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The Utility of Carbanions and Heteroatom-anions in Electroorganic Synthesis

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I. INTRODUCTION

Carbanions and heteroatom-anions (anions formed at atoms other than carbon; henceforth, heteroanions) are among the most important intermediates in organic synthesis. Typically, the precursor conjugate acids are converted to their anions by treatment with different kinds of bases such as alkali metals, hydrides, hydroxides, amides, amines etc. Depending upon their stability, the anions are used in syntheses either by generation *in situ* or with prior isolation as the salt.

The electrochemical method offers the unique possibility of generating at the cathode a wide variety of organic anions under very mild conditions and without the stoichiometric addition of a chemical base. The main advantage of this approach is that it is very easy to control both the solvent and the counterion which can be very useful because the nucleophilic reactivity of anions depends strongly on these factors The cathodic generation of anions is most useful for strongly nucleophilic anions By contrast, thermodynamically stable and weakly nucleophilic anions are useful in anodic processes for generating electrophilic intermediates (radicals and carbenes) Another possibility is to use weak nucleophiles as acceptors of highly reactive anodically generated electrophiles (cation radicals and cations).

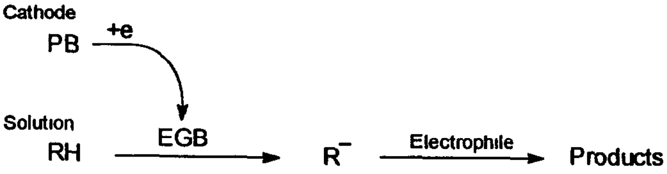
There are two general ways to electrogenerate organic anions The first (which might be called direct generation) is the reductive cleavage of a bond in compounds with potential leaving groups Typical representatives of this process are the reduction of halogen compounds[1] and disulfides [2]

a) $Cl_3CCOOEt + 2e \longrightarrow Cl_2\bar{C}COOEt + Cl^-$

b) $RSSR + 2e \longrightarrow 2RS^-$

Scheme 1

Another way is by indirect generation of anions using electrogenerated bases (EGB) Typically, a "probase" is selected that can be reduced at the cathode producing the EGB, which is an anion radical, anion or dianion. The EGB in turn will deprotonate an appropriate starting organic acid to produce the desired anion that takes part in subsequent chemical reactions



Scheme 2

The use of EGB is a well-known process that has been in existence for more than 20 years and has been used to promote many important synthetic reactions, for example, alkylation,[3a] Michael addition[3b,c] or Wittig-Horner[3d-f] reactions. There are several good reviews[4] on this topic so in the present discussion we will examine only the more recent papers as well as works that have not been previously reviewed. Some investigations in this area will be mentioned for comparison with the results of other methods

A large part of our review will discuss the synthetic utility of anions prepared by direct generation at a cathode by cleavage of an activated element-hydrogen bond of an organic acid.

$$RH \quad + \quad 1e \quad \longrightarrow \quad R^{-} \quad + \quad 1/2H_2$$

Scheme 3

Although this method has been known for quite some time,[5] only in the last few years has rapid progress been made Direct electrogeneration of a variety of organic anions from C-H, N-H, O-H, P-H and S-H acids has been demonstrated and used as a basis for a number of selective organic syntheses

In addition, we also will give examples that demonstrate the possibility of using in synthesis anionic intermediates that are generated from other kinds of precursors such as organic halides, imides or unsaturated substances

Separate sections of the review are dedicated to the use of organic carbanions and heteroanions in synthesis under anodic electrolysis conditions as well as syntheses that use the anodic and cathodic reactions synchronously ("paired electrosynthesis")

II. BRIEF DESCRIPTION OF EXPERIMENTAL METHODS

It is not our intention to review the methods of electroorganic chemistry which are adequately treated in other places [6] Nevertheless, as in any specialized method of synthesis (photochemical, enzymatic, etc.), descriptive terms have been introduced in the electroorganic literature that may have little meaning to the neophyte Thus, we will provide a brief discussion of the salient experimental methods A reader having even a passing acquaintance with electroorganic methods should pass over this section

Electrolyses require two electrodes (anode and cathode) in contact with a conductive medium (solvent plus dissolved salt, the supporting electrolyte) The cathode (where reduction occurs) is attached to the negative lead of a DC power supply and the anode (where oxidation occurs) to the positive lead The electrode (anode or cathode) at which the desired reaction occurs is called the working electrode.

A number of very specialized electrolysis cells have been developed and some are commercially available However, quite acceptable results can be obtained with the ordinary glassware used in organic synthesis. Provision is often needed for purging the solution (usually with nitrogen) to remove dissolved oxygen and the solutions are usually stirred (magnetic stirrer, propeller stirrer) to promote mass transport to the electrode surface

Often it is necessary to separate the cell into two parts, the anode and cathode compartments (divided cell) If a reduction reaction is being carried out, the separator (or diaphragm) serves to prevent products formed at the anode from interfering with the desired cathode reaction In unfavorable cases, the anodic reaction could actually reverse the desired reaction at the cathode if a separator were not used

The requirements for the separator are that it allow easy passage of ions (high conductivity) with minimal movement of solvent (low permeability) and that it be stable under the electrolysis conditions A wide variety of separators has been used including porous ceramics, fritted glass, and ion exchange membranes No perfect separator material exists but, in fact, adequate separation is easily achieved Very simple expedients often suffice, e.g , an anode compartment can be formed by drilling holes in the side of a polypropylene centrifuge tube and wrapping the tube with a few rounds of 100% rag paper held in place by cotton thread.[7] The paper is sufficiently porous to allow efficient passage of ions with almost no mixing of the solutions in the two compartments

Under certain circumstances, a separator is not required and both anode and cathode are immersed in the same solution This is called an undivided cell

Special electrical equipment is required for large scale electrolyses but syntheses at the 1- to 10-gram level can be accomplished with ordinary variable DC power supplies with maximum output capabilities of 30-100 V and 1-5 amperes. Meters usually display the applied voltage and output current There are instances where accurate control of the electrode potential (*vs* a reference electrode) is advantageous requiring the use of an instrument called a potentiostat However, most electroorganic preparations are carried out at (roughly) constant current simply by periodic manual adjustment of the variable DC power supply Currents are usually reported as current density (current divided by the area of the working electrode) because it is a better descriptor of the electrolysis conditions than the current itself.

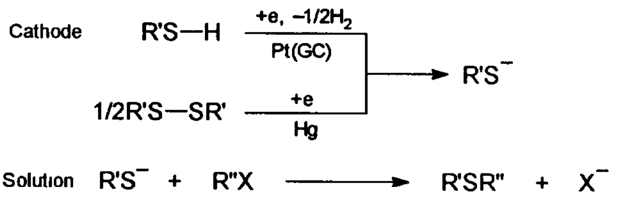
In the ordinary practice of organic synthesis, one chooses the amount of each reagent to use The analog in electroorganic synthesis is the amount of electrical charge introduced per mole of reactant This quantity is usually expressed as Faradays per mole (F/mol), *i e* , the number of moles of electrons added per mole of reactant An equivalent term that is sometimes used is n-value Calculation of F/mol is straightforward When the current is constant, the number of coulombs passed in an electrolysis of duration, t, is [I (in amperes)x(t (in seconds)] Dividing this quantity by the numerical value of Faraday's constant (96485 coulombs) gives the number of Faradays Of course, this can all be done automatically with an electronic device called a coulometer, but the occasional user will probably forego the expense and use the current meter and a laboratory timer

Yields are usually reported in the normal manner as material yields based on the amount of product obtained compared to that theoretically expected on the basis of the amount of starting material taken. Occasionally, yields are reported as current efficiency, i.e , the amount of product obtained compared to that theoretically expected on the basis of the amount of charge passed Unless otherwise specified, the yields reported in this review are material yields

