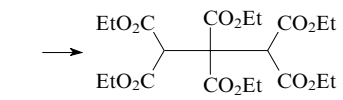
This type of transformations is of particular importance among electrochemically induced reactions, because they provide a convenient approach to the construction of the skeleton of molecules containing various functional groups. Dicarbonyl compounds (malonic and acetoacetic esters, β-diketones), nitro compounds and sulfones were used as CH-acids; nitriles, ketones, acrylic and ethane-1,1,2,2-tetracarboxylic esters, nitroalkenes and unsaturated sulfones acted as Michael acceptors.

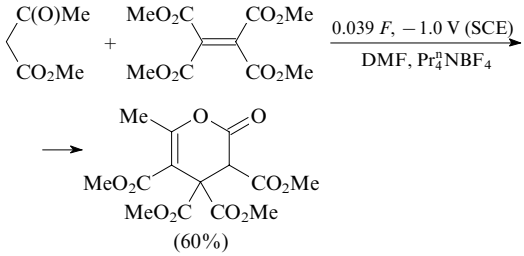
First electrochemically induced Michael reactions with dicarbonyl compounds were performed early in the 1970s by Baizer *et al.*[49, 50] at a controlled electrode potential.





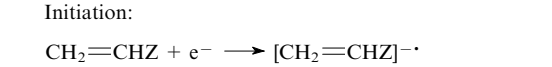




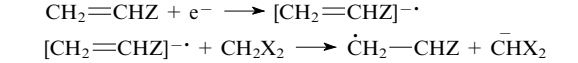


The reactions are generally initiated by the radical anion of activated alkene because, under these conditions, CH-acids are reduced at a more negative potential, if at all.[50]

Initiation:

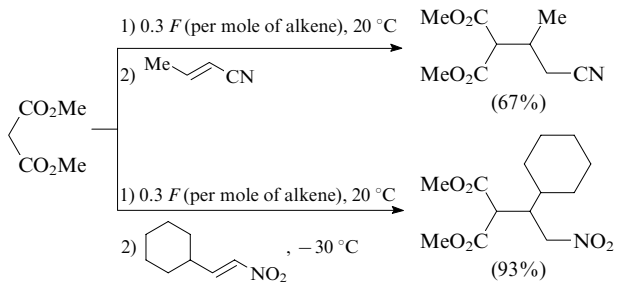


Chain propagation:



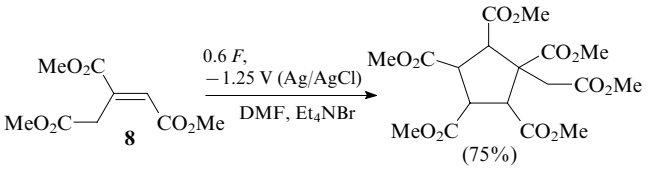
X, Z are electron-withdrawing groups

By performing the pre-electrolysis of pure CH-acid (16-fold excess) under an inert atmosphere at 20 °C followed by the addition of activated alkene to the catholyte, the researchers succeeded in increasing the yield of the addition product, a particularly substantial increase (by a factor of 1.5) being observed in the case of unsaturated nitriles; good results were achieved under these conditions for unsaturated nitro compounds.[31, 32]

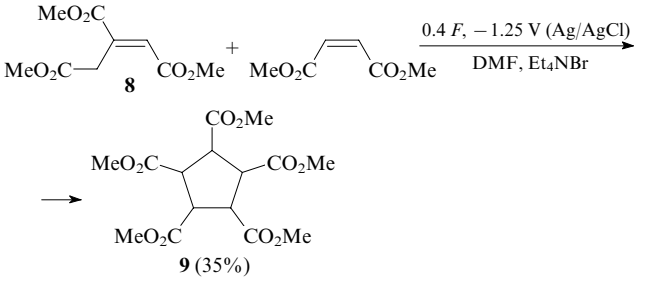


Under similar conditions, addition products of diketones, keto esters and dimethyl malonate with unsaturated ketones and esters were obtained in 82%–98% yield (270%–330% current yield).[31,32] This research group also studied the addition of chiral keto amides and keto esters to methyl vinyl ketone under conditions of pre-electrolysis ($MeCN-Et_4NClO_4$, 0.14 *F*). Mixtures of diastereomers were obtained in a ratio of 73:27 in a total yield of 37%–100%.[51] It should be noted that in all cases, after the pre-electrolysis and the addition of activated alkene to the catholyte, the stirring of the reaction mixture continued for 2–18 (!) h until the reaction was brought to completion. This substantially reduces the advantages of the electocatalytic synthesis.

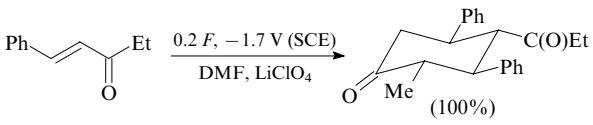
The electrochemically induced cyclodimerization of trimethyl aconitate (**8**), which acts simultaneously as a CH-acid and a Michael acceptor, is an interesting example. The corresponding cyclic dimer was obtained in good yield (130% current yield) with 95% conversion of substrate **8**.[52]



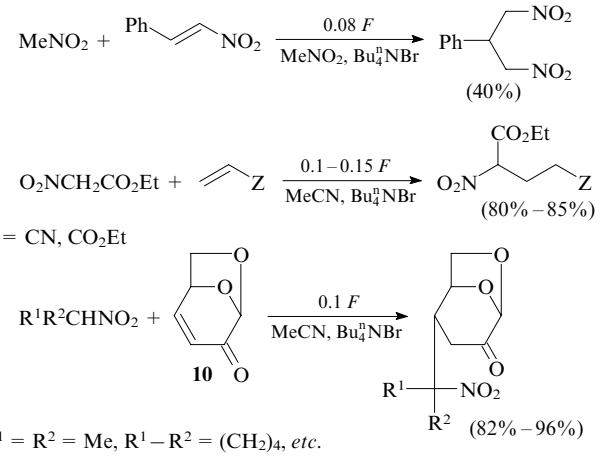
The reaction afforded a mixture of isomers, from which the (1*R**,2*S**,3*R**,4*R**,5*S**) isomer was isolated in 56% yield. The reaction is catalyzed by the radical anion generated from substrate **8**. This radical anion deprotonates the substrate and initiates the cyclization involving two sequential Michael additions to form a cyclodimer. This method was used also to synthesize cyclic product **9** starting from trimethyl aconitate (**8**) and dimethyl maleate.[52]



The cyclization of 1-phenylpent-1-en-3-one, which, like compound **8**, has properties of a CH-acid and contains the activated double bond, proceeds completely regio- and stereoselectively to give cyclic ketone in quantitative yield (500% current yield).[53]



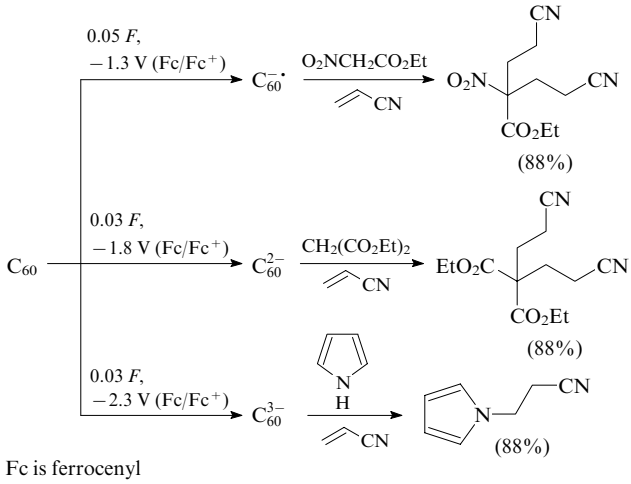
The addition of nitro compounds to activated alkenes was studied by Evans and co-workers.[30,54–58] Nitrostyrene,[30] acrylonitrile, ethyl acrylate[54] and levoglucosenone (**10**), chiral unsaturated ketone prepared by the pyrolysis of cellulose, were used as Michael acceptors.[55–58]



