Russian Chemical Reviews **84** (5) 485 – 497 (2015) © 2015 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RCR4465

Electrochemical synthesis of cyclopropanes

M N Elinson, E O Dorofeeva, A N Vereshchagin, G I Nikishin

N D Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences
Leninsky prosp. 47, 119991 Moscow, Russian Federation

Data on methods of electrochemical synthesis of cyclopropanes are summarized and described systematically. Direct electrochemical methods to afford cyclopropanes in both cathodic and anodic processes are considered. Among indirect electrochemical methods such as the processes employing electrogenerated bases and also those involving electrogenerated metal complexes, attention is focused on the most promising methods for the synthesis of functionally substituted cyclopropanes, namely, the electrocatalytic cascade and multicomponent transformations of CH acids and also the joint electrolysis of CH acids and activated alkenes or carbonyl compounds in the presence of alkali metal halides as mediators. The bibliography includes 62 references.

Contents

I. Introduction 485
II. Direct electrochemical processes giving cyclopropanes 486
III. Indirect electrochemical processes giving cyclopropanes 490
IV. Conclusion 495

I. Introduction

Chemistry of cyclopropanes is an actively developing field of organic chemistry. Cyclopropanes are unique compounds capable of unusual structural transformations with ring expansion and rearrangement, owing to the considerable ring strain. This has determined the wide use of strained ring systems as building blocks (synthons) in the targeted synthesis of organic molecules and also the development of new approaches to the synthesis of functionally substituted small rings.[1]

Compounds of various structure containing the cyclopropane moiety serve as medical and biological products and also as plant-protecting substances (herbicides, fungicides and pesticides). Furthermore, the functionally substituted cyclopropanes are abundant in nature, providing vital biochemical processes in plants, bacteria, fungi and insects.[1] Many of these compounds are of particular interest as they exhibit diverse pharmacological activities.[2 – 5]

During the last decade, several reviews have been published devoted to the chemical synthesis of cyclopropanes and considering the most important methods of cyclopropane synthesis, ranging from the classical methods of 1,3-elimination and alkylation of enolates to the cascade processes involving the Michael addition[6, 7] followed by ring closure and [2 + 1]-cycloaddition.[8 – 10] Although modern organic chemistry has at its disposal numerous approaches to constructing the cyclopropane moiety, the active research along this line is still in progress. The general drawback of the Michael addition reactions followed by ring closure to afford cyclopropanes is that excessive amounts of complex, often expensive precursors and considerable amounts of deprotonating reagents are usually required.

The main approach to the synthesis of cyclopropane derivatives is the [2 + 1]-cycloaddition, which can be illustrated most clearly by the addition of a carbene to a double bond. The limitations of this method are largely associated with the necessity of using equivalent and often even excessive amounts of bases to generate carbenes or fairly expensive catalysts.

Besides the development of chemical methods for building three-membered carbocycles, electrochemical approaches to the synthesis of such structures have been developed since the 1970s.[11] The rapid progress in organic electrosynthesis in the following years was associated with the fact that the electric current is the cheapest and environmentally cleanest 'reagent'. In the last decades, the electrochemical methods were employed to perform a number of targeted electrocatalytic selective transformations of organic compounds which could not be performed by methods of the classical organic chemistry.[12, 13]

M N Elinson Doctor of Chemical Sciences, Professor, Leading Researcher of the ZIOC RAS.
Telephone: + 7(499)137 – 3842, e-mail: elinson@ioc.ac.ru
E O Dorofeeva Candidate of Chemical Sciences, Junior Researcher of the same Institute.
Telephone: + 7(499)137 – 3842, e-mail: e.o.dorofeeva@gmail.com
A N Vereshchagin Candidate of Chemical Sciences, Senior Researcher of the same Institute.
Telephone: + 7(499)137 – 3842, e-mail: vereshchagin@ioc.ac.ru
G I Nikishin Corresponding Member of the Russian Academy of Sciences, Counsellor of the Russian Academy of Sciences.
Telephone: + 7(499)135 – 5328, e-mail: nika@ioc.ac.ru
Current research interests of the authors: organic chemistry, organic synthesis, organic electrosynthesis, chemistry of organic free radicals.

Received 25 April 2014
Uspekhi Khimii **84** (5) 485 – 497 (2015); translated by T Ya Safonova

The present review is aimed at systematization and generalization of the data on electrochemical and electrocatalytic methods for the synthesis of cyclopropane derivatives.

II. Direct electrochemical processes giving cyclopropanes

In direct electrochemical transformations, electrons are transferred from the cathode surface to the substrate in a reduction process and from the substrate to the anode in an oxidation process. Thus, the molecules involved in the reaction are converted into their active state (formation of radicals, anions or cations) directly on the electrode surface.

Direct electrochemical transformations of the following three types are used most extensively: potentiostatic (constant-potential), galvanostatic (constant-current), and constant-voltage processes. As a rule, to carry out a selective electrochemical transformation in the direct mode, the electrolysis is performed at a controlled potential, which requires the use of non-trivial technological equipment and also preliminary determination of the reduction (or oxidation) potentials of the reactants before the reaction.

The direct electrochemical processes carried out at a controlled potential are characterized by the following features:

— as a rule, these methods are implemented in divided cells, often of a complicated design;

— the electrolysis in undivided cells often involves the use of sacrificial anodes; in this case, the isolation of target compounds becomes a difficult task due to the formation of considerable amounts of insoluble metal oxides; special procedures for removing them are cumbersome and commercially unprofitable;

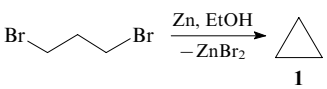
— aprotic media of high purity grades are used (otherwise, the reaction either fails to occur or proceeds nonselectively);

— the processes are performed at low current densities ($\ll 100$ mA cm^{-2}), which increases the reaction time (from 10 h to several days).

II.1. Cathodic reduction

A widely known chemical method for the synthesis of the cyclopropane moiety is cyclization of 1,3-dihalogen derivatives. It is by this method that cyclopropane (**1**) was synthesized for the first time in 1882 in a yield of 56% by treating 1,3-dibromopropane with zinc dust (Scheme 1).[14]

Scheme 1

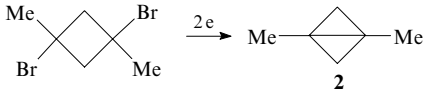


1

In 1967, the electrochemical synthesis of cyclopropane (**1**) from 3-bromopropyltriethylammonium bromide was performed for the first time.[15] The electrolysis at a mercury cathode in a saturated LiBr solution in dry DMF was carried out in the cathode compartment of a divided cell of a complicated design with a platinum anode at a constant voltage of 40 V; the yield of cyclopropane was not specified.

Under similar conditions, bicyclobutane **2** and spiropentane **3** were synthesized (Scheme 2, 3). Electrolysis of 1,3-dibromo-1,3-dimethylcyclobutane in the cathodic part of a divided cell gave in 16 h bicyclobutane **2** in 55% yield.[15]

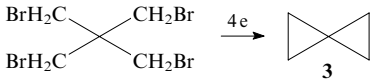
Scheme 2



2

The electroreduction of 1,3-dibromo-2,2-di(bromomethyl)propane affords spiropentane **3** in 50% yield (see Scheme 3).[15]

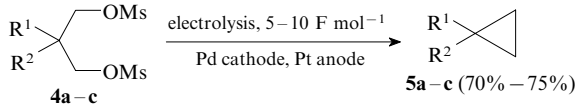
Scheme 3



3

The electroreduction of 1,3-dimethanesulfonates **4a–c** in DMF carried out in the cathode compartment of a divided cell equipped with a lead cathode and a platinum anode produced alkyl- and dialkyl-substituted cyclopropanes **5a–c** in 70%–75% chemical yields and with 15%–30% current efficiency. According to the authors, the electroreduction of compounds **4a–c** was a two-electron process and their complete conversion consumed from 5 to 10 F mol^{-1} (F = 96 485 C) of electricity at a constant current (I) of 0.2 A and current density of 5.7 mA cm^{-2} (the electrolysis time was from 12 to 24 h) (Scheme 4).[16]

Scheme 4



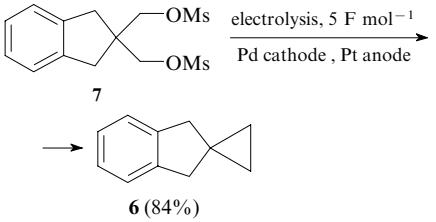
4a–c **5a–c** (70%–75%)

Ms = SO_2Me; R^1 = H, R^2 = n-C_8H_{17} (**a**); $R^1 = R^2$ = Bn (**b**); R^1 = Bn, R^2 = CH=CH_2 (**c**)

This study has demonstrated[16] that the starting compounds **4a–c** are unstable under the electrolysis conditions and should be injected into the cathode compartment gradually and dropwise in order to reach the high yield of cyclopropane.