III. THE CATHODE AS EQUIVALENT TO A STRONG BASE IN ORGANIC SYNTHESIS. PROGRESS IN THE FUNCTIONALIZATION OF ORGANIC COMPOUNDS BY CATHODIC ELECTROLYSIS

1 *Electrosynthesis Based on Thiolate Anions*

Almost 20 years ago Iversen and Lund[2] found that the two- electron reduction of disulfides on a mercury cathode resulted in formation of thiolate anions The anions were efficiently alkylated and acylated (Scheme 4) Later it was shown that thiolate anions can also be easily generated by direct reduction of thiols on solid electrodes[5b,8-10] such as Pt, Fe, Ni, Cu, or glassy carbon (GC) The thiolate anions were electrogenerated *in situ* and allowed to react with appropriate electrophiles to prepare a variety of sulfides[8,9c,10] in high yield (Scheme 4)



R'SSR' (Ref 2)	R"X	Yield, %
$(Me_2S)_2$	$PhCH_2Cl$	63
$(MeCOS)_2$	$PhCH_2Cl$	77
$(PhS)_2$	$PhCH_2Cl$	92
$(PhCH_2S)_2$	*i*-PrCl	76
$(PhCH_2S)_2$	Ac_2O	89
$(o\text{-}O_2NC_6H_4S)_2$	Ac_2O	69
$(o\text{-}O_2NC_6H_4S)_2$	MeCl	91
$(o\text{-}O_2NC_6H_4S)_2$	$(EtO)_2SO_2$	91
$(p\text{-}MeC_6H_4S)_2$	MeCl	86
$(Me_2NCSS)_2$	MeCl	81
$(Me_2NCSS)_2$	Me_2NCOCl	37
$(o\text{-}EtOOCC_6H_4S)_2$	MeCl	89

R'SH (Ref 10)	R'X	Yield, %
n-BuSH	$ClCH_2COOEt$	95
n-BuSH	*n*-$BuSCH_2CH_2Cl$	92
n-$C_6H_{13}SH$	$ClCH_2COOMe$	94
n-$C_8H_{17}SH$	EtBr	85
n-$C_8H_{17}SH$	$BrCH_2CH{=}CH_2$	97
$H_2NCH_2CH_2SH$	*n*-BuBr	72
PhSH	*p*-$O_2NC_6H_4Br$	84
(2-Pyridyl)-SH	$ClCH_2COOEt$	97
(2-Benzoxazolyl)-SH	$ClCH_2COOEt$	97
n-BuSH	$ClCH_2CN$	81
n-BuSH	$ClCH_2C{\equiv}CH$	71
n-BuSH	*n*-BuBr	86

Scheme 4

The use of aprotic solvents (MeCN or DMF) promotes high reactivity of the thiolate anions. This is further enhanced by the use of tetraalkylammonium salts as supporting electrolyte because large cations do not tend to form ion pairs with the thiolate anions and thus reduce their activity.[8,9c,10] Therefore, under these conditions it is possible to carry out the electrochemical alkylation of thiols efficiently at room temperature and in the absence of any added base. The data summarized in Scheme 4 demonstrate that electrogenerated thiolate anions are able to substitute effectively iodide, bromide and chloride in organohalides of various structures The fact that the concentration of base remains low during the reaction suggests that the electrochemical method may be useful for the synthesis of base-sensitive sulfides

Electrolysis of thiols in an undivided cell with a transition-metal cathode and anode allows synthesis of thiolates of transition metals.[9] Here, the undivided cell is used to advantage because the desired end product incorporates the electrolysis products from both the anode and cathode. The thiols are reduced on the cathode to thiolate anions while the anodic process is the dissolution of metal

$$\text{Cathode}\quad nRSH + ne \longrightarrow nRS^- + n/2H_2$$

$$\text{Anode}\quad M - ne \longrightarrow M^{n+}$$

$$\text{Solution}\quad nRS^- + M^{n+} \longrightarrow \underset{53\text{-}94\%}{(RS)_nM}$$

R = n-Bu, t-Bu, n-C_6H_{13}, n-$C_{12}H_{25}$, $PhCH_2$, Ph

M = Zn, Cd, Hg, Fe, Ni, Co, Cu ($n=2$), M = Cr ($n=3$)

$2RSH = HS(CH_2)_mSH$ (m = 2–6), M = Zn, Cd

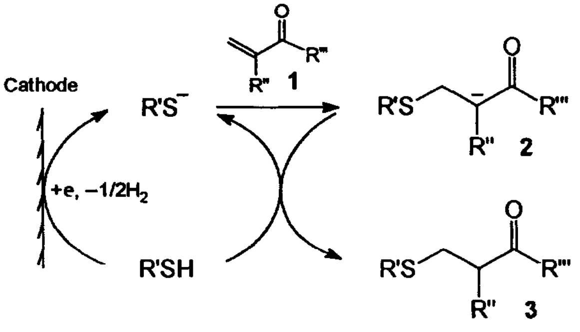
Scheme 5

In the same manner, by use of a sacrificial Mg anode, the magnesium salt of dodecyl thiol was synthesized in a 0.1 M solution of Et_4NBr in MeCN. Subsequent treatment of the reaction mixture with trimethylchlorosilane gave trimethylsilyldodecylsulfide in good yield.[9c]

$$(C_{12}H_{25}S)_2Mg + 2Me_3SiCl \xrightarrow[40^{\circ},\ 1h]{MeCN} 2C_{12}H_{25}SSiMe_3 + MgCl_2$$

Scheme 6

Electrogenerated thiolate anions efficiently initiate the addition of thiols to activated olefins (Scheme 7)[11] This interesting process is an example of a reaction that is catalyzed by the cathode The cathodically generated thiolate anion initiates the process by reacting with olefin **1** to form carbanion **2** Species **2** is quite basic and is protonated by the thiol starting material with the formation of sulfide **3** and regeneration of thiolate anion. The anion enters the cycle again by reacting with **1** to form **2**, etc.

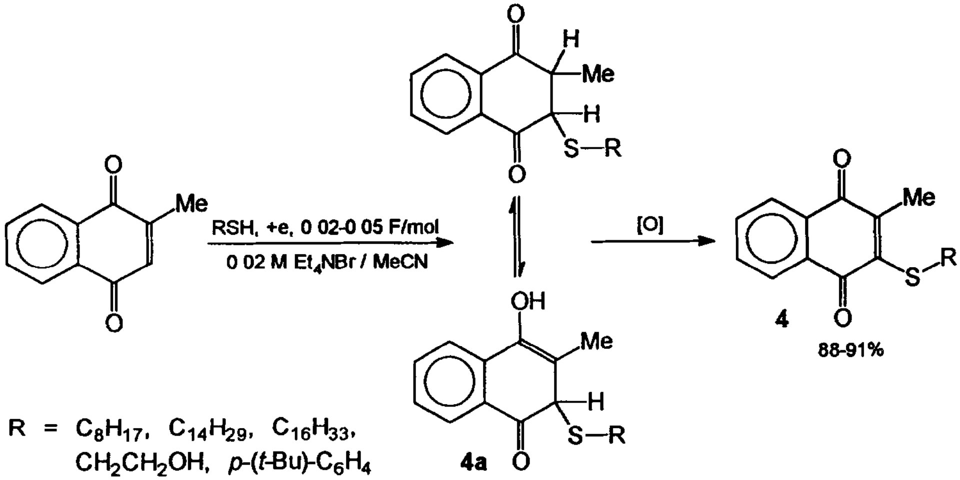


R' = n-C_8H_{17}, n-$C_{12}H_{25}$, CH_2CH_2OH, Ph, R'' = H, Me
R''' = Me, OMe, OEt

Scheme 7

This reaction is very convenient from a preparative point of view and may be carried out either in a divided or undivided cell with a Pt or GC cathode and a Mg anode. The yields of **3** for R' = alkyl, $HOCH_2CH_2$, and Ph are quantitative even after passage of only 0.0008-0.062 F/mol.