$R^1 = R^2 = Me$, $R^1-R^2 = (CH_2)_4$, *etc.*

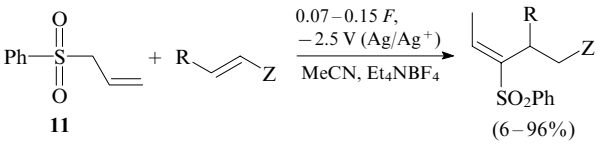
It is noteworthy that the *exo* addition giving the *erythro* isomer always occurs in the case of compound **10** regardless of the type of the nitro compound (2-nitropropane, nitrocyclopentane, dinitromethane, ethyl nitroacetate or diethyl 2-nitroglutarate).

Nitro compounds are generally activated by electrogenerated superoxide.[54,58] The use of cathodically generated radical anions, di- and trianions of fullerene C_{60}, as initiators,[59] is worthy of notice.



Fc is ferrocenyl

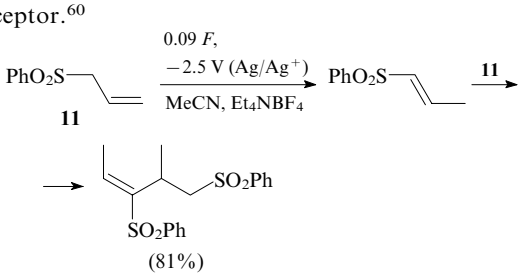
Sulfones were also used as CH-acids; in these reactions, unsaturated nitriles, ketones, esters and sulfones served as Michael acceptors.[60,61]



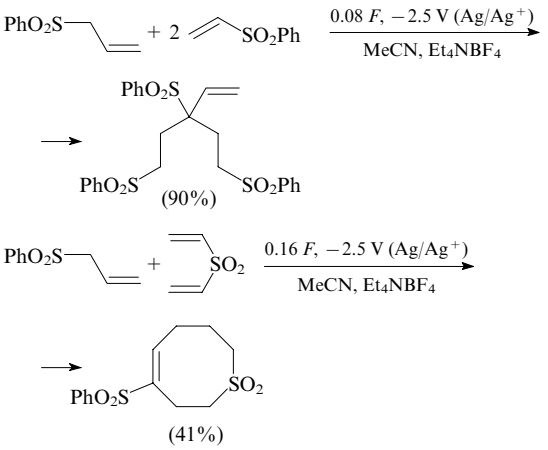
11

R = H, Me, CO_2Et; Z = CN, Ac, C(O)Et, CO_2Me, CO_2Et, CO_2Ph, SO_2Ph, SO_2Me, SO_2Et.

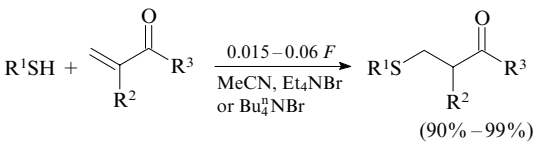
The proposed reaction mechanism[60,61] involves the reduction of allyl phenyl sulfone (**11**) to the radical anion, which deprotonates the starting sulfone **11**. The resulting carbanion adds to the activated double bond. The reaction is accompanied by the double bond migration in the addition product catalyzed by the electrogenerated base (a radical anion or a carbanion). In the dimerization of compound **11**, the isomerization of the double bond occurs not only in the product but also in the substrate; the resulting phenyl propenyl sulfone acts as a Michael acceptor.[60]



In some cases, the electrogenerated base initiates two sequential Michael additions to form 2 : 1 linear adducts; the cyclization of the addition product is also observed.[60,61]



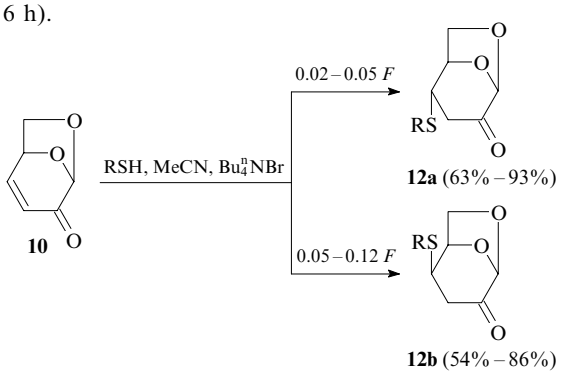
The electrochemically induced addition of thiols to activated alkenes[22,58,62] involves thiolate anions generated at the cathode and is generally much more efficient than the addition of CH-acids (the yield of addition products is nearly quantitative, the current yield is up to 6400%). This fact was attributed to the higher nucleophilicity of thiolate anions compared to carbanions.[62]



R^1 = n-C_8H_{17}, n-$C_{12}H_{25}$, CH_2CH_2OH, Ph; R^2 = H, Me; R^3 = Me, OMe, OEt

This conclusion is confirmed by a substantial decrease in the efficiency of the reaction when using less nucleophilic hetarylthiols (pyridine-2-thiol, benzoxazole-2-thiol). In these cases, the yield of the products decreases to 70%, and the current yield reduces to 500%–1000%.

In the study of the addition of thiols to levoglucosenone (**10**), Samet *et al.*[58] found that under kinetically controlled conditions (current density 0.2–0.3 mA cm^{-2}, reaction time 0.5–1 h), the reaction gives *erythro* isomers **12a**, whereas *threo* isomers **12b** are generated under thermodynamically controlled conditions (0.01–0.02 mA cm^{-2}, 4–6 h).



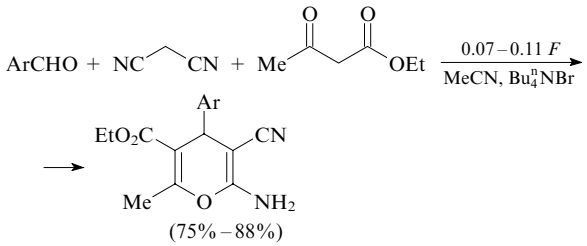
10

R = n-C_8H_{17}, n-$C_{10}H_{21}$, 4-ClC_6H_4, 4-$MeOC_6H_4$, 4-$O_2NC_6H_4$, 2 naphthyl

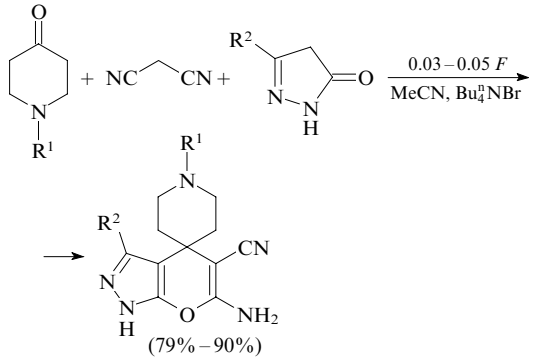
Compounds **12a** isolated in the pure form are transformed into isomers **12b** during the long-term electrolysis at a low current density according to the mechanism involving the retro-Michael reaction.

b. Tandem Knoevenagel–Michael reactions followed by cyclization

These transformations are of particular interest from the point of view of synthetic organic chemistry because they can be applied to the one-pot synthesis of complex compounds. For example, electrochemically induced multicomponent reactions in an aromatic aldehyde–



Ar = Ph, 4-ClC_6H_4, 3-$O_2NC_6H_4$, 2-thienyl, 4-pyridyl



R^1 = Ac, CO_2Et; R^2 = Pr^n, CH_2OMe

malononitrile – acetoacetic ester system [63] or in a piperidin-4-one – malononitrile – pyrazol-5-one system [64, 65] give the corresponding substituted 2-amino-4*H*-pyrans.