Spirocyclopropane **6** containing the dihydro-1*H*-indene moiety was obtained in a chemical yield of 84% with a current efficiency of 34% by the electrolysis of dimethanesulfonate **7** in DMF in the presence of tetraethylammonium *p*-toluenesulfonate as the supporting electrolyte; in the process, 5 F mol^{-1} of electricity was passed in 12 h (Scheme 5).[16]

Scheme 5



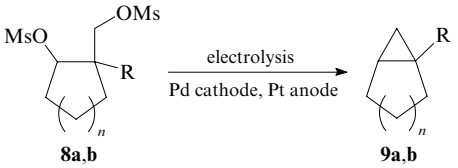
7

6 (84%)

The electroreduction of cyclic dimethanesulfonates **8a**,**b** under the conditions described above afforded fused bicyclic compounds **9a**,**b** in 55% and 52% yields, respectively, (Scheme 6).[16]

Annulated cyclopropane **9b** is formed non-streoselectively, as a mixture of *cis*- and *trans*-isomers in the 1 : 2.7 ratio. The isomers were separated by liquid chromatography.[16]

Scheme 6



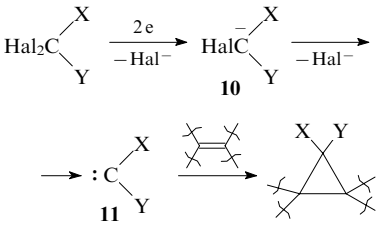
8a,b **9a,b**

R = n-C_6H_{13}, *n* = 1 (**a**); R = H, *n* = 8 (**b**)

The [2 + 1]-cycloaddition is the key step in many procedures of preparation of strained cyclopropane structures. The popular chemical method of cyclopropanation with halocarbenes, attractive due to its simplicity, was discussed in detail in a review.[17] Halocarbenes are generated *in situ* by treatment with alkali metal alkoxides or hydroxides.

Apart from the chemical methods of carbene generation, an electrochemical method which does not require large amounts of expensive alkaline reagents was successfully used in the practice of organic synthesis. The electrochemical generation of carbenes in cathodic processes involves the intermediate formation of thermodynamically unstable anions. For instance, the electroreduction of the C–Hal bond in compounds of the general composition $CHal_2XY$ affords anion **10**; the fragmentation of the latter produces carbene **11** (Scheme 7).[18, 19]

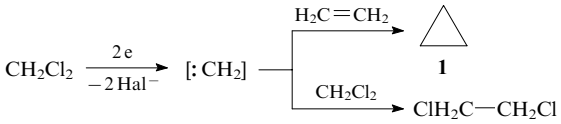
Scheme 7



A series of dihalocarbenes and their analogues [$:CCl_2$, $:CBr_2$, :CBrCl, $:CF_2$, $:C(CN)_2$] were generated by elimination of a halide anion from an electrogenerated α-halocarbanion and were successfully used to prepare the corresponding cyclopropanes by the [2 + 1]-cycloaddion to alkenes (see Scheme 7).[13]

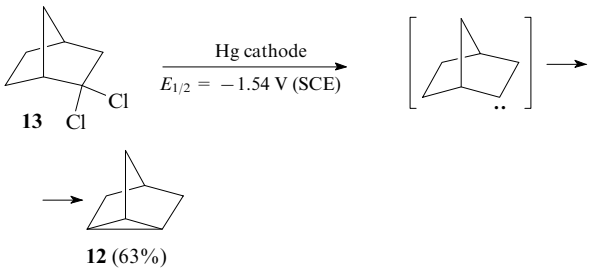
An example of this type of reaction is the electroreduction of dichloromethane at an Al cathode to form a mixture of 1,2-dichloroethane, ethylene and cyclopropane (**1**) (no yields or product ratios were reported) (Scheme 8).[20]

Scheme 8



Tricyclo[2.2.1.$0^{2,6}$]heptane (**12**) was synthesized in a yield of 63% *via* electroreduction of 2,2-dichloronorbornane (**13**) in DMF at a Hg cathode by passing 2 F mol^{-1} of electricity under potentiostatic conditions (Scheme 9).[21]

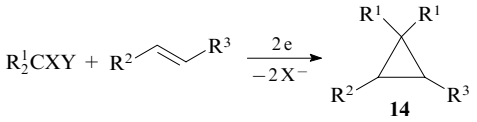
Scheme 9



SCE is saturated calomel electrode

In the 1990s, the electrochemical version of the Simmons–Smith reaction was proposed. The electrolysis of dihalomethane in an undivided cell equipped with a steel cathode and a sacrificial zinc anode was carried out in the presence of alkenes to afford the corresponding cyclopropanes **14** (Scheme 10, Table 1). Presumably, the cyclopropanation proceeded *via* the formation of zinc carbenoid CH_2-Zn-I_2.[22]

Scheme 10



In this electrochemical process, an excess of dihalomethane was gradually added to the reaction mixture up to complete conversion of the original alkene *via* its constant-current electrolysis (I = 0.2 A, cathode surface area 20 cm^2, reaction time from 3 to 8 h) in argon flow at 40 °C. The reaction was monitored by GLC.[22]

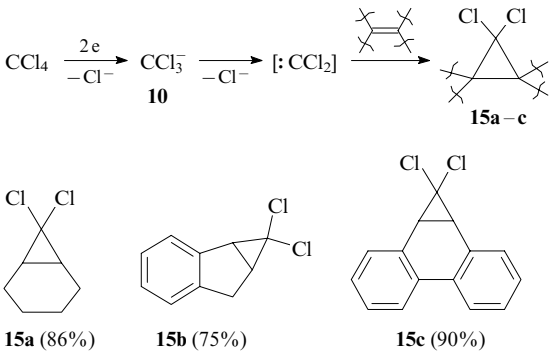
A series of fused dichlorocyclopropanes **15a–c** were synthesized in 75%–90% chemical yields by electrolysis of CCl_4 and alkenes in anhydrous chloroform in the presence of quaternary ammonium salts as the supporting electrolytes. The electrolysis was carried out in the cathode compartment of a divided electrolytic cell equipped with a lead cathode and a platinum anode at a constant current of 0.2 A for 3–6 h. The current efficiency for cyclopropane **15a–c** was 13%–45% (Scheme 11, the chemical yields are shown).[23]

The nucleophilic addition of organic anions to the activated double bond in the presence of bases, *i.e.*, the Michael reaction,[6, 7] is a fundamental method for the formation of carbon–carbon bonds in classical organic chemistry. For the synthesis of functionally substituted cyclopropanes, a version of the Michael reaction with the subsequent closure of a three-membered ring was used. In

Table 1. Electrochemical cyclopropanation of alkenes by dihalomethanes (the electrochemical version of the Simmons–Smith reaction).[22]

Alkene	R^1_2CXY	Yield of **14** (%)	Alkene	R^1_2CXY	Yield of **14** (%)
MeCH=CHCH$_2$OH	CH_2Br_2	56	PhCH=CHCH$_2$OH	CH_2BrCl	59
MeCH=CHCH$_2$OH	CH_2BrCl	54	CH_2=CHCH$_2$OPh	CH_2Br_2	52
MeCH=CHCH$_2$OH	CH_2I_2	47	Geraniol	CH_2Br_2	70
MeCH=CHCH$_2$OH	CMe_2Br_2	51	Cyclooctene	CH_2I_2	75

Scheme 11

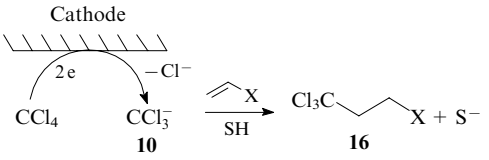


this case, the added carbanion should contain a good leaving group at the anionic site.[8]

Some geminal polyhalo compounds are suitable precursors for the preparation of halo carbanions. The use of electric current to generate halo anions makes it possible to sharply decrease the consumption of auxiliary reagents and improve the environmental characteristics of the process.

As mentioned above, in the media having low proton-donor properties, the fragmentation of unstable halo carbanion **10** affords carbene **11**, which reacts with electron-donating alkenes to form the cyclopropane ring (see Scheme 7). However, in the presence of alkenes with a double bond activated for the subsequent nucleophilic attack, carbanion **10** can rapidly add to the alkene by the Michael mechanism to afford linear adduct **16** (Scheme 12).[17]

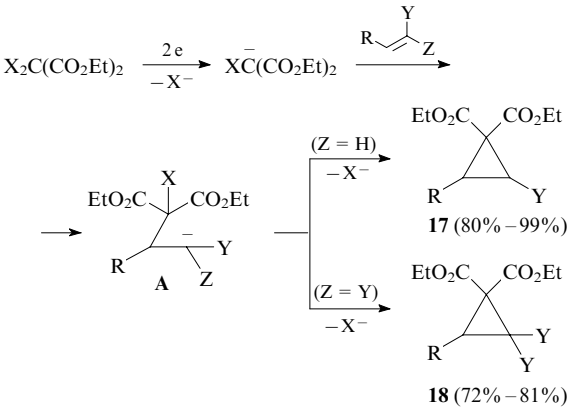
Scheme 12



X = CO_2Et, CN; SH is protic solvent

This feature of halo carbanions was used in the electrosynthesis of cyclopropanes. The Michael addition of the ethyl chloro- or bromomalonate anion to an alkene followed by ring closure in the intermediate carbanion **A** with elimination of a halide anion afforded cyclopropanes **17** and **18** (Scheme 13).[24, 25]

Scheme 13

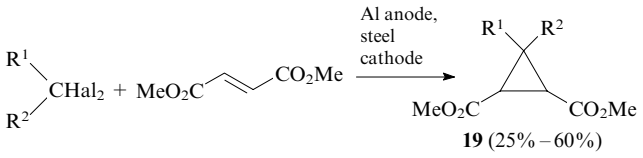


X = Cl, Br; R = H, Me, Ph, 4-MeC_6H_4; Y = CHO, Ac, CO_2Et, CN

The electrolysis was carried out in the cathode compartment (mercury or platinum cathode) of a divided cell in argon atmosphere for 8 h in the constant-current mode (20 mA); 2 F mol^{-1} of electricity was passed.[24, 25] The yield of cyclopropanes **17** and **18** was substantially higher upon the electrochemical activation of chloro- or bromomalonate anions as compared with their chemical activation under the action of bases.[24, 25]