The electrochemical method is clearly a superior method for preparation of vitamin K-related thio compounds **4**.[11c] The reaction proceeds via electrocatalytic addition of thiolate anions to the double bond of 2-methyl-1,4-naphthoquinone (as in scheme 7) followed by oxidation of the intermediate product **4a** with air

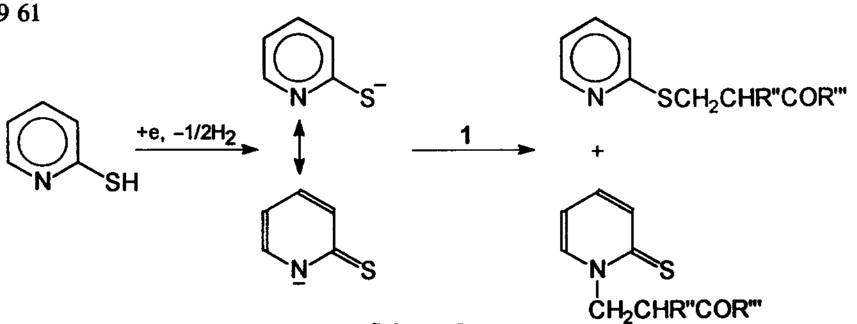


R = C_8H_{17}, $C_{14}H_{29}$, $C_{16}H_{33}$, CH_2CH_2OH, p-(t-Bu)-C_6H_4

Scheme 8

Usually the chemical version of this reaction proceeds very slowly even at high temperature and the yield of **4** is 30-40% because the intermediate **4a** is oxidized by the 2-methyl-1,4-naphthoquinone starting material (see ref. 11c and papers cited therein). It is possible to increase the yield of **4** by introducing an additional oxidation step with $FeCl_3$ or $CuSO_4$ (see ref. 11c and papers cited therein). In the electrochemical method, the use of MeCN as solvent and quaternary ammonium salt as electrolyte allows completion of the reaction at room temperature in less than 0.5 h. Moreover, under the conditions of the electrolysis, intermediate **4a** was efficiently oxidized to **4** by oxygen from the air.

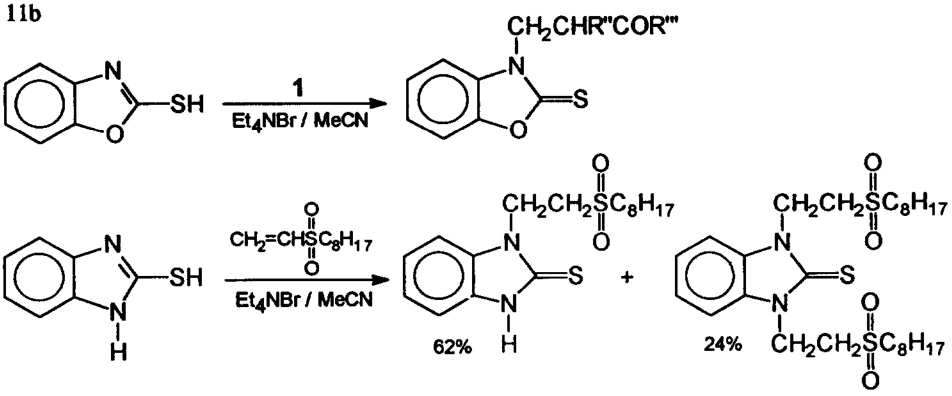
Heterocyclic thiols that can form ambidentate anions react with olefins **1** (cf. Scheme 7) with the formation of both S-alkylated and N-alkylated products[11b] with the ratio of products depending on the structure of the thiol, the reactivity of the olefin and the cation of the supporting electrolyte. For example, electrolysis of 2-pyridylthiol with ethyl acrylate in 0.1 M Bu_4NBr/MeCN gives S- and N-alkylated products in the ratio 39:61.



Scheme 9

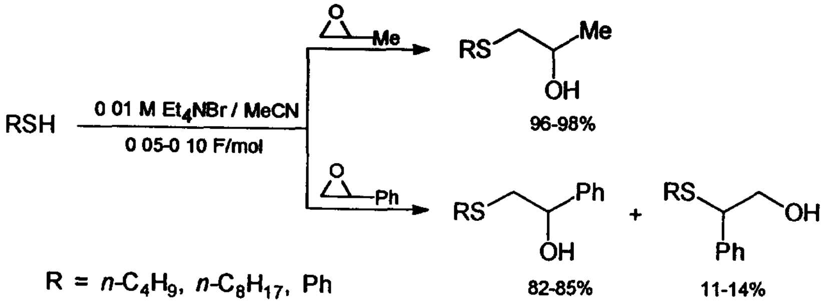
Under the same conditions, the reaction with butyl vinyl sulfone gives a 77:23 product ratio. However, if the reactions are carried out in 0.1 M $NaClO_4$/MeCN, S-alkylation increases and the ratio of S- to N-isomers is 69:31 for ethyl acrylate and 92:8 for butyl vinyl sulfone.

Only N-alkylated products were isolated after electrolysis of 2-mercaptobenzoxazole with activated olefins and for 2-mercaptobenzimidazole with octyl vinyl sulfone, both N- and N,N'-alkylated products were obtained.[11b]



Scheme 10

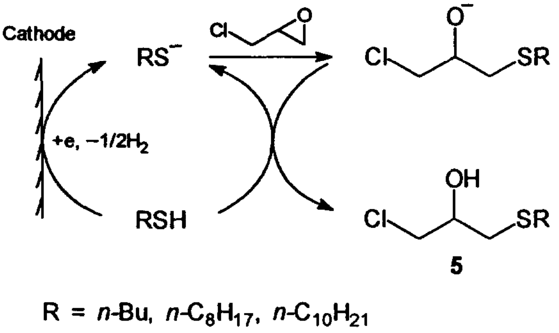
Electrogenerated thiolate anions effectively promote addition of thiols to epoxides.[11b,12] It has been found that addition of aliphatic and aromatic thiols to propylene oxide is regioselective while this reaction with styrene oxide results in formation of two isomeric products.



Scheme 11

The advantage of the electrochemical method is nicely illustrated by the reactions of the epoxide, epichlorohydrin.[11b,12,13] By simple and logical manipulation of the experimental conditions, it is possible to synthesize three types of products

For example, when an equimolar mixture of thiol and epichlorohydrin, containing 15-20% MeCN and small amounts of Bu_4NBr and water, was electrolyzed in an undivided cell, a catalytic amount of electricity was passed resulting in the quantitative formation of β-chloro alcohol **5**



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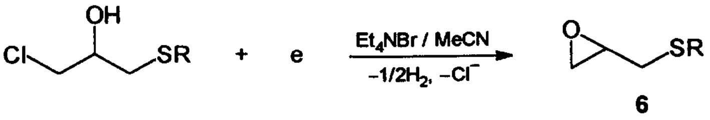
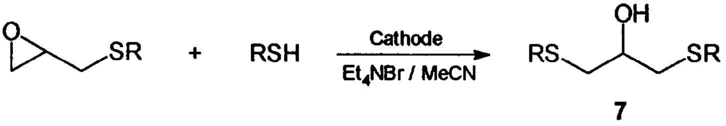
Scheme 12

When this reaction mixture was further electrolyzed in a divided cell, epoxysulfide **6** was formed This is an example of the cathodic generation of an alkoxide followed by intramolecular displacement of chloride



Scheme 13

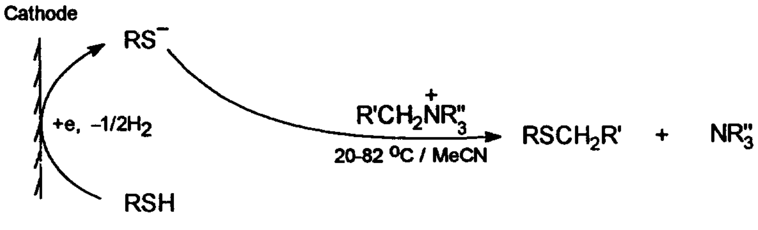
Finally, the electrocatalytic addition of a second molecule of thiol to epoxysulfide **6** resulted in formation of di(alkylthio)-alcohol **7**.