Electrogenerated superoxide, which abstracts a proton from malononitrile,[63] or the malononitrile anion formed directly from $CH_2(CN)_2$ if the reaction is carried out under an inert atmosphere,[64, 65] serve as an initiator. The subsequent reaction in solution is the typical tandem Knoevenagel – Michael reaction followed by intramolecular cyclization of the resulting adduct and its tautomeric transformation to yield 2-amino-4*H*-pyran as the final product.

c. Other addition reactions to the activated double bond

If radical anions generated by the electroreduction of the substrate are unable to abstract a proton from the reagents that are present in the system, they react with the substrate.

Initiation:

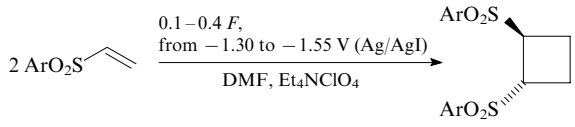
$$X + e^- \rightleftharpoons X^{-\cdot}$$

Chain propagation:

$$X^{-\cdot} + X \longrightarrow X_2^{-\cdot}$$

$$X_2^{-\cdot} + X \longrightarrow X_2 + X^{-\cdot}$$

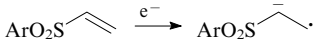
The cyclodimerization of aryl vinyl sulfones performed by Simonet and co-workers [66–71] was the first process of this type.



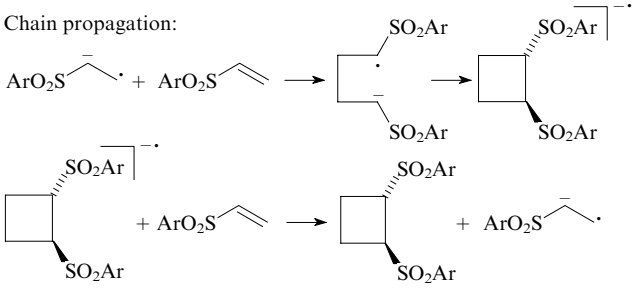
Ar = Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 2-naphthyl (20% – 67%)

The reaction mechanism proposed by Bergamini *et al.*[72] involves the coupling of the radical anion with the starting molecule and the cyclization of the resulting symmetric dimeric radical anion. The chain propagation is provided by the electron transfer from the cyclic radical anion to the substrate.

Initiation:

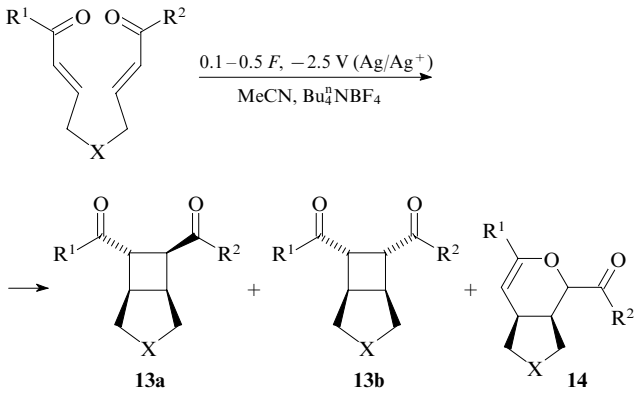


Chain propagation:



The replacement of the hydrogen atom at the double bond by an alkyl substituent gives rise to a mixture of unsymmetric linear dimeric products.[69] A comparative analysis and the theoretical explanation of the mechanism of the formation of cyclic and linear products were reported.[73]

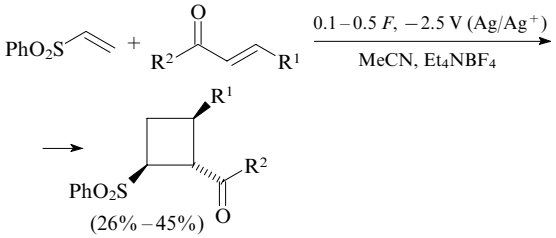
The intramolecular anion-radical cyclobutanation of unsaturated ketones and esters has been performed recently.[74, 75]



R^1, R^2 = Ph, 4-ClC_6H_4, 3,4-$Cl_2C_6H_3$, 2-naphthyl, Me, OEt;
X = CH_2, O

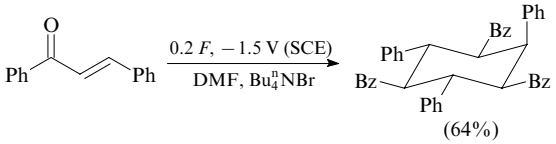
The yield of the products depends on the structure of the substrate and the supporting electrolyte. For example, in the case of X = CH_2, compounds **13** and **14** were prepared in a total yield of 88% with $Bu_4^nNBF_4$ supporting electrolyte and only in 45% yield with $LiClO_4$. In the case of X = O, both electrolytes provide a moderate yield of compounds **13** and **14** (43% – 53%); however, $Mg(ClO_4)_2$ unexpectedly proved to be efficient (yield 88%), that was attributed [75] to the difference in stability of ion pairs of radical anions with the corresponding cations. The role of ion pairs in the stereoselectivity of cyclobutanation is discussed also in another study.[73]

The formation of cyclobutanes with the involvement of unsaturated ketones was also observed in the intermolecular reaction of two substrates.[76]



R^1 = H, Me; R^2 = Me, Et, Ph

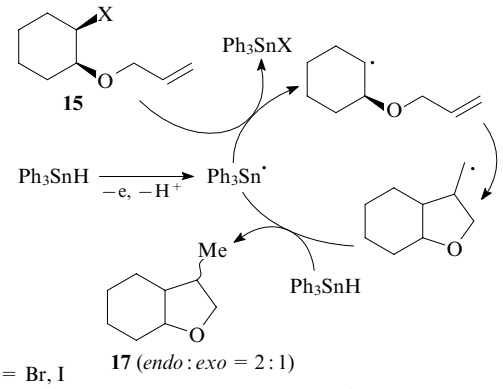
The electrochemically induced stereoselective cyclotrimerization of chalcone also proceeds *via* a radical-anion mechanism.[77]



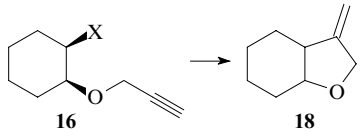
5. Redox reactions

Among a few reactions of this type, radical chain reactions induced by electrogenerated tin compounds are of particular interest.[78, 79] The cyclization of halogen-substituted alkenes **15** and alkynes **16** to the corresponding 3-methyl- and 3-methylidene-substituted octahydrobenzofurans **17** and **18** and the transformations of β-lactams **19** – **21** to products **22** and **23** (Scheme 2) [78] are examples of these reactions.