The addition of electrochemically generated halo carbanions to dimethyl fumarate afforded substituted cyclopropanedicarboxylates **19** in moderate yields (Scheme 14). The current with the density of 20 mA cm^{-2} was passed through a DMF solution of activated alkene containing an excess of halo compounds in an undivided cell equipped with a sacrificial aluminium anode and a stainless steel cathode until alkene was completely converted.[26]

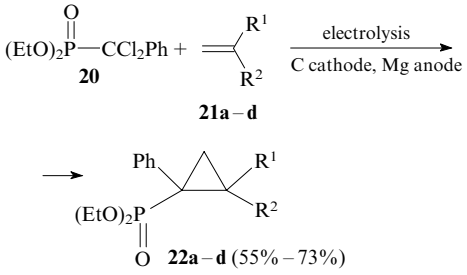
Scheme 14



R^1 = H, Me, Hal; R^2 = Me, Ph, CO_2Me; Hal = Cl, Br

The constant-current electroreduction of (α,α-dichlorobenzyl)phosphonates **20** in the presence of a five-fold excess of Michael acceptors **21** carried out in an undivided cell with a carbon felt cathode and a sacrificial magnesium anode[27] afforded cyclopropylphosphonates **22** (Scheme 15). A constant current (100 mA) was passed through a reactant solution in DMF until phosphonates **20** were completely consumed (according to ^{31}P NMR monitoring). After the treatment of magnesium oxide formed with a hydrochloric acid solution, cyclopropylphosphonates **22** were isolated by column chromatography in 55%–73% yields.[27]

Scheme 15

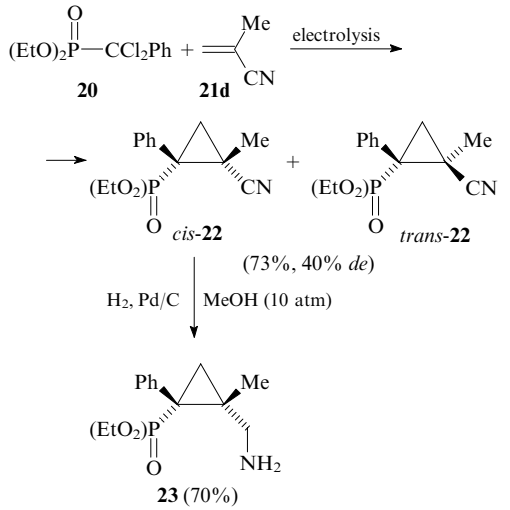


R^1 = H: R^2 = CO_2Me (**a**), CO_2Bu^t (**b**);
R^1 = Me: R^2 = CO_2Me (**c**), CN (**d**)

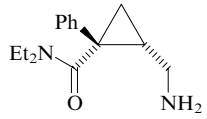
This electrochemical approach was used in a highly efficient two-step synthesis of compound **23** [an analogue of Milnacipran (**24**)], a clinically efficacious antidepressant drug belonging to the group of selective serotonin and noradrenalin reuptake inhibitors (Scheme 16).[27]

An electrochemical version of the Perkin reaction was implemented in an acetonitrile medium in the cathode compartment (Pt foil) of a divided cell *via* joint constant-current (80 mA) electrolysis of compounds **25** containing an activated methylene group and 1,2-dibromoethane.

Scheme 16



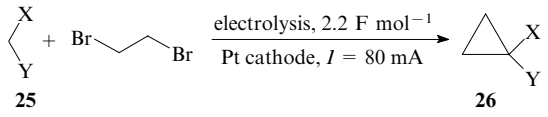
Structure 24



Milnacipran (**24**)

1,1-Disubstituted cyclopropanes **26** were formed as 2.2 F mol^{-1} of electricity was passed (glassy carbon anode, Pt cathode) (Scheme 17, Table 2).[28]

Scheme 17



The addition of azobenzene as the mediator (electrocatalytic process) made it possible to increase the yield of cyclopropanes up to 80%–85% (see Table 2).[28]

The cyclopropane moiety was formed upon electrochemical reduction of methyl abscisate (**27**) carried out at a mercury cathode in a divided cell at a constant potential of −2.0 V *vs.* Ag/AgCl electrode in a H_2O–MeCN (4 : 1) mixture in argon atmosphere during 4.5 h (Scheme 18).[29] To obtain bicyclo[4.1.0]heptane **28**, the constant acidity of the medium (pH 7) had to be maintained in the cathode part of the cell.[29]

Scheme 18

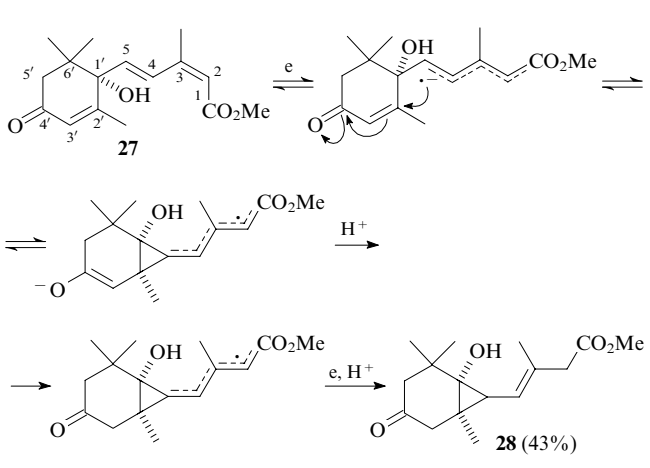


Table 2. Electrochemical and electrocatalytic methods for the synthesis of 1,1-disubstituted cyclopropanes **26**.[28]

X	Y	Yield of **26** (%)	
		electrochemical process	electrocatalytic process
Ac	Ac	25	31
CN	CN	60	64
Ac	CO_2Et	12	85
CN	CO_2Et	12	85
CO_2Et	CO_2Et	12	80

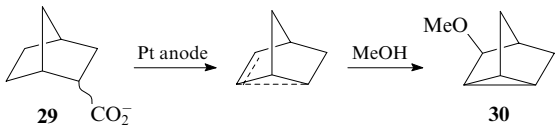
According to the mechanism proposed by the authors, compound **28** was formed in the consecutive two-electron reduction of methyl ester **27** with the addition of two protons. The experiments using isotope labels have shown that two protons add to the C(2) and C(3′) atoms.[29]

II.2. Anodic oxidation

To our knowledge, only two descriptions of electrochemical anodic processes to afford cyclopropane have been reported.[30, 31]

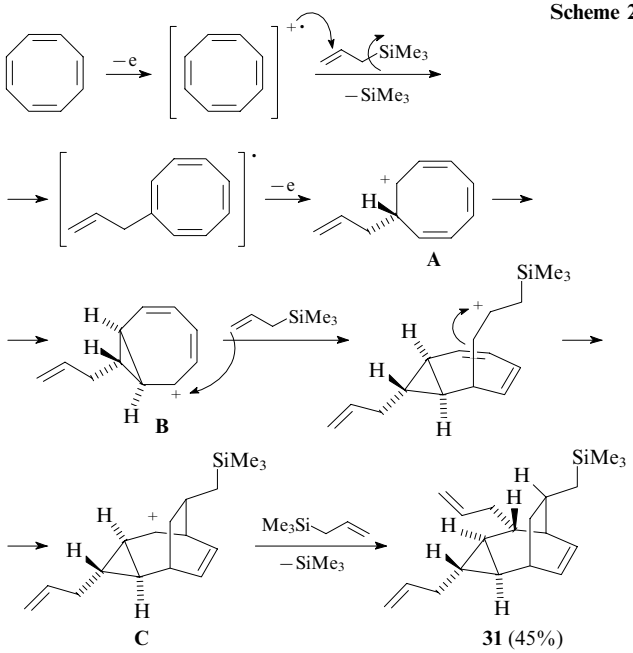
The electrooxidation of *exo*- and *endo*-5-norbornen-2-carboxylic acids **29** in methanol at a platinum anode affords 3-methoxynortricyclene (**30**) in a yield of 56% (Scheme 19). However, no experimental details for this process were published.[30]

Scheme 19



Tricyclic system **31** containing a fused three-membered carbocycle was synthesized in 45% chemical yield and with 10% current efficiency by electrooxidation of cyclooctatetraene (COT) in the presence of allyltrimethylsilane (Scheme 20). A COT solution containing a 20-fold excess

Scheme 20



of allyltrimethylsilane in acetonitrile was subjected to oxidation at a platinum anode under constant-current conditions (0.1 A) for 4 h.[31] The reaction was carried out in a divided cell (in an undivided cell, the cyclooctatetraene reduction produced a mixture of trienes). The following mechanism was proposed for this process: COT is oxidized at the anode to afford a radical cation, which adds to allyltrimethylsilane with subsequent electron transfer to afford cation **A**. The rearrangement of cation **A** to give cyclopropane **B**, the nucleophilic attack by silane, the ring closure to form carbocation **C** and the second nucleophilic attack by silane afford tricyclic adduct **31** (see Scheme 20).[31]

III. Indirect electrochemical processes giving cyclopropanes

In the recent years, the indirect electrochemical oxidation or reduction has been among the most actively developing areas of organic electrosynthesis. This method includes the electrochemical formation and regeneration of redox reagents (mediators). This substantially extends the scope of applicability and simplifies the equipment of the classical electrosynthesis. In these processes, the mediator is either oxidized or reduced at the electrodes to subsequently react in solution with the substrate; hence, the mediator serves as a a redox catalyst, *i.e.,* the electron carrier. The subsequent electrochemical process at the electrode regenerates the active form of the mediator. As a result, an indirect electrocatalytic process takes place.