Scheme 14

Alternatively, one can proceed directly to compound **6** in a one-pot reaction by starting with an equimolar mixture of thiol and epichlorohydrin and electrolyzing in a divided cell with passage of 1 1-1 15 F/mol electricity The logic of this procedure is that addition of thiol to epichlorohydrin is catalytic and requires very little electrical charge, but reforming the epoxide ring in **6** requires the stoichiometric passage of 1 F/mol Similarly, **7** can be formed in good yield simply by starting with a thiol/epichlorohydrin mole ratio of two

Due to the very high reactivity of cathodically-generated thiolate anions in acetonitrile, it is possible to achieve efficient dealkylation of quaternary ammonium salts[14] (QAS) This reaction proceeds by a nucleophilic substitution mechanism according to the following scheme



R = n-C_8H_{17}, n-$C_{12}H_{25}$, Ph, p-(t-Bu)-C_6H_4, p-Cl-C_6H_4

R' = H, Me, n-Pr, Ph, R'' = Me, Et, n-Bu

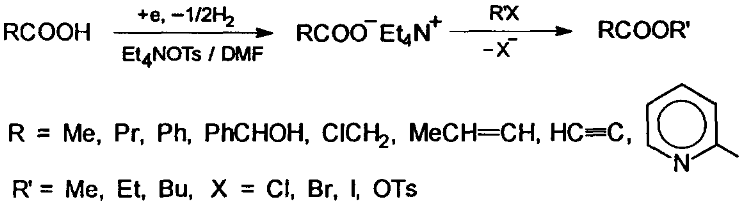
Scheme 15

The electrochemical nucleophilic dealkylation of QAS is a convenient alternative to reported chemical methods,[15] that usually require sodium hydrogen telluride,[15a] alkali metal or copper salts of thiophenol[15b,c] under reflux in various solvents Therefore the selectivity of the process is not very high Only in the expensive and toxic solvent, hexamethylphoshoramide, did the reaction of the lithium salt of propyl thiolate with QAS proceed at relatively low temperature [15d]

The electrochemical version of dealkylation of QAS proceeds in the preparatively convenient solvent acetonitrile under mild conditions and is more selective than the chemical alternatives.[14] For example, debenzylation of triethylbenzylammonium chloride with electrogenerated thiophenolate anion proceeds at 23-25 °C with a yield of benzyl phenyl sulfide of 98% and for dealkylation with dodecanethiolate anion the reaction occurs rapidly at 42-45 °C It should be noted that a variety of aliphatic, aromatic and heteroaromatic thiols can be used as dealkylating agents, not only the volatile and toxic propylthiol or thiophenol

2 *Electrochemical Esterification, Etherification and Transesterification*

In 1957 Coetzee and Kolthoff showed that cathodic electrolysis of acetic acid in acetonitrile results in hydrogen evolution [16] Of course, the other product was the acetate anion Later on, this cathodic reduction was made the basis of an efficient method of esterification of carboxylic acids under mild conditions (Scheme 16) [8,17] The esterification proceeds smoothly at room temperature by the reaction of different kinds of alkylating reagents with quaternary ammonium carboxylates formed in the cathode compartment



Scheme 16

It has been shown[17] that acids with groups such as chlorides, olefins, or acetylenes could be esterified without the simultaneous reduction of these groups

In the same manner, etherification of alcohols can be carried out under cathodic electrolysis conditions [8,18a] It has been shown[18a] that this process proceeds through intermediate formation of alkoxide ions at the cathode The reactivity of alkoxide ions depends dramatically on the nature of the counterion.

$$\mathrm{ROH} \xrightarrow[\text{QAS / DMF}]{+e,\ -1/2H_2} \mathrm{RO^-Q^+} \xrightarrow[-X^-]{R'X} \mathrm{ROR'}$$

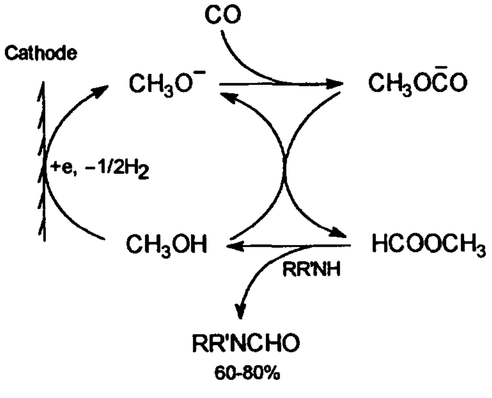
R	R'	X	Curr effic ,%	Ref.
Me	$PhCH_2$	Cl	72 4	18a
Et	$PhCH_2$	Cl	52	18a
Ph	Me	I	82	18a
Ph	p–C_6H_4-NO_2	I, Br, Cl, F	72-95 (yield)	8

Scheme 17

For example, etherification of phenol with *p*-bromonitrobenzene in a DMF solution of Et_4NOTs produced ether in 75% yield while with $NaClO_4$ as supporting electrolyte only a trace of product was formed [8]

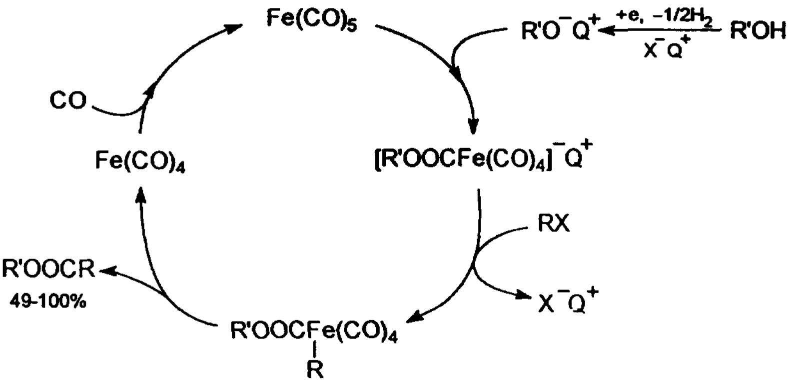
When electrolysis of alcohols and carboxylic acids was carried out in an undivided cell with sacrificial anodes, cyclohexanolato,[18a] catecholato[18b] and carboxylato[18c] derivatives of main group and transition metals were obtained in high yield.

An interesting application of electrogenerated anions is found in the area of C-1 chemistry The electrolysis of methanol/Bu_4NBF_4 under 100 atm of carbon monoxide gave methyl formate as the main product.[19] When this process was carried out in the presence of alkylamines, the corresponding formamides were obtained. It was suggested that in the first step methyl formate is formed which then reacts with the alkylamine.[19]



Scheme 18

The use of catalytic amounts of iron(0) pentacarbonyl allows one to synthesize esters from alcohols and alkyl halides with low pressure (one atmosphere) carbon monoxide[20]



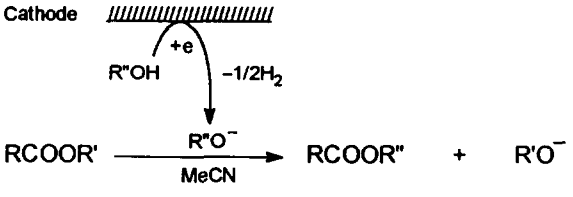
RX = $PhCH_2Br$, p-Me-$C_6H_4CH_2Br$, p-Br-$C_6H_4CH_2Br$, MeI

R'OH = MeOH, EtOH, i-PrOH

Scheme 19

For comparison it was shown that the yields of esters from the cathodic method were higher than those from a chemical route in which alkoxide ions were generated with sodium hydride[20]