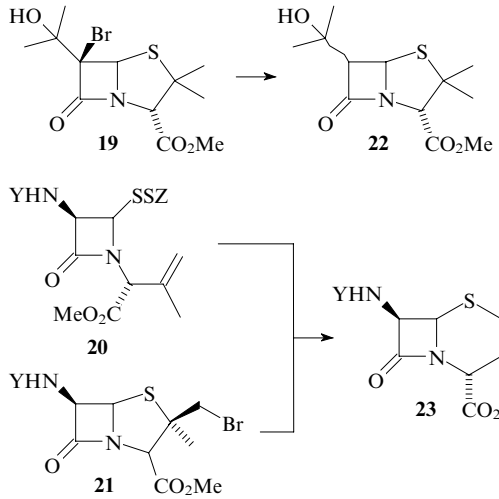
Scheme 2



X = Br, I



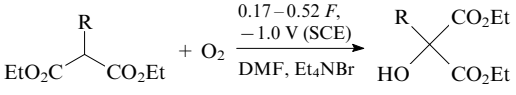
X = Br, I



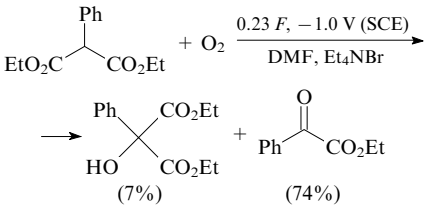
Y = $PhOCH_2C(O)$, Z is benzothiazol-2-yl

These reactions were carried out in the anode compartment of a divided cell in THF with the $Bu^n_4NClO_4$ electrolyte by passing 0.2–0.5 *F* of electricity; the yields of products **17** and **18** were 63%–72%; those of products **22** and **23** were 80%–98%.

Substituted malonic esters are oxidized by molecular oxygen; the reaction is initiated by superoxide.[80]



R = Me, Et



The proposed reaction mechanism[80] involves the deprotonation of malonic ester by superoxide and oxidation of the resulting anion by molecular oxygen.

Initiation:

$$O_2 + e^- \longrightarrow O_2^{-\bullet}$$

$$2\,O_2^{-\bullet} + RH \longrightarrow O_2 + HO_2^- + R^-$$

Chain propagation:

$$R^- + O_2 \longrightarrow ROO^-$$

$$ROO^- + R^- \longrightarrow 2\,RO^-$$

$$RO^- + RH \longrightarrow ROH + R^-$$

RH is malonic ester

The electrochemically induced oxidation of alcohols by aromatic halides in liquid ammonia to form carbonyl compounds was investigated.[81,82]

Initiation:

$$ArX + e^- \rightleftharpoons ArX^{-\bullet}$$

$$ArX^{-\bullet} \longrightarrow Ar^{\bullet} + X^-$$

Chain propagation:

$$ArX^{-\bullet} \longrightarrow Ar^{\bullet} + X^-$$

$$Ar^{\bullet} + >CH{-}OH \longrightarrow >\dot{C}{-}OH + ArH$$

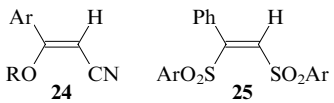
$$>\dot{C}{-}OH + NH_3 \longrightarrow >\dot{C}{-}O^- + NH_4^+$$

$$>\dot{C}{-}O^- + ArX \longrightarrow >C{=}O + ArX^{-\bullet}$$

This method has a limited scope in the synthesis because these reactions require complicated apparatus and liquid ammonia as the solvent.

6. Isomerization and exchange reactions

The electrochemically induced *cis–trans* isomerization efficiently proceeds in the case of sufficient reduction potential difference between the isomers ($\Delta E^\circ > 0.1$ V), the less stable isomer being more easily reduced. These conditions are realized for the isomerization of *Z*-enol ethers **24** (Ref. 83) and (*Z*)-1,2-di(arylsulfonyl)phenylethenes **25** (Ref. 84) to *E*-isomers.



Initiation:

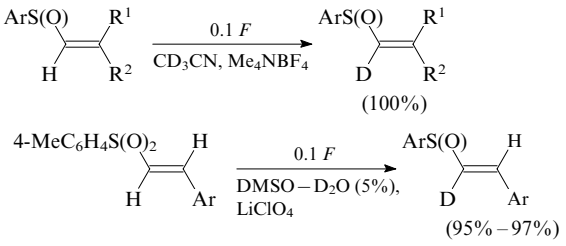
$$Z + e^- \rightleftharpoons Z^{-\bullet}$$

Chain propagation:

$$Z^{-\bullet} \rightleftharpoons E^{-\bullet}$$

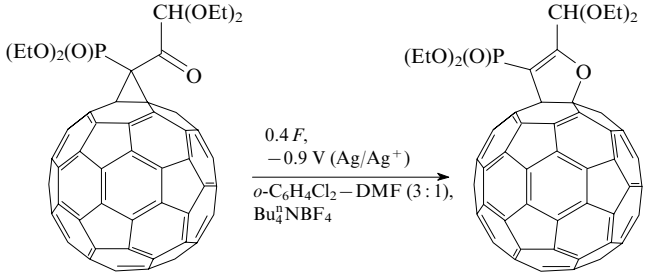
$$E^{-\bullet} + Z \rightleftharpoons E + Z^{-\bullet}$$

The hydrogen–deuterium exchange in α-unsaturated aryl sulfoxides[85] and aryl sulfones[86] proceeds during their electrolysis in MeCN-d_3 or DMSO-d_6, as well as in the presence of D_2O.

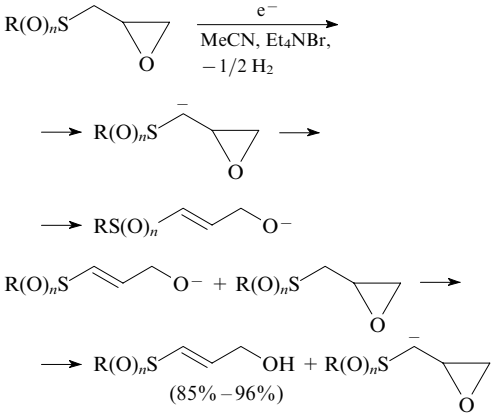


Deuterium is incorporated into the molecule upon the deuteron abstraction from a deuterated solvent by the radical anion of the substrate; if the starting compounds are mixtures of *Z*- and *E*-isomers, the reaction is accompanied by isomerization to give exclusively the *E*-isomer.[86] The double bond migration in unsaturated aryl sulfones most likely proceeds *via* a radical-anion mechanism as well.[60, 69, 73]

The radical-anion mechanism was proposed also for the isomerization of methano[60]fullerenes to dihydrofullerofurans.[87, 88]



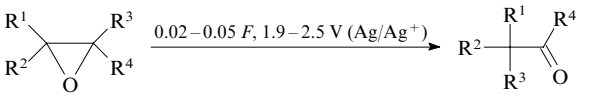
The isomerization of 2,3-epoxy alkyl sulfoxides and 2,3-epoxy alkyl sulfones to the corresponding allylic alcohols proceeds *via* a carbanion mechanism.[89]



R = Bu^n, n-C_8H_{17}, n-$C_{10}H_{21}$; *n* = 1, 2

During the reaction, 0.2 *F* and 0.1 *F* of electricity is passed in the case of sulfoxides (*n* = 1) and sulfones (*n* = 2), respectively.