The important advantages of the indirect electrochemical treatment of the substrate are the higher reaction rate and selectivity due to the combination of specially selected successive electrochemical and chemical reactions and also the use of undivided cells and the constant-curent mode of the process.

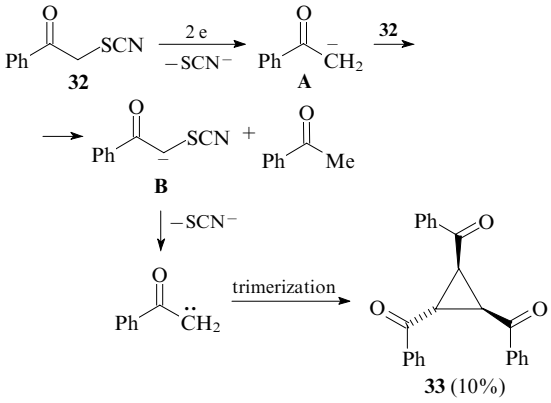
III.1. Electrochemical transformations involving electrogenerated bases

The aforementioned joint electrolysis of compounds **25** containing an activated methylene group and 1,2-dibromoethane in the cathode compartment of a divided cell (see Scheme 17 and Table 2) was implemented also through the electrocatalytic route with the use of an electrogenerated base.[28] In the latter case, the mechanism of formation of cyclopropane **26** includes the electroreduction of azobenzene at a platinum cathode to form a radical anion or dianion capable of deprotonating compound **25** in solution. The subsequent nucleophilic attack of the 1,2-dibromoethane molecule by the $CHXY^-$ anion and the successive elimination of two halide anions affords cyclopropane **26**.

The addition of azobenzene as the mediator leads to higher yields of cyclopropanes **26** due to suppression of the competitive direct reduction of vicinal dihaloalkane to alkene. If the azobenzene reduction potential ($E_{1/2}$ = −1.8 V *vs.* Ag/0.1 M Ag^+) is far below the reduction potentials of compounds **25** containing the activated methylene group, the yields of cyclopropanes **26** substantially increase (to 80%–85%, see Table 2).[28]

Yet another example of this approach is the cathodic reduction of phenacyl thiocyanate (**32**), which was carried out in DMF at a mercury cathode at the constant potential of −1.2 V *vs.* SCE and afforded anion **A**. It was assumed[32] that further chemical process in the solution leads stereoselectively to *trans*-1,2,3-tribenzoylcyclopropane **33** (Scheme 21).

Scheme 21

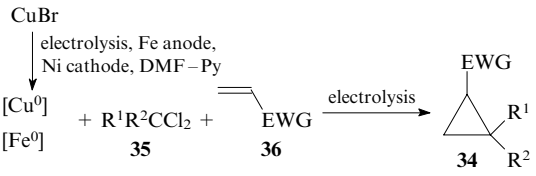


The two-electron reduction of phenyl thiocyanate (**32**) afforded anion **A** which, being an electrogenerated base, can deprotonate molecule **32** in solution. The elimination of the thiocyanate ion from enolate **B** followed by carbene trimerization yields cyclopropane **33**.[32]

III.2. Processes involving electrogeneratied metal complexes

A group of French scientists carried out the electrochemical synthesis of cyclopropanes which involved electrogenerated metal complexes and used the sactificial-anode approach.[33–36] Thus, several functionally substituted cyclopropanes **34** were synthesized by the indirect electroreduction of geminal polyhalo derivatives **35** in the presence of activated alkenes **36** in an undivided cell with a nickel cathode and a sacrificial iron anode in argon atmosphere in the presence of catalytic amounts of copper(I) bromide (Scheme 22).[33–36]

Scheme 22



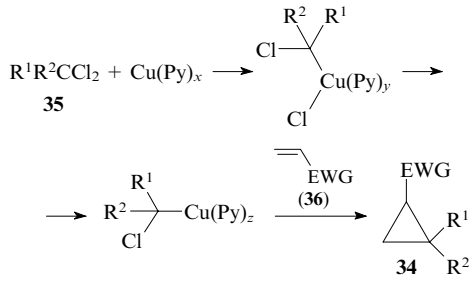
34, **35**: $R^1 = R^2$ = Ph; R^1 = H, R^2 = Ph; R^1 = Cl: R^2 = Ph, CO_2Me;
36: acrylonitrile, methyl acrylate, dimethyl itaconate, coumarin, dimethyl maleate, dimethyl fumarate, α,β-unsaturated aldehydes and ketones;
34, **36**: EWG = CN, CO2Me, CHO, C(O)R, *etc.*
(EWG is the electron-withdrawing group)

In the authors' opinion,[36] the catalytic reagent, *i.e.*, the copper(0) complex with pyridine, is formed in the preliminary electrolysis of copper(I) bromide at −10 °C before the injection of the main reactants to the reaction zone, is regenerated during the electrochemical process and is directly involved in the cyclopropanation step (Scheme 23).[37] In the absence of copper(I) bromide (direct electroreduction), the electrochemical process turned out to be less selective.

This transformation was also carried out with the use of nickel(II) bromide.[34]

The proposed[33–36] method of joint electrolysis of alkenes and geminal polyhalo derivatives is an efficient alternative to the classical methods of cyclopropane synthesis with the use of substituted diazomethanes, diazonitriles, *etc*.[33] This electrochemical process is carried out in an

Scheme 23



undivided cell and can proceed with commercial chemicals and solvents used as received.

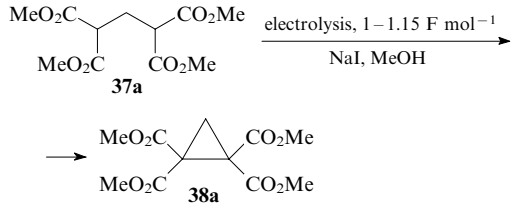
However, this protocol has certain drawbacks, namely, the reaction must be carried out in an argon atmosphere using a sacrificial anode, which necessitates the use of special equipment and complicates the isolation of the synthesized cyclopropanes due to the formation of considerable amounts of insoluble metal oxides. Furthermore, the electroreduction occurs at a low current density (7.5 mA cm^{-2}) because of which the electrochemical process continues for no less than 8 h.

III.3. Electrocatalytic synthesis of cyclopropanes involving salts of hydrohalic acids as the mediators

The electrocatalytic oxidation involving salts of hydrohalic acids as the mediators is among the most vigorously developing areas of electroorganic synthesis. In some cases, the use of such mediators enables targeted selective electrocatalytic transformations of organic compounds that are unreactive in the direct electrochemical processes.[13] The method comprises generation of the oxidant (bromine or iodine) at the anode and the activation of the substrate by transferring it into the anionic form.[13]

The cyclization of tetramethyl propane-1,1,3,3-tetracarboxylate (**37a**) carried out back in the 1970s (Ref. 38) was the first electrosynthesis of cyclopropane derivatives that employed alkali metal halides as the mediators. Tetramethyl cyclopropanetetracarboxylate (**38a**) was synthesized in an undivided cell in boiling methanol in the presence of NaI as the mediator in a chemical yield of 40% and a current efficiency of 82% (Scheme 24).

Scheme 24

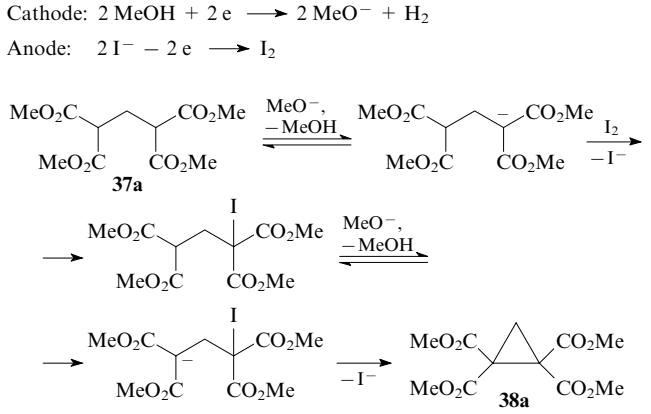


Scheme 25 demonstrates the mechanism proposed for this electrocatalytic process.

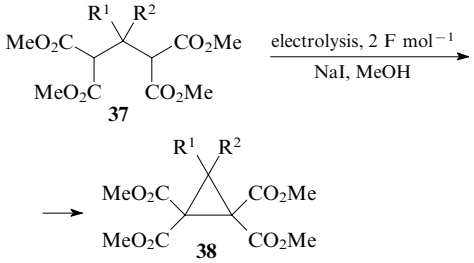
This protocol was improved in the 1990s (the yield of cyclopropane **38a** was raised from 40% to 98%)[39] and applied to the synthesis of substituted cyclopropanetetracarboxylates **38**.[40] The electrolysis at 30 °C with 2 F mol^{-1} of electricity passed afforded cyclopropanes **38** in a yield of 50% –95% (Scheme 26).[40]

Cyclization of 1,3-diaroylpropanes was carried out in the presence of the NaI–MeONa mediator system in methanol in an undivided cell (Pt anode, Ni cathode, 2.4–2.8 F mol^{-1}) (Scheme 27).[41] The chemical yield of

Scheme 25



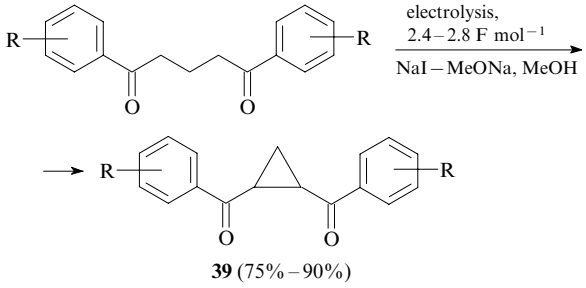
Scheme 26



$R^1 = R^2$ = H (**a**), CO_2Me (**b**), Me;
R^1 = H: R^2 = Me, Pr^n, Ph, CO_2Me, Bu^t

1,2-diaroylcyclopropanes **39** was 75%–90% and the current efficiency was 60% –75%.