The direct cathodic generation of alkoxide ions provides a way of accomplishing the important synthetic operation of transesterification under very mild conditions[21,22] Electrolysis of a mixture of ester RCOOR' and excess alcohol R"OH in acetonitrile results in transesterified product RCOOR"[21a]

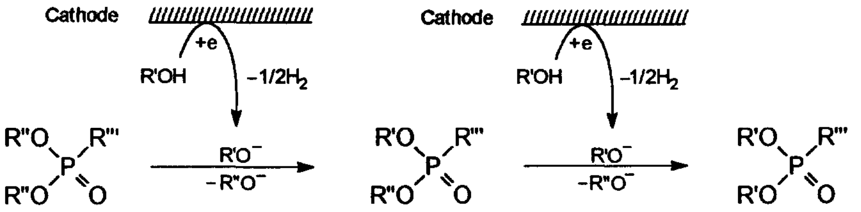


R = $PhCH_2$, PhCH=CH, PhC(O), R' = Me, $PhCH_2$, (-)-menthyl, (-)-bornyl, (-)-2-methylbutyl, R" = $PhCH_2$, (-)-menthyl, (-)-2-methylbutyl, (-)-bornyl

Scheme 20

When R was benzyl or cinnamyl, tetraethylammonium perchlorate was used as the supporting electrolyte while for R = benzoyl, transesterification was performed with lithium perchlorate.[21a] In the last case, the lability of the alkoxy group is obviously higher and the reaction proceeds even with the less reactive lithium alkoxide. The maximum yield of transesterified product was found after passing 0.5 F/mol current and when conversion of starting material was not more than 50% because the reaction of esters with alkoxide ions is reversible.[21a] However, in the case of methyl benzoates with a 5-fold excess of aminoalcohol, the tranesterified product was obtained in 58-92% yield after passing 1.2 F/mol.[21b]

The cathodic electrolysis of aliphatic alcohols and esters of alkylphosphonic acids (alkylphosphonates), **8**, in acetonitrile with Et_4NClO_4 as the supporting electrolyte leads to either mono- (**9**) or ditransesterified (**10**) alkylphosphonates depending on the charge passed.[22] The key step of this method is the cathodic generation of alkoxide ion that then takes part in a nucleophilic substitution reaction at the phosphorous atom in phosphonate **8**, leading to **9** and **10**.



8 **9** **10**

No	R'	R"	R'''	Cathode[a]	Charge, F/mol	Yield (isolated), % 9	10
1	*n*-Pr	Me	Me	GC	2.3	–	65
2	*n*-Bu	Me	Me	GC	0.5	48	–
3	*n*-Bu	Me	Me	GC	2.3	–	61
4	*n*-Bu	Me	Me	GC	1.05	50	10
5	*n*-Bu	Me	Me	Pt	2.3	–	68
6	*i*-C_5H_{11}	Me	Me	GC	1.00	45	15
7	*i*-C_5H_{11}	Me	Me	Pt	2.10	–	63
8	*n*-C_6H_{13}	Me	Me	GC	1.01	46	16
9	*n*-C_6H_{13}	Me	Me	Pt	2.2	–	65
10	*n*-C_6H_{13}	Et	Me	GC	1.50	65	5
11	*n*-Bu	Me	$CH(OMe)_2$	GC	1.80	11	5
12	*n*-C_6H_{13}	Et	$CH_2CH(OEt)_2$	GC	2.00	–	30
13	*n*-Bu	Me	Ph	GC	2.00	–	60

a) GC - glassy carbon

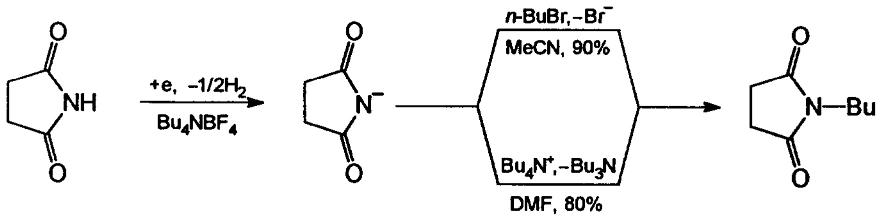
Scheme 21

The yield and ratio of products **9** and **10** are largely functions of the nature of the starting phosphonate **8** and the amount of current passed For example, dimethyl methylphosphonate readily undergoes electrochemical transesterification with various alcohols Passing 0 5 F/mol leads to exclusive formation of monosubstituted product **9** (Scheme 21, No. 2) whereas *ca.* 1 F/mol gives a mixture of mono- and disubstituted esters (No 4, 6) Disubstituted ester **10** was the only electrolysis product found upon passage of >2 F/mol (No 1, 3, 5, 7, 9 and 13).

Interest in the transesterification of esters of alkylphosphonic acids is related to the possibility of synthesizing higher esters from readily available lower esters However, the known chemical variants[23] of this reaction require heating and base catalysis Electrochemical transesterification proceeds under mild conditions without any base and can be considered to be a good alternative to the chemical versions of this reaction

3 Electrochemical Generation of N-Anions and their Use in Synthesis

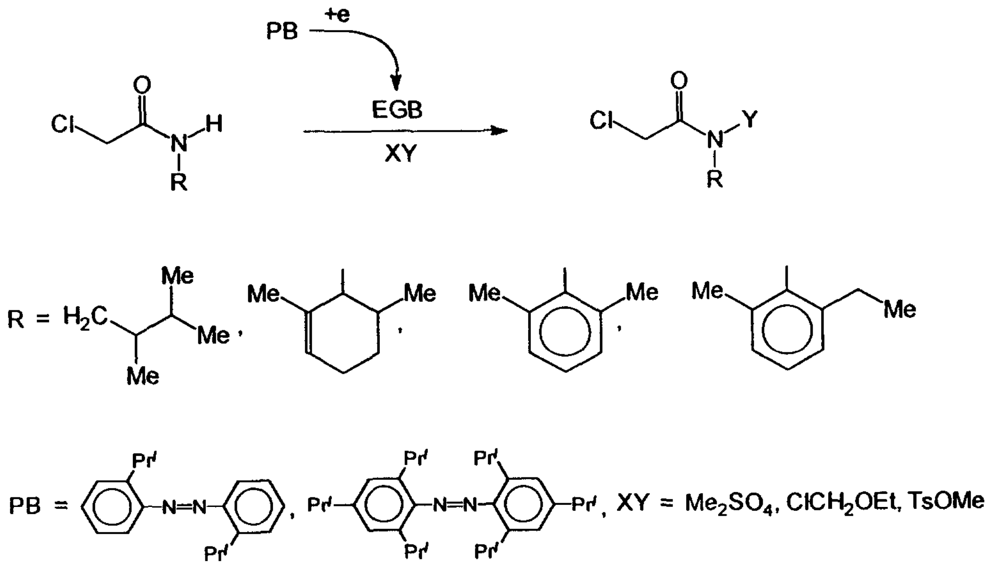
The first example[5c] of the direct electrochemical generation of N-anions involved the reduction of succinimide (which is a relatively strong acid, pK_a 9 6) in either MeCN or DMF containing Bu_4NBF_4 The electrolysis proceeds *via* one-electron transfer, hydrogen evolution and formation of the succinimide anion which then can be alkylated by both *n*-BuBr and tetrabutylammonium cation



Scheme 22

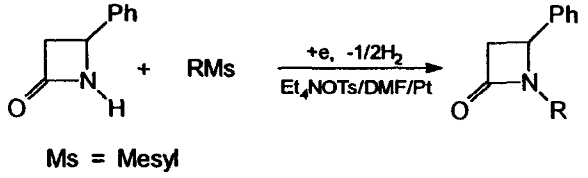
Due to the low nucleophilicity of succinimide anion, the reaction with QAS proceeds at a reasonable rate only in refluxing DMF (b p 153 °C), while the more nucleophilic thiolate anions react with QAS in MeCN under much milder conditions (see part **III.1**).