The isomerization of epoxides to ketones was observed during the electrolysis in MeCN with the $LiClO_4$ electrolyte or in CH_2Cl_2 with the $Bu^n_4NClO_4$ electrolyte in the anode compartment of a divided cell.[90]



R^1, R^2, R^3 = H, Me, Ph; R^4 = Me, Ph

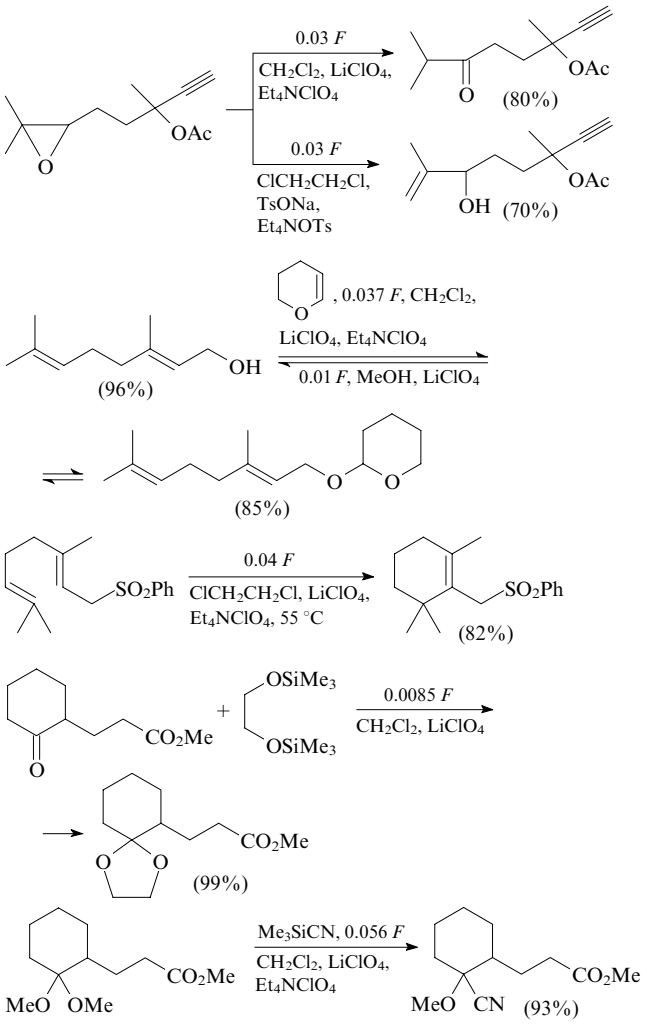
The proposed reaction mechanism involves the oxidation of epoxide to form the oxygen-centred radical cation, the epoxide ring opening and the rearrangement. However, in our opinion, it is more likely that the rearrangement induced by electrogenerated acid ($HClO_4$) takes place.

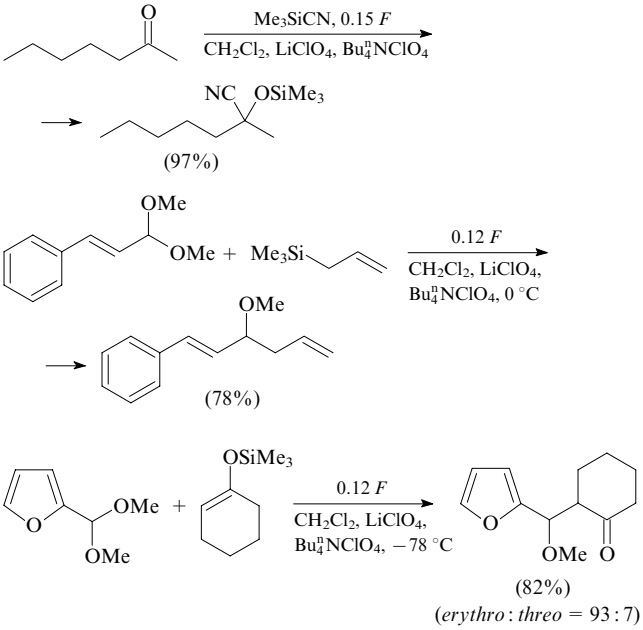
III. Electrochemically induced chain reactions in an undivided cell

1. Reactions initiated by electrogenerated acid

The oxidation of trace amounts of water at the anode in an aprotic solvent gives rise to solvated protons exhibiting extremely strong acid properties.[91]

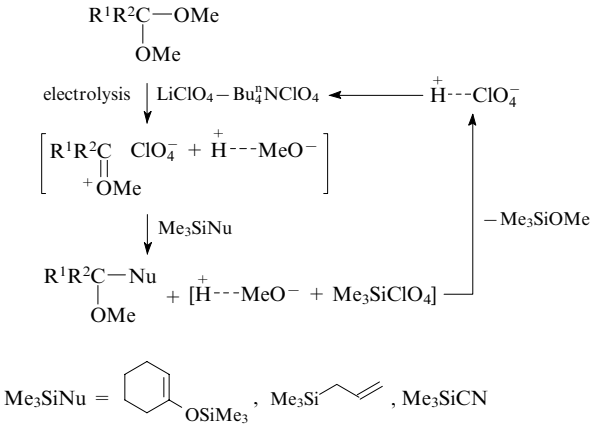
As a result, the electrolysis in an undivided cell produces, at the vicinity of the anode, a medium, in which acid-catalyzed reactions proceed, the system as a whole being neutral. This method was developed by Torii and co-workers for various electrochemically induced reactions, such as the epoxide opening giving ketones[91] and allylic alcohols,[92] the tetrahydropyranyl protection – deprotection of alcohols,[93] the cyclization of isoprenoids,[94] the acetalization of carbonyl compounds[95] and various reactions of carbonyl compounds and their acetals, including cyanation,[96, 97] allylation[97] and aldol reactions.[97, 98] The most typical examples of the above-mentioned reactions are given below.





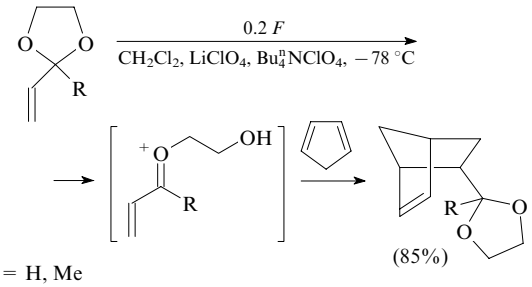
The general reaction mechanism for these transformations[97] involves the formation of a catalytic amount of a protic acid ($HClO_4$ for the $CH_2Cl_2-LiClO_4$ system) at the anode and the protonation of the substrate by this acid to form a cationic intermediate stabilized by the counterion (the perchlorate anion). The subsequent transformations of this cationic intermediate depend on the character of the nucleophile that is present in the system. Scheme 3 shows the probable mechanism of the reaction of acetals with organosilicon nucleophiles Me_3SiNu initiated by electrogenerated acid.[97]

Scheme 3



The best yields were achieved when the electrolysis was performed in CH_2Cl_2, dichloroethane or THF; MeCN showed good results in aldol reactions of acetals.[98] Lithium perchlorate with an additive of perchlorate of the quaternary ammonium cation (to increase the electrical conductivity of the solution) was generally used as the supporting electrolyte. The conversion of epoxides into allylic alcohols was carried out with the use of Et_4NOTs.[92]