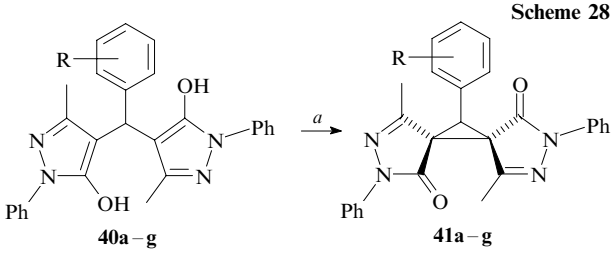
Scheme 27



R = H, 4-Me, 4-MeO, 4-Bu^nO, 4-PhO, 4-Cl, 4-Br

The stereoselective electrocatalytic cyclization of 4,4′-(arylmethylene)bis(1*H*-pyrazol-5-ols) **40** afforded (5*R**,6*R**)-tetraazadispiro[4.0.4.1]undeca-3,9-diene-1,7-diones **41** containing a cyclopropane moiety spiro-coupled with

Scheme 28

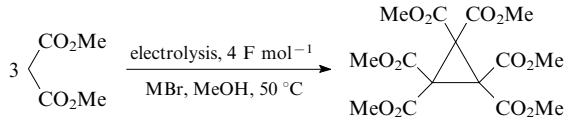


R = H (**a**), 3-Br (**b**), 2-Cl (**c**), 4-Me (**d**), 2-MeO (**e**), 3-Cl (**f**), 4-Et (**g**);
(*a*) electrolysis, 2.5 F mol^{-1}, NaBr, MeOH

two pyrazolone rings in a chemical yield of 85% –97% and with 68%–78% current efficiency (Scheme 28).[42]

The electrocatalytic cyclotrimerization of dimethyl malonate was carried out in an undivided cell with a Pt anode and a Fe cathode (Scheme 29).[43] Hexamethyl cyclopropanehexacarboxylate (**38b**) was synthesized in a yield of 70%.

Scheme 29

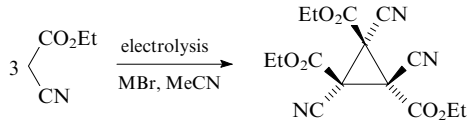


M = Li, Na, K

38b (70%)

Under analogous conditions, cyclotrimerization of ethyl cyanoacetate occurs stereosevectively giving the *trans*-isomer of triethyl 1,2,3-tricyanocyclopropane-1,2,3-tricarboxylate (**42**) in 85% yield (Scheme 30).[44]

Scheme 30



M = Li, Na

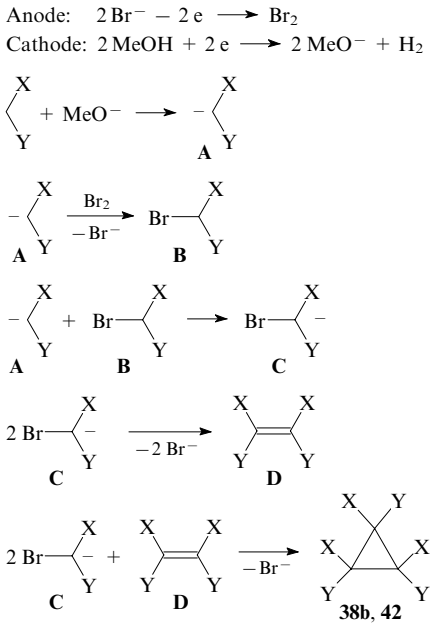
42 (85%)

Scheme 31 illustrates the mechanism of electrocatalytic cyclotrimerization. The formation of bromine at the anode can be detected by sight based on solution colouring when electrolysis is carried out without stirring.

In solution, anion **A** is brominated to give bromo-CH acid **B**. It reacts with anion **A** being converted to CH acid anion **C**, which dimerizes to form alkene **D**.[45] The Michael addition of anion **C** to alkene **D** followed by ring closure results in cyclopropanes **38b** and **42** (see Scheme 31).

Systematic studies of cascade and multicomponent transformations involving electrocatalytically generated anions of CH acids have been carried out in the past decades at the N D Zelinsky Institute of Organic Chemistry

Scheme 31



X = Y = CO_2Me (**38b**); X = CN, Y = CO_2Et (**42**)

of the Russian Academy of Sciences.[13,46] Based on the data obtained there, a new approach to constructing the cyclopropane moiety has been developed, namely, the joint electrocatalytic transformation of CH acids and activated alkenes or carbonyl compounds.[13]

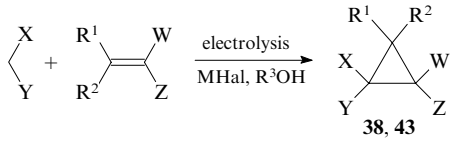
The electrolysis of malonic acid derivatives (malonates or cyanoacetates, malononitrile) together with activated alkenes produced functionally substituted cyclopropanes **38** and **43** in chemical yields of 50%–95% and with current efficiency of 40%–80% (Scheme 32, Table 3).[47–54]

When alkylidenecyanoacetate was used as the activated alkene, the electrolysis proceeded stereoselectively to form 3-substituted (*E*)-2-cyanocyclopropane-1,1,2-tricarboxylates **43** (Scheme 33). It deserves mention that the electrocatalytic reaction described above can proceed under mild conditions for alkylidenemalononitriles and benzylidenecyanoacetates

Table 3. Joint electrochemical transformation of malonic acid derivatives (alkyl malonates and cyanoacetates, malononitrile) and activated alkenes.

Compounds	X	Y	W	Z	R^1	R^2	Yield of **38**, **43** (%)	Ref.
38b	CO_2Me	CO_2Me	CO_2Me	CO_2Me	CO_2Me	CO_2Me	58	47
38	CO_2Me	CO_2Me	CO_2Me	CO_2Me	Me, Pr^n, n-C_5H_{11}, Ph	H	75–95	47
43	CO_2Me	CO_2Me	CO_2Me	CN	Me, Et, Pr^n, Pr^i, Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 2-ClC_6H_4, 4-ClC_6H_4, 3-BrC_6H_4	H	74–85	50, 54
43	CO_2Et	CO_2Et	CO_2Et	CN	Ph, 4-ClC_6H_4	H	82–83	50, 54
43	CO_2Me	CO_2Me	CN	CN	Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-$BnOC_6H_4$, 2-ClC_6H_4, 4-ClC_6H_4, 4-$O_2NC_6H_4$, Me, Et, Pr^n	H	75–84	53
43	CO_2Et	CO_2Et	CN	CN	Ph, 4-MeC_6H_4	H	71–88	53
43	CO_2Me	CN	CO_2Me	CN	Me, Et, Pr^n, cyclo-C_3H_5	Me, Pr^n	56–78	48
43	CO_2Et	CN	CO_2Et	CN	Me, Et, Pr^n, cyclo-C_3H_5	Me	86–95	48
43	CO_2Et	CN	CO_2Et	CN	$(CH_2)_5$, $(CH_2)_6$		84–95	48
43	CN	CN	CO_2Me	CO_2Me	Et, Ph	H	50–67	53
43	CN	CN	CN	CN	$(CH_2)_4$, $(CH_2)_5$, $(CH_2)_6$, $(CH_2)_{11}$, $(CH_2)_2CHMe(CH_2)_2$, $(CH_2)_2CHPh(CH_2)_2$, $(CH_2)_2CHBu^t(CH_2)_2$		51–87	51, 52

Scheme 32

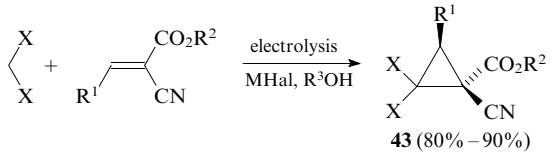


38, **43**

M = Na, K; Hal = Br, I; R^3 = Me, Et

which have either electron-donating or electron-withdrawing substituents in the phenyl moiety.[50, 54]

Scheme 33

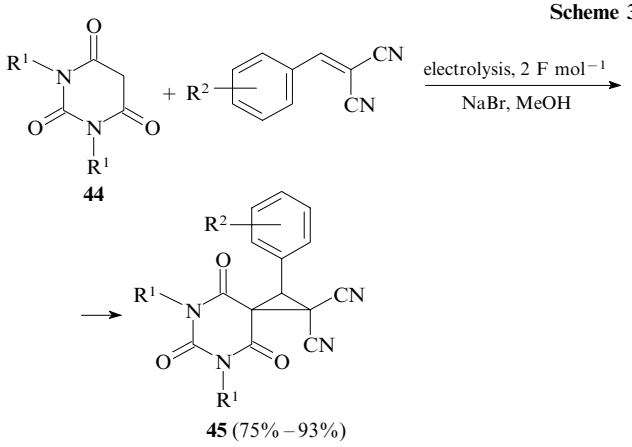


43 (80% – 90%)