Baizer and coworkers have used EGB for generation of N-anions of less acidic amides and their subsequent alkylation gave the desired N,N-dialkylamides in high yield [24]



Scheme 23

Later it was found[5d,25a] that electrochemical reduction of 2-pyrrolidinone results in formation of the N-anion which was successfully used as an EGB to promote base-catalyzed reactions.[4c] It was subsequently shown[25b] that cathodic alkylation of different kinds of amides as well as carbamates and some N-heterocycles can be carried out without using any EGB. Obviously, in practice this method is more convenient than Baizer's method in which isolation of the products is complicated by the presence of the PB in the reaction mixture. (Azobenzenes can be difficult to separate from the desired products). Another advantage of the direct electrolysis is that the reaction medium remains neutral because the highly basic electrogenerated N-anion reacts rapidly with electrophile thus preventing the buildup of strong bases in the reaction medium. For example, β-lactams, which are quite unstable under basic conditions, can be N-alkylated in good yield by cathodic electrolysis.[25b]



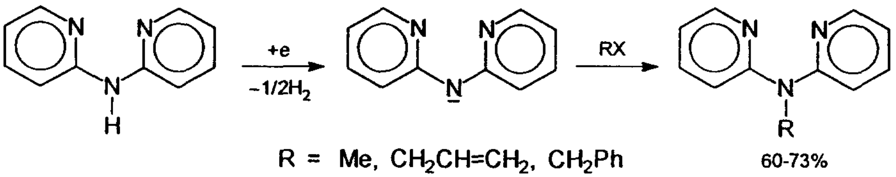
R	Yield, %
Me	91
s-Bu	60

Scheme 24

Voltammetric investigations of the cathodic behavior of NH-containing heterocyclic compounds,[26a,27a] aliphatic carboxamides[26b,d] and derivatives of urea[26c] showed that the reduction of these compounds on transition metal electrodes in aprotic media proceeds *via* one-electron transfer and formation of the N-anion. This conclusion was supported by the subsequent alkylation[26b-d] of the N-anions as well as by the synthesis of a number of organometallic compounds[26] when sacrificial anodes were used.

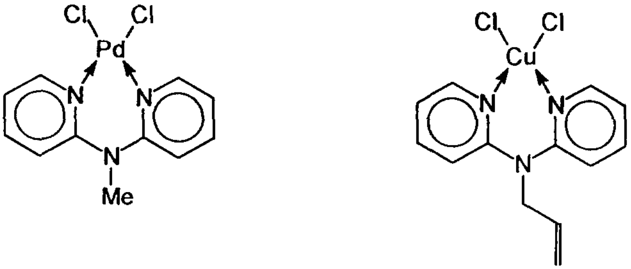
It should be noted that under cathodic electrolysis conditions it is possible to alkylate even amines such as diphenylamine or piperidine[27b] which are very weak acids and their reduction as well as that of ammonia obviously proceeds via N-anion formation.[28]

According to data from voltammetric measurements, 2,2'-dipyridylamine in 0.1 M Bu_4NBF_4 solution in MeCN is reduced with cleavage of the N-H bond and formation of the N-anion.[27c] On the basis of this observation a method of regioselective alkylation of 2,2'-dipyridylamine was developed.



Scheme 25

The alkyl(2,2'-dipyridyl)amines so obtained were used as bidentate ligands for synthesis of complexes of bivalent metals.[27c]



Scheme 26

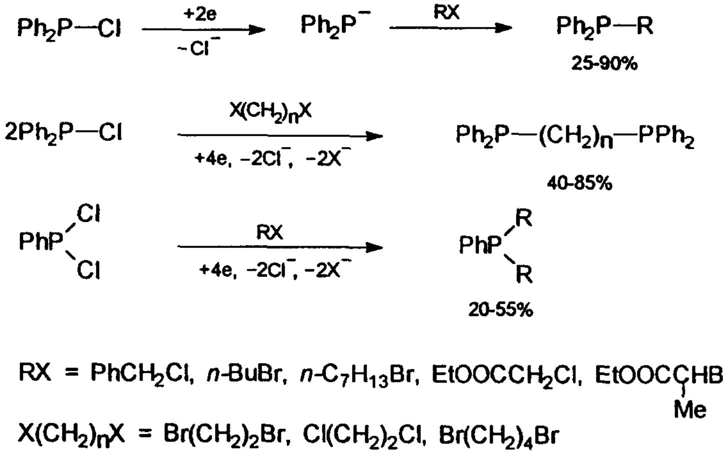
It is known that chemical alkylation of 2-aminopyridine and 2-alkylaminopyridines normally occurs at the nitrogen atom of the pyridine ring. Only in the presence of strong bases, such as $NaNH_2$, is it possible to achieve alkylation at the amino group.[29] Webb *et al.*[30] attempted to obtain methyl(2,2'-dipyridyl)amine by the reaction of MeI in the presence of NaH, but the desired product was obtained only in very low yield.

The direct cathodic reduction of 2,2'-dipyridylamine (dpa) in an undivided cell with sacrificial anodes results in the preparation of various metal complexes $M(dpa)_n$ (M = Cu, Ag, Tl, $n=1$, M = Zn, Cd, n = 2) in approximately 90% yield.[31]

4 *Electrochemical Generation of other Heteroatom Anions and their Use in Synthesis*

Generally speaking, the electrochemical method allows one to generate any heteroatom-centered anion that is capable of existence in solution. Depending upon the nature of the available starting materials, any of the procedures that were mentioned in the Introduction (*cf.* Schemes 1-3) can be used for generation of these anions.

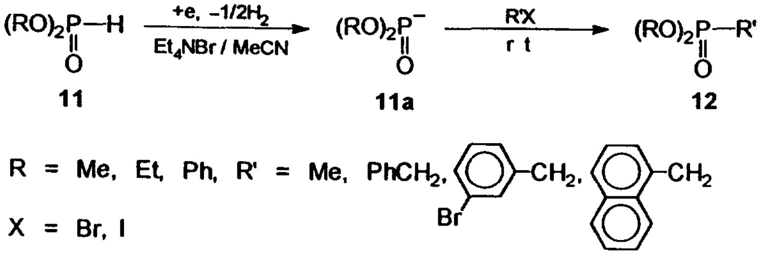
P-Anions It is clear that the well known reductive coupling of halodiphenylphosphines[32] proceeds via intermediate formation of P-anions.[33] This was made the basis of a very simple method for synthesis of different kinds of tertiary phosphines starting from chlorodiphenyl- or dichlorophenylphosphines [34] The electrolysis was carried out either in a DMF or N-methylpyrrolidone solution of Bu_4NBF_4 (0 02 M) and Bu_4NI (0 02 M) in an undivided cell with a stainless steel cathode and Mg anode



Scheme 27

The anion Ph_2P^- can also be generated by the direct reduction of diphenylphosphine Thus, electrolysis of this phosphine in MeCN in an undivided cell with a Pt cathode and sacrificial anode gives metal-phosphido complexes $M(PPh_2)$ (M = Cu, Ag, Au) or $M(PPh_2)_2$ (M = Co, Zn, Cd) in high yield.[35] Electrolysis of a mixture of Ph_2PH and bis(diphenylphosphino)methane (dppm) results in formation of $Cu_4(PPh_2)_4(dppm)_2$ It should be noted that the main advantages of the direct electrochemical preparation of such complexes are simplicity and high yield (>90%) compared with the chemical methods described previously [35]

The cathodic electrolysis of dialkyl and diaryl phosphites **11** (for R = Et, the pKa in DMSO is 20 8[36]) in the presence of alkyl halides gives phosphonates **12** in 55-65% isolated yields [37,38] The reaction apparently proceeds through the intermediate formation of anion **11a**, which acts as a nucleophile on the alkyl halide