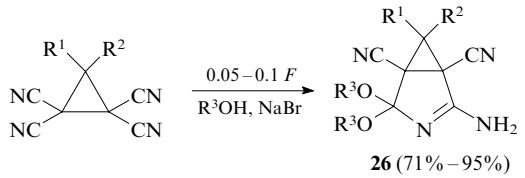
It should be noted that in some cases, the reactions initiated by electrogenerated acid are much more efficient than the corresponding chemical transformations. In particular, the epoxide opening in the presence of 60% aqueous $HClO_4$ or $BF_3 \cdot Et_2O$ affords ketones in a yield 20% lower than that achieved in the corresponding electrochemical reactions.[91] In some cases, electrochemically induced reactions are more selective. For example, the electrochemical Diels–Alder reaction of α,β-unsaturated acetals and cyclopentadiene results in a substantially higher *endo* to *exo* product ratio (50 : 1, R = Me) compared to that obtained earlier (3 : 1) in the synthesis by conventional chemical method. In addition, the electrochemical initiation leads to a substantial suppression of the polymerization of the substrate.[99]



R = H, Me

2. Reactions initiated by electrogenerated base

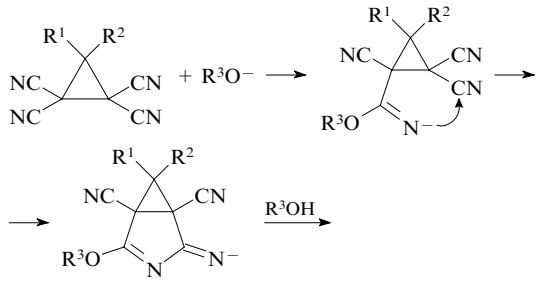
In the 1990s, a new class of electochemical chain reactions initiated in an undivided cell was discovered in the Laboratory of Homolytic Reactions of the N D Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences. Chain reactions are initiated by alkoxide anions electrogenerated at the cathode. These anions act as nucleophiles and are regenerated in subsequent chain chemical transformations to give the target product. The cyclization of 1,1,2,2-tetracyanopropanes to bicyclic pyrrolines **26** in an undivided cell in alcohols (700%–1900% current yield)[100–102] is the first discovered reaction of this type.

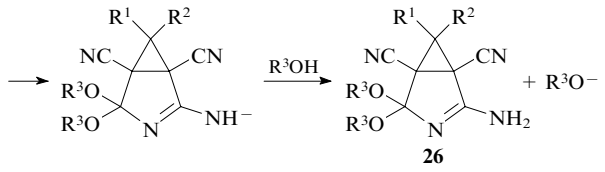


26 (71%–95%)

R^1 = Me, Et, Pr^n, Ph; R^2 = H, Me; $R^1-R^2 = (CH_2)_4$;
R^3 = Me, Et

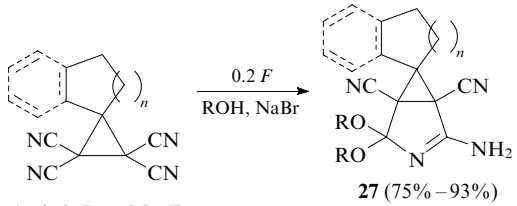
The reaction involves the addition of alkoxide anions to the CN group as the first step. The subsequent cyclization, the protonation of the intermediate and the addition of the second alkoxide anion followed by the protonation afford pyrroline systems. The regenerated alkoxide anion initiates the next cycle:





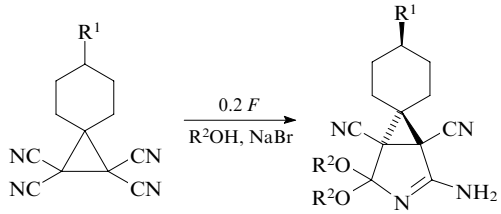
26

This method was used for the synthesis of various, including benzannulated, polycyclic pyrrolines **27** and **28**; in the case of substituted rings, the reactions are stereoselective.[103]



27 (75%–93%)

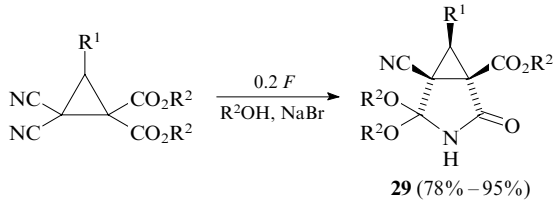
n = 1–3, 8; R = Me, Et



28 (51%–89%)

R^1 = Me, Bu^t, Ph; R^2 = Me, Et

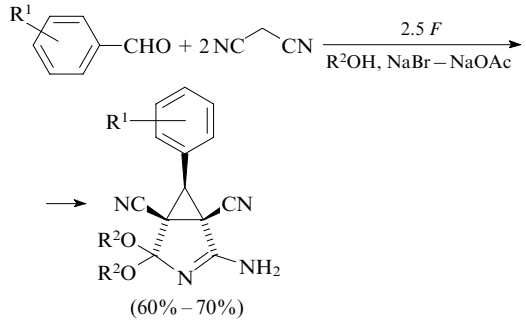
2,2-Dicyanocyclopropane-1,1-dicarboxylates give the corresponding pyrrolidones **29**.[104]



29 (78%–95%)

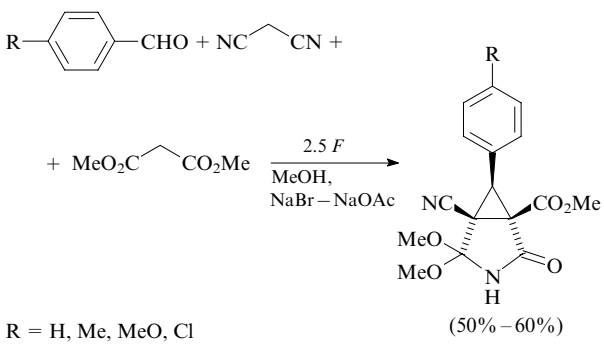
R^2 = Me: R^1 = Me, Et, Pr^n, Ph, 4-MeC_6H_4, 2-FC_6H_4, 2-ClC_6H_4, 4-$MeOC_6H_4$, 4-$O_2NC_6H_4$; R^1 = Ph, R^2 = Et

This procedure was successfully applied to the electrocatalytic, including multicomponent, synthesis of pyrrolines [105, 106] and pyrrolidones [107, 108] from acyclic reactants.



(60%–70%)

R^1 = H, 4-Me, 4-MeO, 2-Cl, 3-Br, 4-I; R^2 = Me, Et



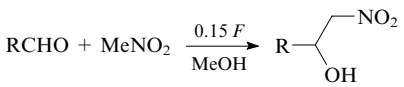
R = H, Me, MeO, Cl

(50%–60%)

In these processes, the synthesis of the cyclopropane moiety requires the stoichiometric amount of electricity (2 F), and at the final stage, the electrochemically induced chain reaction results in the closure of the pyrroline ring.

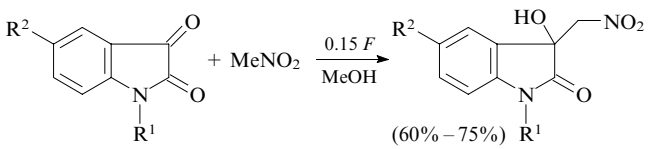
Electrochemically induced chain condensation reactions of carbonyl compounds with CH-acids were considered in a series of publications.