X = CO_2Me, CO_2Et; R^1 = Alk, Ar; R^2, R^3 = Me, Et;
M = Na, K; Hal = Br, I

A new approach to one-step synthesis of functionally substituted cyclopropanes spiro-coupled with a heterocyclic moiety was implemented. Thus electrolysis of barbituric acids **44** together with benzylidenemalononitriles or benzylidenecyanoacetates in methanol carried out in an undivided cell in the presence of sodium bromide as the mediator

Scheme 34

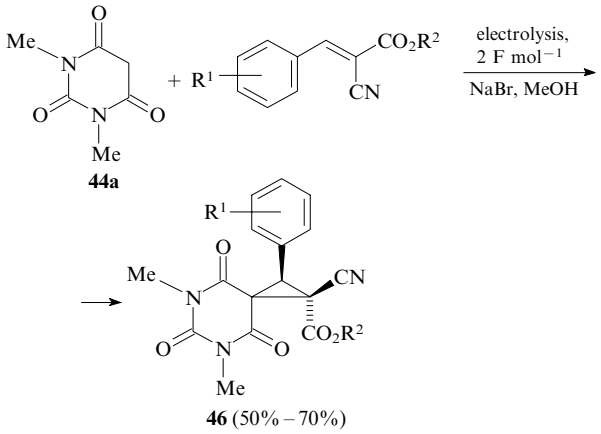


44

45 (75% – 93%)

R^1 = Me, Et, H; R^2 = EWG, EDG (EDG is an electron-donating group, EWG is electron-withdrawing group)

Scheme 35



44a

46 (50% – 70%)

R^1 = EWG, EDG; R^2 = Me, Et

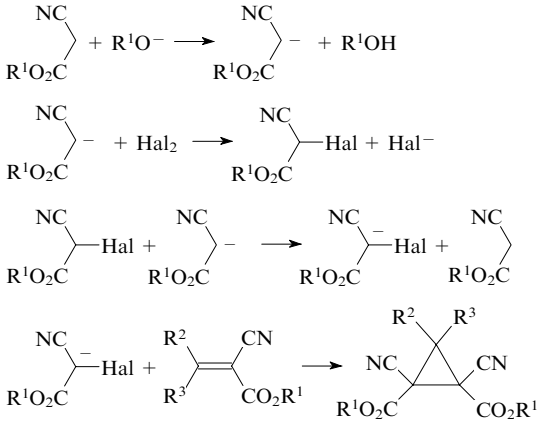
afforded 4,6,8-trioxo-5,7-diazaspiro[2.5]octanes (spirocyclopropylbarbiturates) **45** and **46** (Schemes 34, 35).[55]

Under the optimal conditions (current density 100 mA cm^{-2}, quantity of electricity 2 F mol^{-1}, NaBr as the mediator, MeOH, 10 or 0 °C), the reaction proceeds over a period of 32 min and the yield of substituted spirocyclopropyl barbiturates **45** can be as high as 93%.[55]

When benzylidenecyanoacetates were used, the electrocatalytic process was stereoselective and furnished the corresponding spirocyclopropyl barbiturates **46** with the aryl and alkoxycarbonyl substituents arranged in the *E* configuration with respect to the cyclopropane plane (see Scheme 35).

The mechanism of joint electrolysis of CH acids and activated alkenes can be illustrated by the example of electrocatalytic transformation of cyanoacetate and alkylidenecyanoacetates (see Scheme 34). The bromine evolution at the anode and the alkoxide anion generation at the cathode are illustrated above in Scheme 31. In solution, the cyanoacetate anion is formed and then undergoes halogenation with abstraction of the second proton. The Michael addition of halocyanoacetate anion to activated alkenes with subsequent ring closure produces cyclopropanes as mixtures of *cis*- and *trans*-isomers in high yields (Scheme 36).[48]

Scheme 36

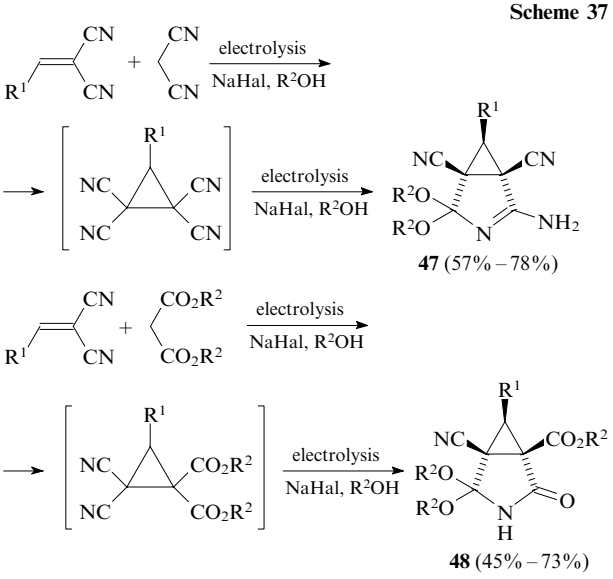


Thus, this electrocatalytic transformation represents a multistep cascade process implemented in an undivided cell with a graphite cathode and an iron anode in ethanol in the presence of alkali metal halides.

The further progress in the synthesis of cyclopropanes from activated alkenes and CH acids was associated with the use of stereoselective multicomponent processes for the preparation of bicyclic compounds with the fused cyclopropane moiety (Scheme 37).[56, 57] A larger quantity of electricity (2.5 F mol^{-1}) passed in the final step of this reaction brings about the electrocatalytic chain process of transformation of the functionally substituted cyclopropane into the corresponding bicyclic fused system **47** or **48**.

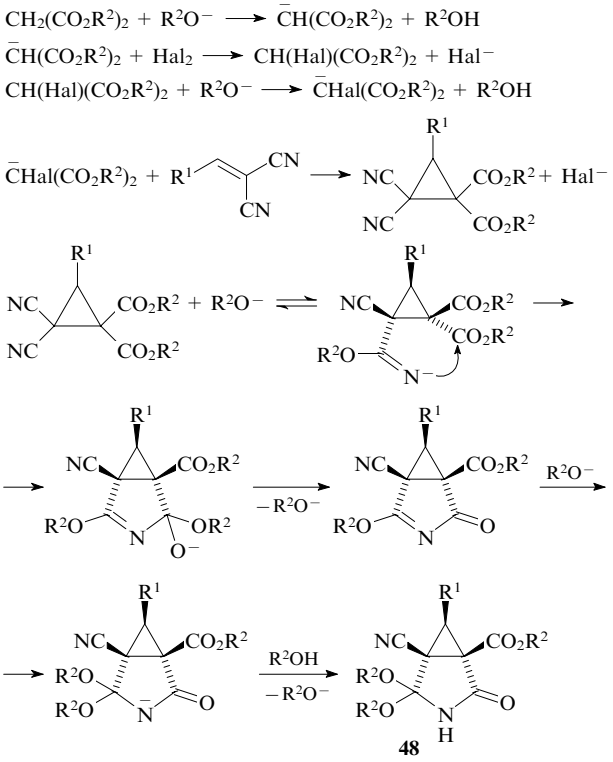
Thus, the electrolysis of alkylidene- or benzylidenemalononitrile together with malononitrile or alkyl malonate in an undivided cell results in cyclopropanes which could easily be transformed into bicyclic pyrrolines **47** and pyrrolidones **48** under the action of catalytic amounts of electrogenerated base. The pyrroline or pyrrolidone rings are formed *via* a chain electrocatalytic process initiated by electrogenerated alkoxide anions in the undivided cell.[56, 57] Scheme 38 illustrates the mechanism of formation of pyrrolidones **48** from alkyl malonate and activated alkene.[57]

Scheme 37



R^1 = Alk, Ar; R^2 = Me, Et; Hal = Br, I

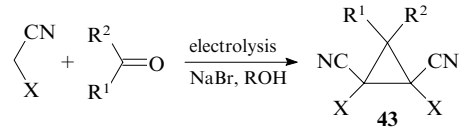
Scheme 38



In the mid-1990s, a new stage started in the development of electrochemical synthesis of cyclopropanes, which was characterized by the use of carbonyl compounds apart from CH acids and alkenes as the starting reactants. The combined electrochemical transformation of malononitrile or alkyl cyanoacetate together with aldehydes or ketones in the presence of sodium bromide produces substituted cyclopropanes **43** (Scheme 39, Table 4).[58–60]

In this case, the activated alkene is formed directly in the cell as a result of the Knövenagel condensation of the carbonyl compound with the CH acid catalyzed by the base generated at the cathode to be involved subsequently in the cascade process mentioned above to give a cyclopropane moiety.

Scheme 39



X = CN, CO_2Me, CO_2Et

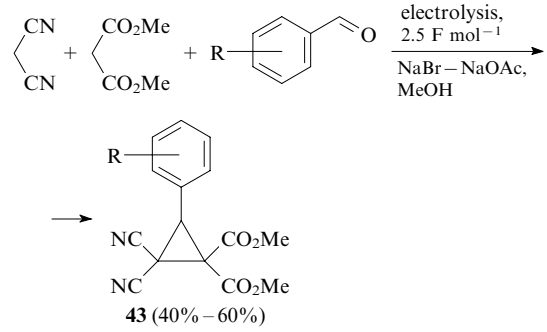
Table 4. Electrosynthesis of cyclopropanes directly from CH acids and carbonyl compounds.