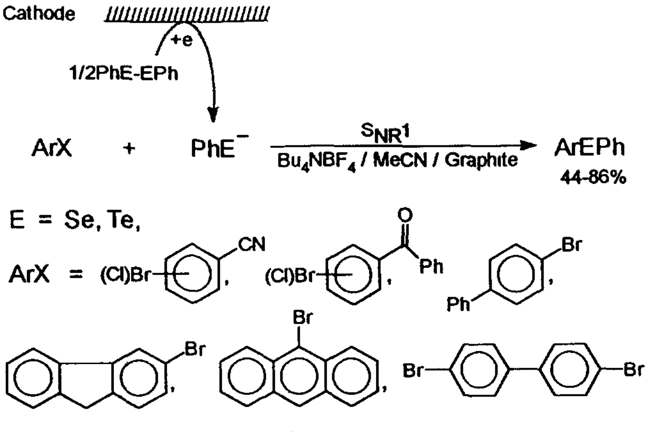
Scheme 28

In support of this scheme is the observation[39] that the reduction of dialkylphosphites in QAS solution in MeCN on transition metals occurs by a one-electron mechanism with cleavage of the P-H bond and formation of the anion. Electrolysis in an undivided cell with a Ni cathode and sacrificial anode allowed the preparation of Ni, Co, Cr and Ti derivatives of phosphites.[39]

Very interesting results were obtained when alkylation of dialkylphosphites with alkyl halides was carried out in DMF.[40] It has been found that this process is more effective in DMF containing a small amount of water and the reaction was completed by passing 1.0-1.2 F/mole of electricity. In dry DMF, alkylation of dialkyl phosphites also took place, but two equivalents of alkyl iodide and 2 F/mole of electricity were required. It was concluded that in the presence of water, OH^- is generated at the cathode, and this strong base (pKa of H_2O is 35 in DMF, 31 in DMSO) deprotonates the dialkylphosphites.[40]

Compared to the preparation of phosphonates by the Arbuzov reaction, the electrochemical method uses the more readily available dialkyl phosphites **11** instead of tertiary phosphites and the reaction conditions are quite mild. The Michaelis-Becker reaction[41] can also be used but the electrochemical method eliminates the necessity of prior preparation of the salt of **11** with sodium or sodium alkoxide. It should be noted that electrochemical alkylation of **11** is selective: although anion **11a** is an ambidentate anion, no O-alkylated products were formed during electrolysis. Another advantage of the electrochemical method is the possibility to prepare *in situ* alkyl phosphonates with an activated α-H bond and use them in a subsequent Horner reaction.[38] This sequence allows the synthesis of olefins starting from dialkyl phosphites, alkyl halides and ketones (see Section III.5).

Se- and Te-Anions. The electrochemical reduction of diphenyl diselenide and ditelluride (by analogy with the disulfides[2]) results in the formation of $PhSe^-$ and $PhTe^-$ which will react with aromatic halides ArX by the electrochemically induced $S_{RN}1$ aromatic nucleophilic substitution to give unsymmetrical diaryl chalcogenides.[42-48]



Scheme 29

It should be noted that ultrasound-enhanced reduction of Se and Te powders with generation of Se^{2-} and Te^{2-} followed by addition of alkyl halides resulted in formation of dialkyl dichalcogenides in high yields [46] Direct synthesis of diaryl dichalcogenides was more effective when sacrificial Se and Te cathodes were used [48]

Electrogenerated Se- and Te-anions have been used principally in electroinduced $S_{RN}1$ reactions (for more information see refs 42-48 and papers cited therein). However, by analogy with thiolate anions, there are good prospects for the synthetic utility of these anions by using them as typical anionic nucleophiles

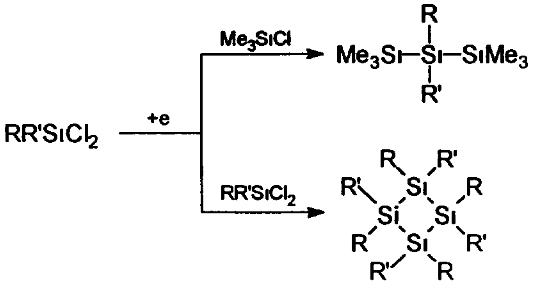
Si- and Ge-Anions. Detailed investigations of the electrochemical reduction of halosilanes[49-53] in aprotic media showed[52,53] that this process, at least in the case of triarylhalosilanes, proceeds *via* intermediate formation of Si-anions On this basis, a facile electrochemical method of forming Si-Si bonds was created that allows synthesis of both symmetric and asymmetric disilanes as well as polysilanes[50,53] with current yields up to 100%.

$$R_2R'SiCl + 2e \xrightarrow{-Cl^-} R_2R'Si^- \xrightarrow[-Cl^-]{R''_2R'''SiCl} R_2R'SiSiR''_2R'''$$

R	R'	R"	R"'	Current efficiency, %	Ref
Ph	Ph	Me	Me	95-100	50b, 53
Ph	Me	Me	Me	90 (yield)	54a
Ph	Ph	Ph	Ph	100	50b, 53
p-F-C_6H_4	p-F-C_6H_4	p-F-C_6H_4	p-F-C_6H_4	82	53
p-F-C_6H_4	Me	p-F-C_6H_4	Me	50	53
p-F-C_6H_4	p-F-C_6H_4	Me	Me	46	53
p-Me-C_6H_4	p-Me-C_6H_4	Me	Me	61	53
Me	Me	Me	Me	95-100	50a, 53

Scheme 30

Tri- and tetrasilanes are formed by electrolysis of dichlorosilanes



R (Ref 54a)	R'	Yield, %
Me	Ph	25
Me	Me	60

R (Ref 53)	R'	Curr effic , %
Ph	Ph	100
p-F-C_6H_4	p-F-C_6H_4	70

Scheme 31

1,1,3,3-Tetramethyl-1,3-disilacyclobutane (yield 34%) and polycarbosilanes (40%) were obtained as the principal products after electrolysis of (chloromethyl)dimethylchlorosilane while electrolysis of this compound in the presence of dimethyldichlorosilane resulted in formation of bis(dimethylchlorosilyl)methane in 60% yield [54b]

Although cathodic electrolysis of trimethylhalosilane results in formation of hexamethyldisilane,[50,53] the question of the intermediacy of the anion, Me_3Si^-, has not been answered However, electrolysis of mixtures of trimethylchlorosilane (TMClS) and organic halides resulted in formation of Si-C bonds with the products formed in good yields [55-58]

$$RX + Me_3SiCl \xrightarrow{+e} RSiMe_3$$

$$R'R''CCl_2 + 2Me_3SiCl \xrightarrow{+e} R'R''C(SiMe_3)_2$$

RX	Yield, %	Ref
$PhCH_2Br$	89, 70	55,57a
(1-naphthyl)-CH_2Cl	81	55
$C_3H_7CH{=}CHCH_2Cl$	60	55
$PhCH{=}CHCH_2Cl$	70	56b
trans-PhCH=CHI	51	56b
p-MeO-C_6H_4-I	53	56b
Ph-Br	55	57a
3-bromopyridine	55	56b
3-iodobenzothiophene	62	56b

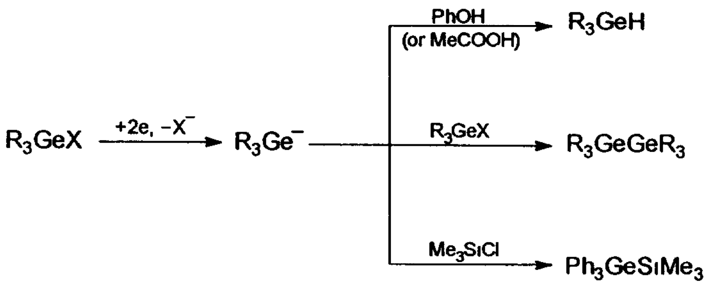
R'	R"	Yield, %	Ref
Cl	Cl	68	57b
Cl	H	56	57b
H	H	88	57b
Ph	H	74	58
o-Me-C_6H_4	H	88	58
m-Me-C_6H_4	H	78	58
p-Me-C_6H_4	H	87	58
p-F-C_6H_4	H	91	58
2-Cl-6-F-C_6H_3	H	72	58