The electrochemically induced Henry reaction (the addition of nitromethane to aldehydes, isatins, acenaphthenequinone and phenanthrene-9,10-dione) in methanol was documented; the corresponding β-nitro alcohols were prepared in 60%–75% yield (400%–500% current yield).[109]



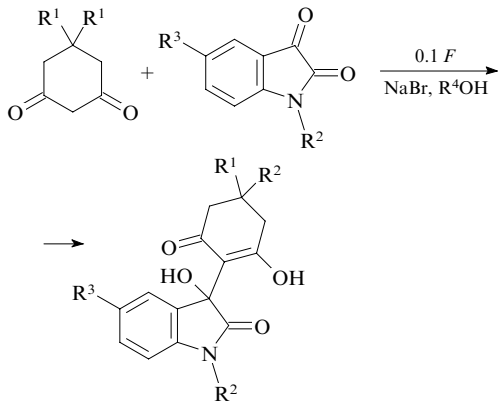
(60%–75%)

R = Ph, 4-MeC_6H_4, 3-BrC_6H_4, 4-$O_2NC_6H_4$, 3-$O_2NC_6H_4$, 2-furyl, n-C_5H_{11}



R^1 = H, Me, $PhCH_2$; R^2 = H, Me, Cl, Br

The reactions of isatins and cyclic 1,3-diketones gave aldol adducts **30**.[110]

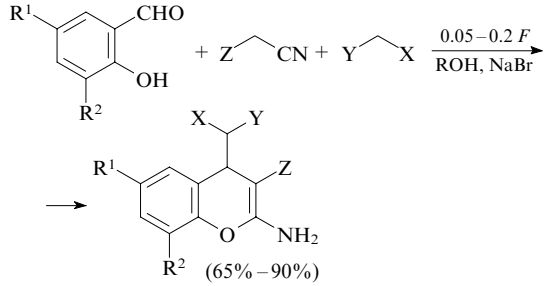


30 (70%–87%)

R^1 = H, Me; R^2 = H, Me, $PhCH_2$, Ac; R^3 = H, Me, Cl; R^4 = Me, Et

Due to the low current concentration of the base during the electrolysis performed in an undivided cell, the reaction can be terminated at the step of the aldol addition of the CH-acid to the carbonyl group, thus avoiding the subsequent dehydration, that is typical of the related both acid- and base-catalyzed chemical processes.

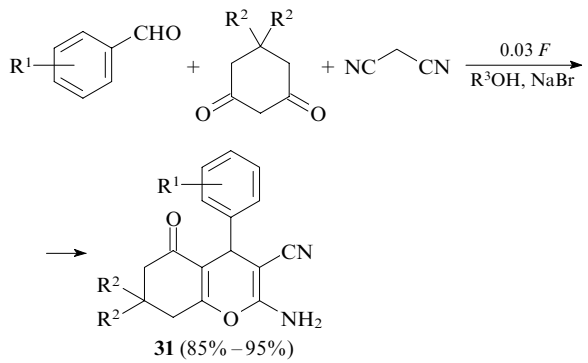
Methods for the synthesis based on electrochemically induced multicomponent reactions involving CH-acids and carbonyl compounds have been extensively developed in recent years. For example, the condensation of salicylic aldehydes with two CH-acids [malononitrile or cyanoacetate served as one acid and malonic ester, cyanoacetate, cyanoacetamide, malononitrile, phenylacetonitrile, pyrazolone or nitromethane acted as the other one (XCH_2Y)] afforded various 4*H*-chromenes (320% – 1900% current yield).[111–114]



X = CN: Y = CN, CO_2Me, $C(O)NH_2$, Ph; X = Y = CO_2Me;
X = H, Y = NO_2, *etc.*; Z = CN, CO_2Me

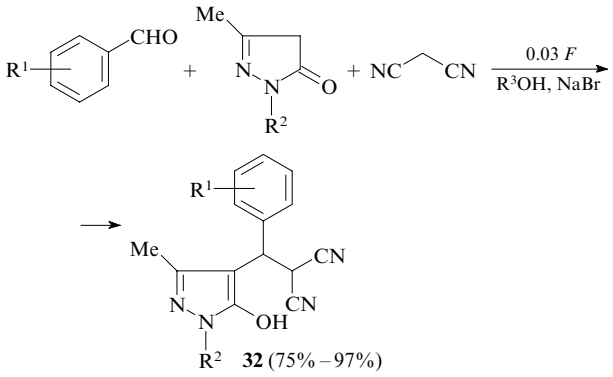
It should be noted that this electrocatalytic system distinguishes CH-acids based on their reactivity. Thus, the chromene ring is always formed with the involvment of the stronger CH-acid, which provides the synthesis of compounds containing substituents in a defined position.

The addition of pyrazolones to aromatic aldehydes produced 4,4′-(arylmethylene)bis(1*H*-pyrazol-5-ols) (80% – 96% yields).[115] The electrochemically induced multicomponent reactions of benzaldehydes, malononitrile and cyclic 1,3-diketones or pyrazolones giving 4-aryl-5,6,7,8-tetrahydro-4*H*-chromenes **31** (Ref. 116) or 3-aryl-2-cyano-3-(5-hydroxy-3-methylpyrazol-4-yl)propionitriles **32**,[117] respectively were described.



31 (85% – 95%)

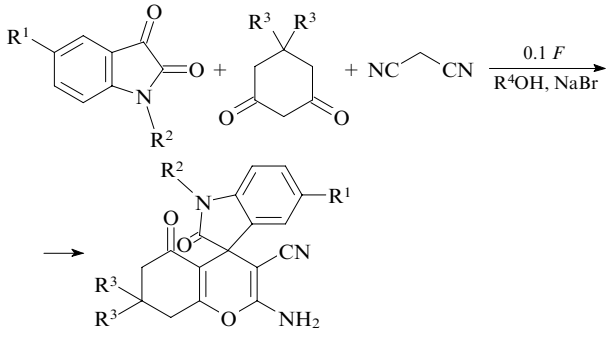
R^1 = H, 4-Me, 4-MeO, 4-Cl, 3-Br, 4-O_2N; R^2 = H, Me;
R^3 = Me, Et, Pr^n



32 (75% – 97%)

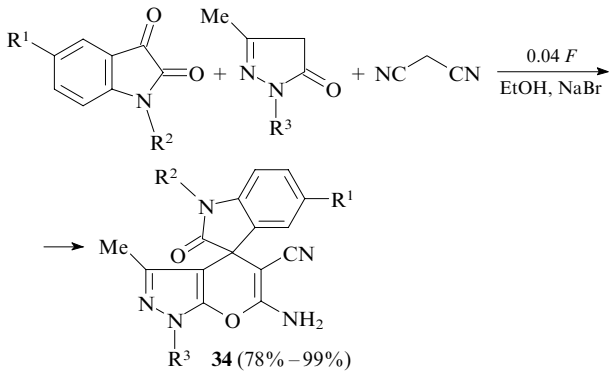
R^1 = H, 4-Me, 4-MeO, 4-Cl, 3-Br, 4-O_2N; R^2 = H, Ph;
R^3 = Me, Et, Pr^n

The condensation of isatins with two CH-acids [malononitrile was used as one CH-acid and cyclic 1,3-diketone, pyrazolone, barbituric acid or 4-hydroxyquinolin-2(1*H*)-one served as the other CH-acid] gave various spirocyclic structures (500% – 2500% current yield): spiro(5,6,7,8-tetrahydro-4*H*-chromene-4,3′-oxindoles) **33**,[118] spiro(indole-3,4′-pyrano[2,3-*c*]pyrazoles) **34**,[119] spiro(indole-3,5′-pyrano[2,3-*d*]pyrimidines) **35** (Ref. 120) and spiro(indole-3,4′-pyrano[3,2-*c*]quinolines).[121]