X	R^1	R^2	Yield of **43** (%)	Ref.
CN	Me, Et, Pr^n, Bu^n, Ph, n-C_6H_{13}	Me, Pr^n	50–91	58, 60
CN	$(CH_2)_4$, $(CH_2)_5$, $(CH_2)_6$		50–86	58, 60
CO_2Me	H, $MeOC_6H_4$, Ph, 4-ClC_6H_4	H	63–93 [a]	59
CO_2Et	H, Ph, 4-IC_6H_4, 4-ClC_6H_4, 4-BrC_6H_4	H	57–98	59

[a] In some cases, a mixture of *cis*- and *trans*-isomers is formed; the total yield for both isomers is indicated.

One of the latest and remarkable achievements in this field of chemistry is implementation of the first multicomponent process for the synthesis of functionally substituted cyclopropanes from three different molecules (Scheme 40). In this reaction, each carbon atom of the cyclopropane moiety has originally been involved in a different molecule of the three starting compounds.[61]

Scheme 40



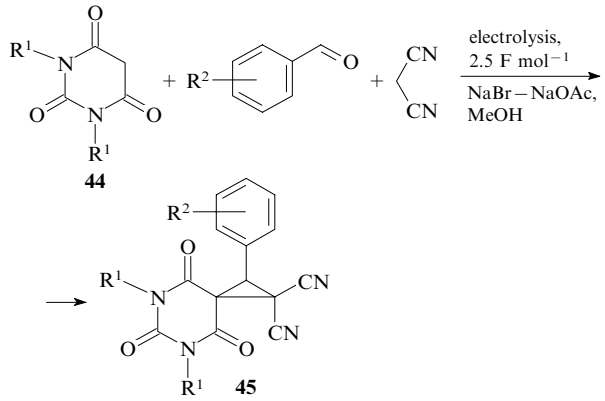
R = H, 4-Me, 4-MeO, 2-MeO, 4-Cl, 2-Cl, 4-Br, 4-F, 2-F

The electrolysis of an aromatic aldehyde, malononitrile and dimethyl malonate in methanol carried out in the presence of the NaBr–NaOAc mediator system in an undivided cell with a graphite anode and an iron cathode at 0 °C afforded 3-substituted 2,2-dicyanocyclopronane-1,1-dicarboxylates **43** in 40%–60% yields. It deserves mention that cyclopropanes **43** are crystallized in the reaction mixture and can be isolated by filtration; they require no additional purification.[61]

The multicomponent synthesis of spirocyclopropylbarbiturates **45** in yields of 50%–65% was also performed by a similar protocol based on three different molecules: aromatic aldehyde, malononitrile and barbituric acid (Scheme 41).[62]

A solution of an aromatic aldehyde and malononitrile in methanol was stirred in the presence of the NaBr–NaOAc mediator system at room temperature for 30 min. Then, the

Scheme 41



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

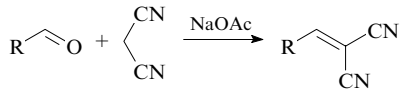
reaction mixture was cooled, barbituric acid was added and 2 F mol^{-1} of electricity was passed at a constant current density of 100 mA cm^{-2} at 10 °C for 32 min. The target cyclopropanes **45** were isolated by filtration; they required no additional purification. The electrocatalytic process developed can occur under mild conditions for aromatic aldehydes containing either electron-donating or electron-withdrawing substituents in the phenyl moiety.[62]

The spiro cyclopropanes formed in the course of electrolysis represent a unique ring system that includes the cyclopropane moiety spiro-coupled with the pyridimine-2,4,6-trione heterocycle and pertain to a highly promising class of compounds having sedative, anticonvulsive and antiepileptic properties and also acting as transarterial chemoembolization (TACE) inhibitors and matrix metalloproteinases (MMP).

Thus, the above electrocatalytic transformation provides the synthesis of spirocyclopropyl barbiturates in one step in yields of several grammes in a 25-ml undivided cell. The process is easily scaled, providing the target compounds in amounts up to 20 g without any loss in efficiency.

The multicomponent electrocatalytic transformations are complex multistep cascade processes.[61,62] They include the formation of bromine at the anode and generation of methoxide anions at the cathode. In the first step, in a solution containing sodium acetate, the base-catalyzed Knövenagel reaction takes place between malononitrile and carbonyl compound to afford a substituted arylmethylidenemalononitrile (Scheme 42).

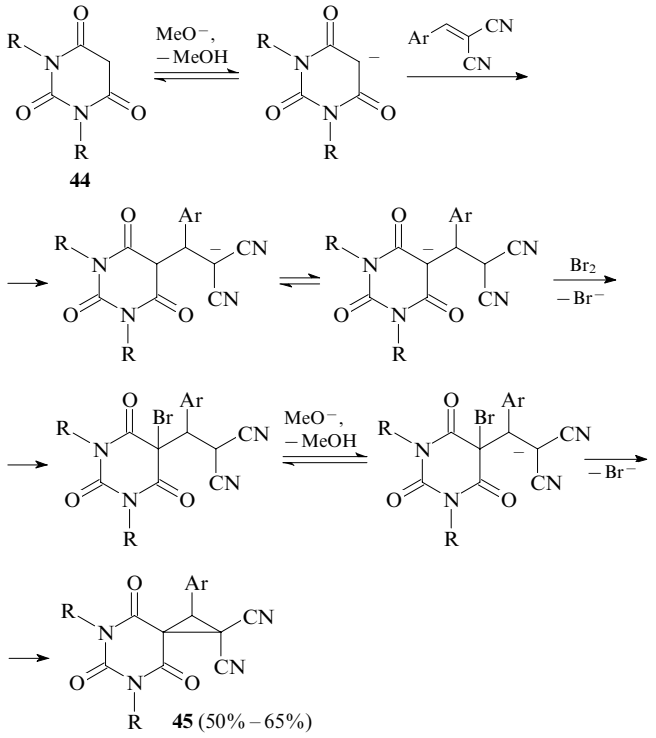
Scheme 42



When ethyl malonate is used as the second CH acid, the ethyl malonate anion is formed in solution, then it is halogenated and gives off the second proton. The Michael addition of a halomalonate anion to arylmethylidenemalononitrile followed by ring closure affords 3-substituted 2,2-dicyanocyclopropane-1,1-dicarboxylates **43** in 40%–60% yields.[61]

When barbituric acid **44** is taken as the second CH acid, the subsequent process includes a cascade of reactions to afford spirocyclopropylbarbiturates **45** (Scheme 43).[62]

Scheme 43



R = Me, Et; Ar = XC_6H_4 (X = H, 4-Me, 4-Bu^t, 2-MeO, 2-Cl, 3-Cl, 3-Br, 4-O_2N)

IV. Conclusion

The modern organic chemistry has at its disposal numerous methods for the synthesis of cyclopropane structures. Among these methods, the electrochemical synthesis gains in importance. The progress in organic electrochemistry is associated with the increasing scientific and practical interest in electrochemical transformations and the methods based on them. Taking into account the fact that electric current is the cheapest 'reagent', organic electrosynthesis should become even more demanded in the future.

Cyclopropane structures can be synthesized by both direct and indirect electrochemical treatment of the starting compounds.

The methods of direct electroreduction and electrooxidation require the use of divided cells of intricate design and carrying out the electrochemical processes at low current densities and in high-purity aprotic solvents. Moreover, to carry out the majority of direct electrochemical transformations, the electrolysis should be performed at a controlled potential, which requires non-trivial technological equipment and preliminary determination of the reduction (oxidation) potentials for the starting reactants.

There are two main approaches to the indirect electrocatalytic oxidation or reduction to afford cyclopropanes in diaphragm cells:

— the use of electrogenerated bases for the formation of CH acid anions and subsequent chemical processes with participation of these species;[24–26,28,32]

— joint electrolysis of polyhalo derivatives and alkenes carried out in the presence of copper and nickel salts, which involves the use of electrogenerated metal complexes and sacrificial anodes.[33–36]

However, these reactions also require the use of complex and expensive equipment, they are carried out in cells of intricate design at low current densities and, hence, long reaction times are needed.

At present, promising electrochemical methods for the synthesis of cyclopropanes include the indirect electrocatalytic cascade type and multicomponent transformations of CH acids, such as alkyl malonates and cyanoacetates, and also joint electrolysis of CH acids with activated alkenes or carbonyl compounds. These transformations are carried out in the presence of mediators (alkali metal halides) under the action of the halogen and the base generated in the undivided cell. These processes consume catalytic amounts of the mediator, which is then regenerated. Such reactions are simple as regards their experimental implementation, they do not require cumbersome equipment and are carried out at high current densities in the constant-current mode, *i.e.*, no control over the electrode potential is needed, which allows selective construction of the cyclopropane moiety at high concentrations of the reactants.

The best-known electrocatalytic methods for the synthesis of substituted cyclopropanes are as follows: the oxidative cyclization of CH acids;[38–42] cyclotrimerization of CH acids;[43, 44] transformations of CH acids and activated alkenes;[47–57] transformations of CH acids and carbonyl compounds;[58–60] multicomponent synthesis of cyclopropanes *via* electrocatalytic transformation of two different CH acids and a carbonyl compound.[61, 62]

The electrolysis of organic compounds in an undivided cell without control over the electrode potential in the presence of alkali metal halides as the mediators combines the advantages of electrochemical and chemical processes. The factors listed above make these methods easily available and versatile for the use in conventional chemical laboratories.