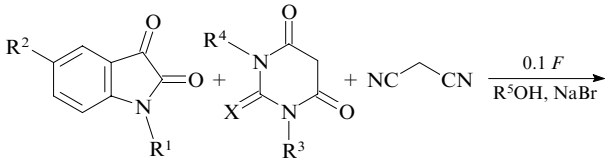
33 (83% – 97%)

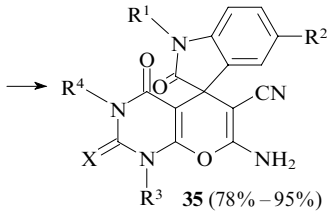
R^1 = H, Br; R^2 = H, Me, CH_2Ph, Ac; R^3 = H, Me; R^4 = Me, Et, Pr^n



34 (78% – 99%)

R^1 = H, Me, Cl; R^2 = H, Me, CH_2Ph; R^3 = H, Ph





35 (78% – 95%)

R^1 = H, Me, Ac; R^2 = H, Br; R^3 = Me, Et, Ph; R^4 = H, Me, Et, Ph; R^5 = Me, Et; X = O, S

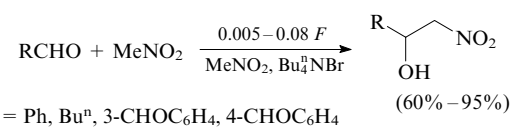
Therefore, the electrolysis in an undivided cell produces, at the vicinity of the cathode, a medium in which base-catalyzed reactions proceed, the system as a whole being neutral. The yield of products in the electrocatalyzed reaction is comparable [104] with or even higher [114] than that obtained in base-catalyzed reactions, the reaction time being substantially shorter.[114, 115] The choice of the solvent (methanol, ethanol, propanol) was generally dictated by the completeness of the crystallization of the product from the reaction mixture. In most cases, the products were isolated by the simple filtration and did not require additional purification. As for the supporting electrolyte, the use of NaBr is not necessary. Thus, similar results were obtained with $LiNO_3$ and NaOAc.[103, 104] In the one-pot synthesis of pyrrolines and pyrrolidones from acyclic compounds, the use of NaI instead of NaBr led to a decrease in the yield of the target product by 10% – 15%;[105, 107] in some cases, the addition of NaOAc resulted in the increase in the rate of the Knoevenagel condensation, thus enhancing the efficiency of the process as a whole.[106, 108]

In addition to investigations of Russian researchers,[100 – 121] who showed the synthetic scope of electrochemically induced chain reactions with the use of cathodically generated bases in an undivided cell, the Knoevenagel condensation of carbonyl compounds and malononitrile under solvent-free conditions without a supporting electrolyte (0.007 – 0.04 *F*, 12% – 100% yield) [34] and the cyclodimerization of aryl vinyl sulfones (0.1 *F*, 70% – 95%) [72] were studied. However, these processes have considerable drawbacks. The time of the reaction described in the study [34] is 12 h (!) *versus* 15 – 40 min in the studies,[109 – 121] and the cyclodimerization of aryl vinyl sulfones requires thoroughly dried and degassed solvents (DMF, DMSO), whereas usual commercial alcohols were used in the investigations.[100 – 121]

3. Reactions with the use of a soluble anode

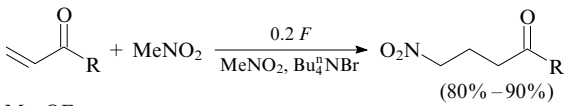
This type of reactions is considered in a special section because the process, being performed in an undivided cell, is accompanied by real alkalization of the reaction medium due to the formation of solvates of metal cations with a cathodically generated base.

A soluble Mg anode was used to perform the electrocatalytic addition of nitromethane to aldehydes and dialdehydes,[30] as well as the addition of nitro compounds [30] and thiols [22, 30, 58, 62] to activated alkenes.



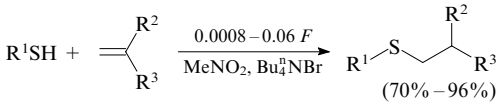
(60% – 95%)

R = Ph, Bu^n, 3-$CHOC_6H_4$, 4-$CHOC_6H_4$



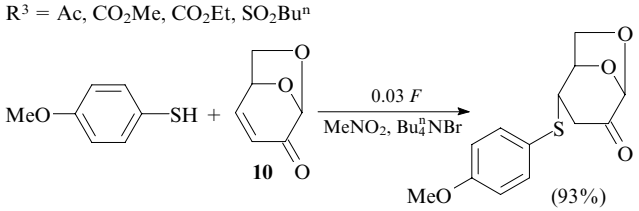
(80% – 90%)

R = Me, OEt



(70% – 96%)

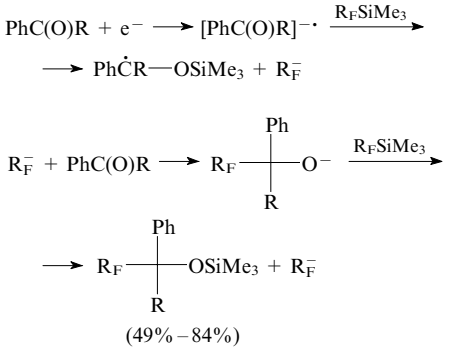
R^1 = n-C_8H_{17}, $HOCH_2CH_2$, Ph; R^2 = H, Me; R^3 = Ac, CO_2Me, CO_2Et, SO_2Bu^n



(93%)

In these reactions, the current yield varies from 400% to 123 000%. In some cases, magnesium solvates that are formed during electrolysis substantially affect the course of the reaction. For example, the addition of thiols to levoglucosenone (**10**) gives exclusively the *erythro* isomer, because magnesium solvates hinder the subsequent isomerization to the thermodynamically more stable *threo* isomer,[58] whereas no conversion was observed in the reaction of nitromethane with *o*-phthalaldehyde, and the researchers were forced to return to a divided cell.[30]

A soluble Al anode was used to perform the addition of fluoroalkyl(trimethyl)silanes to carbonyl compounds (0.012 – 0.3 *F*, DMF, Et_4NBF_4).[122, 123]



(49% – 84%)

R = H, CF_3; R_F = CF_3, $CFCl_2$, CF=CFCl

The reduction potential of chlorine-containing silanes (R_F = $CFCl_2$, CF=CFCl) is substantially lower and is comparable with the reduction potential of the carbonyl compound. The electron transfer to this silane is accompanied by elimination of Cl^- and the chain termination, resulting in a decrease in the yield of addition products by 20% – 30%.

IV. Conclusion

This review surveys the state-of-the-art of the research on organic electrosynthesis based on electrochemically induced chain reactions. Due to the use of the electric current as the 'environmentally friendly reactant' and the catalytic character of the process, electrochemically induced chain reactions are very attractive from a green chemistry perspective. The observed increase in the number of publications on the development of synthetic methods based on these reactions is largely due to the development of a new promising area of electrochemistry of organic compounds, that is electrochemically induced chain reactions involving CH-acids in an undivided cell in the presence of catalytic amounts of

electrogenerated base. In addition to engineering simplicity and a high yield of the product per unit of reactor volume, an advantage of an undivided cell is that the system is, as a whole, neutral. Due to this fact, the reaction can be performed under very mild conditions, which enables the synthesis of compounds sensitive to acids and bases, and the application of a catalytic amount of electricity reduces possible undesirable direct redox reactions at electrodes. Further progress in the development of new methods of organic electrosynthesis, the design of promising electrochemical modifications of known chemical reactions and the discovery of reactions, which have no analogues in conventional organic chemistry, would be expected in the near future.

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