This review was prepared with the financial support by the grant of President of the Russian Federation for the support of young Russian scientists — candidates of sciences (MK-899.2014.3).

References

1. R R Kostikov *Sorosovsk. Obrazovat. Zh.* (8) 52 (1997) [a]
2. L A Yanovskaya, V A Dombrovskii, A Kh Khusid *Tsiklopropany s Funktsional'nymi Gruppami. Sintez i Primenenie* (Cyclopropanes with Functional Groups. Synthesis and Application) (Moscow: Nauka, 1980)
3. W A Donaldson *Tetrahedron* **57** 8589 (2001)
4. R E Taylor, F C Engelhardt, M J Schmitt *Tetrahedron* **59** 5623 (2003)
5. M Ohkita, S Nishida, T Tsuji *Recent Advances in Synthesis of Cyclopropanes (Patai's Chemistry of Functional Groups)* (New York: Wiley, 2009)
6. A Michael *J. Prakt. Chem.* **35** 349 (1887)
7. A Michael, P C Freer *J. Prakt. Chem.* **43** 390 (1891)
8. V A Smit, A D Dilman *Osnovy Sovremennogo Organicheskogo Sinteza* (Foundationals of Current Organic Synthesis) (Moscow: BINOM. Laboratoriya Znanii, 2009)
9. E David, G Milanole, P Ivashkin, S Couve-Bonnaire, P Jubault, X Pannecoucke *Chem.–Eur. J.* **18** 14904 (2012)
10. M Yu, B P Pagenkopf *Tetrahedron* **61** 321 (2005)
11. *Organic Electrochemistry* (Ed. H Lund) (New York: Marcel Dekker, 2000)
12. M E Niyazymbetov, D H Evans *Tetrahedron* **49** 9627 (1993)
13. Yu N Ogibin, M N Elinson, G I Nikishin *Russ. Chem. Rev.* **78** 89 (2009)
14. A Freund *J. Prakt. Chem.* **26** 367 (1882)
15. M R Rifi *J. Am. Chem. Soc.* **89** 4442 (1967)
16. T Shono, Y Matsumura, K Tsubata, Y Sugihara *J. Org. Chem.* **47** 3090 (1982)
17. M Fedorynski *Chem. Rev.* **103** 1099 (2003)
18. V A Petrosyan, M E Niyazymbetov *Russ. Chem. Rev.* **58** 644 (1989)
19. M M Baizer, J L Chruma *J. Org. Chem.* **37** 1951 (1972)
20. E H Mottus, M R Ort *J. Electrochem. Soc.* **117** 885 (1970)
21. A J Fry, R G Reed *J. Am. Chem. Soc.* **94** 8475 (1972)
22. S Durandetti, S Sibille, J Perichon *J. Org. Chem.* **56** 3255 (1991)
23. V A Petrosyan, M E Niyazymbetov, T K Baryshnikova *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **37** 81 (1988) [*Izv. Akad. Nauk SSSR, Ser. Khim.* 91 (1988)]
24. J-C Le Menn, J Sarrazin, A Tallec *Electrochim. Acta* **35** 563 (1990)
25. J C Le Menn, J Sarrazin, A Tallec *Bull. Soc. Chim. Fr.* **128** 562 (1991)
26. E Léonel, J P Paugam, S Condon-Gueugnot, J-Y Nédélec *Tetrahedron* **54** 3207 (1998)
27. C Duquenne, S Goumain, P Jubault, C Feasson, J-C Quirion *Org. Lett.* **2** 453 (2000)
28. V A Petrosyan, A A Vasil'ev, V I Tatarinova *Russ. Chem. Bull.* **43** 84 (1994) [*Izv. Akad. Nauk, Ser. Khim.* 89 (1994)]
29. N Hirai, K Iwami, M Horiuchi, K Kano, Y Todoroki, H Ohigashi *Phytochemistry* **80** 89 (2012)
30. E J Corey, N L Bauld, R T La Londe, J Casanova, E T Kaiser *J. Am. Chem. Soc.* **82** 2645 (1960)
31. J Bours, M Morton, A J Fry *Tetrahedron Lett.* **53** 1015 (2012)
32. B Batanero, R Horcajada, R Mallmann, M G Quintanilla, F Barba *Electrochim. Acta* **47** 1761 (2002)
33. S Sengmany, E Léonel, J P Paugam, J-Y Nédélec *Synthesis* 533 (2002)
34. S Sengmany, E Léonel, J P Paugam, J-Y Nédélec *Tetrahedron* **58** 271 (2002)
35. S Oudeyer, E Léonel, J P Paugam, J-Y Nédélec *Tetrahedron* **59** 1073 (2003)
36. S Oudeyer, E Léonel, J P Paugam, C Sulpice-Gailletb, J-Y Nédélec *Tetrahedron* **62** 1583 (2006)
37. T Saegusa, Y Ito *Synthesis* 291 (1975)
38. D A White *J. Electrochem. Soc.* **124** 1177 (1977)
39. M N Elinson, S K Fedukovich, S V Lindeman, M S Aleksanyan, Yu T Struchkov, G I Nikishin *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **38** 1467 (1989) [*Izv. Akad. Nauk SSSR, Ser. Khim.* 1603 (1989)]
40. M N Elinson, S K Fedukovich, G I Nikishin *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **39** 2523 (1990) [*Izv. Akad. Nauk SSSR, Ser. Khim.* 2783 (1990)]
41. M Okimoto, Y Takahashi, T Kakuchi *Bull. Chem. Soc. Jpn.* **76** 207 (2003)
42. M N Elinson, A N Vereshchagin, E O Tretyakova, I S Bushmarinov, G I Nikishin *Synthesis* 3015 (2011)
43. G I Nikishin, M N Elinson, S K Fedukovich *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **35** 1749 (1986) [*Izv. Akad. Nauk SSSR, Ser. Khim.* 1919 (1986)]
44. M N Elinson, T L Lizunova, M O Dekaprilevich, Yu T Struchkov, G I Nikishin *Mendeleev Commun.* 192 (1993)
45. G I Nikishin, M N Elinson, S K Fedukovich *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **33** 1970 (1984) [*Izv. Akad. Nauk SSSR, Ser. Khim.* 2154 (1984)]
46. A I Ilovaisky, V M Merkulova, M N Elinson, G I Nikishin *Russ. Chem. Rev.* **81** 381 (2012)
47. M N Elinson, S K Feducovich, S G Bushuev, A A Zakharenkov, D V Pashchenko, G I Nikishin *Mendeleev Commun.* 15 (1998)
48. M N Elinson, S K Fedukovich, S G Bushuev, D V Pashchenko, G I Nikishin *Russ. Chem. Bull.* **47** 1133 (1998) [*Izv. Akad. Nauk, Ser. Khim.* 1165 (1998)]

49. M N Elinson, S K Feducovich, A A Zakharenkov, G I Nikishin *Mendeleev Commun.* 20 (1999)
50. M N Elinson, S K Feducovich, Z A Starikova, O S Olessova, A N Vereshchagin, G I Nikishin *Tetrahedron Lett.* **41** 4937 (2000)
51. M N Elinson, S K Feducovich, A N Vereshchagin, A S Dorofeev, D E Dmitriev, G I Nikishin *Russ. Chem. Bull.* **52** 2235 (2003) [*Izv. Akad. Nauk, Ser. Khim.* 2117 (2003)]
52. M N Elinson, S K Feducovich, T A Zaimovskaya, A N Vereshchagin, G I Nikishin *Russ. Chem. Bull.* **52** 2241 (2003) [*Izv. Akad. Nauk, Ser. Khim.* 2122 (2003)]
53. M N Elinson, S K Feducovich, T A Zaimovskaya, A N Vereshchagin, S V Gorbunov, G I Nikishin *Russ. Chem. Bull.* **54** 1593 (2005) [*Izv. Akad. Nauk, Ser. Khim.* 1547 (2005)]
54. M N Elinson, S K Feducovich, Z A Starikova, A N Vereshchagin, P A Belyakov, G I Nikishin *Tetrahedron* **62** 3989 (2006)
55. E O Dorofeeva, M N Elinson, A N Vereshchagin, N O Stepanov, I S Bushmarinov, P A Belyakov, O O Sokolova, G I Nikishin *RSC Adv.* **2** 4444 (2012)
56. M N Elinson, S K Feducovich, Z A Starikova, A N Vereshchagin, G I Nikishin *Tetrahedron* **60** 11743 (2004)
57. M N Elinson, S K Feducovich, Z A Starikova, A N Vereshchagin, S V Gorbunov, G I Nikishin *Tetrahedron Lett.* **46** 6389 (2005)
58. G I Nikishin, M N Elinson, T L Lizunova, B I Ugrak *Tetrahedron Lett.* **32** 2655 (1991)
59. M N Elinson, T L Lizunova, B I Ugrak, M O Dekaprilevich, G I Nikishin *Tetrahedron Lett.* **34** 5795 (1993)
60. M N Elinson, S K Feducovich, T L Lizunova, G I Nikishin *Tetrahedron* **56** 3063 (2000)
61. M N Elinson, S K Feducovich, A N Vereshchagin, S V Gorbunov, P A Belyakov, G I Nikishin *Tetrahedron Lett.* **47** 9129 (2006)
62. A N Vereshchagin, M N Elinson, E O Dorofeeva, N O Stepanov, T A Zaimovskaya, G I Nikishin *Tetrahedron* **69** 1945 (2013)

[a] — *Soros Educ. J. (Engl. Transl.)*