Scheme 32

On the basis of the structures of the products and the relative reduction potentials, it was supposed that this process proceeds *via* reduction of the organic halides with formation of carbanions, which in turn react with TMClS by a nucleophilic substitution mechanism It is known that halosilanes are reduced in the range of -2 0 to -2 5 V vs SCE (determination of the reduction potential of trimethylhalosilanes at low concentration is complicated by the fast hydrolysis of these compounds with traces of water present in nominally anhydrous solvents).[51,52] The reduction potentials of some organic halides (-1 8 to -2.5 V vs SCE) are close to the reduction potential of TMClS Moreover, it can be expected that many organic halides will be cathodically inactive on solid electrodes such as Pt, GC or stainless steel (excluding, of course, polychloromethanes,[57b] which can be reduced at less negative potentials) Usually preparative electrolyses are carried out at relatively high current density without control of the potential and in the presence of a large excess of silylating agent. Therefore the possibility of the reduction of TMClS during electrolysis with formation of Si-anions can not be excluded

Of course, for the purposes of organic synthesis it is not so important whether the carbanion or Si-anion is formed Of much greater interest are the products that can be obtained, their yields, and the general convenience of the method. In any case, the electrochemical method of synthesis of organosilicon compounds has the notable advantages of mild conditions, no need for metal reducing agents (see ref 54-58 and papers cited therein), and the electrosynthesis can be carried out either in divided[50a,53,55,56] (electrolyte Bu_4ClO_4/1,2-dimethoxyethane or Et_4NOTos/DMF) or undivided[54,57,58] (Et_4NBF_4/THF or $LiClO_4$/DMF) cells using Pt,[55,56] Hg,[50a] Pb,[53] stainless steel[54,57,58] or GC[54,57] cathodes In the more convenient undivided electrolyses, sacrificial Al, Mg or Zn anodes were used

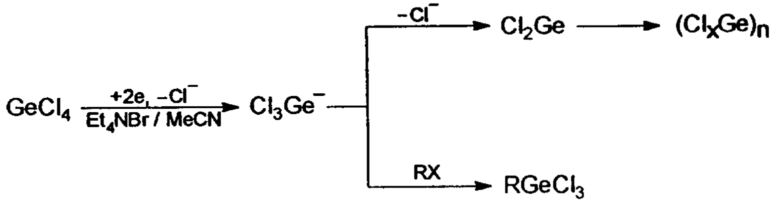
Electrochemical investigation of the mechanism of reduction showed that the two-electron reduction of triorganylhalogermanes proceeds *via* the formation of Ge-anions which can be protonated or, in an aprotic medium, used in nucleophilic substitution reactions [52a]



R_3 = Ph_3, $(p\text{-}CF_3\text{-}C_6H_4)_3$, Ph_2Me, (1-naphthyl)PhMe, $(n\text{-}Bu)_3$
X = Br, Cl, F

Scheme 33

In analogous fashion, electrochemical reduction of tetrachlorogermane resulted in the generation of Cl_3Ge^-, whose oxidation wave was detected by using a rotating ring-disk electrode [59,60] This anion can eliminate chloride ion to form dichlorogermylene,[59,60] which converts to germanium subchlorides However, Cl_3Ge^- can also react with organic halides to form organotrichlorogermanes.[60]



R = Me, Ph, $PhCH_2$, $CH_2CH{=}CH_2$, MeC(O), X = Cl, Br, I

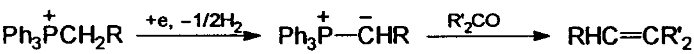
Scheme 34

These results hold considerable promise for future development of methods for the electrochemical synthesis of organogermanium compounds from readily accessible germanium chlorides

5 *Electrogeneration of Carbanions and their Use in Synthesis*

The electrochemical method opens up excellent synthetic opportunities in carbanion chemistry, which plays such a central role in synthetic organic chemistry

More than twenty years ago, it was shown that direct electrochemical reduction of phosphonium,[5a] sulfonium[61] and ammonium[62] salts resulted in formation of the corresponding ylides which were then used in subsequent reactions Perhaps the electrogeneration of phosphonium ylides was the most important since it permitted the Wittig reaction to be performed under mild conditions without using any base.



$$Ph_3\overset{+}{P}CH_2R \xrightarrow{+e,\ -1/2H_2} Ph_3\overset{+}{P}-\overset{-}{C}HR \xrightarrow{R'_2CO} RHC{=}CR'_2$$

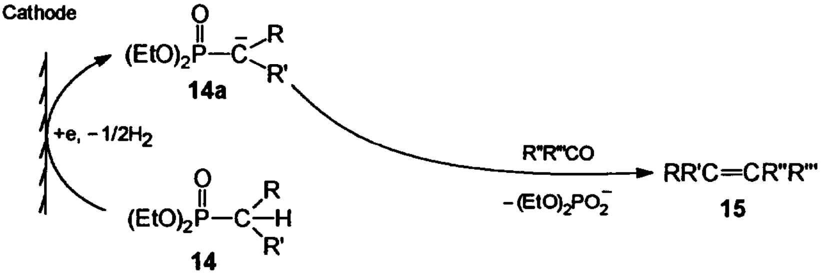
13

R (Ref 5a)	R'_2CO	Yield of 13, %
H	PhCHO	84
Me	PhCHO	95
Ph	PhCHO	72
Ph	*n*-PrCHO	95
Ph	cyclohexanone	75
COOEt	*n*-PrCHO	50
COOEt	PhCHO	75

Scheme 35

This reaction was successfully repeated using an electrogenerated base (EGB).[3d,f] In an analogous fashion, an EGB was also used to promote the Horner reaction,[3e,f,4a,63] which proceeds *via* intermediate generation of phosphonate carbanions. Electroreductive cleavage of the C-halogen bond in α-halophosphonates on a Hg cathode allows the generation of phosphonate carbanions without using any base.[63,64] The subsequent reaction of these anions with carbonyl compounds resulted in the formation of olefins with satisfactory yields.

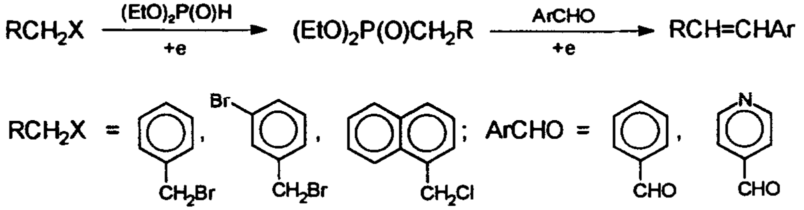
Actually, the Horner reaction can be carried out by the direct electrolysis of phosphonates on Pt or glassy carbon cathodes in a solution of Et_4NBr in MeCN.[65] The cleavage of the activated C-H bond of phosphonates **14** proceeds with selective formation of the carbanion **14a** which further reacts with the carbonyl compound with formation of olefins **15**.



R (Ref 65)	R'	R''	R'''	Cathode	Yield of **15**, %
COOEt	H	Ph	H	Pt	68
COOEt	H	Ph	H	GC	84
COOEt	H	Et	H	Pt	42
COOEt	H	$(CH_2)_5$		Pt	50
CN	H	Ph	H	Pt	83
CN	NMe_2	Ph	H	Pt	61
CN	NMe_2	Ph	H	GC	60
$(EtO)_2P(O)$	H	Ph	H	Pt	68

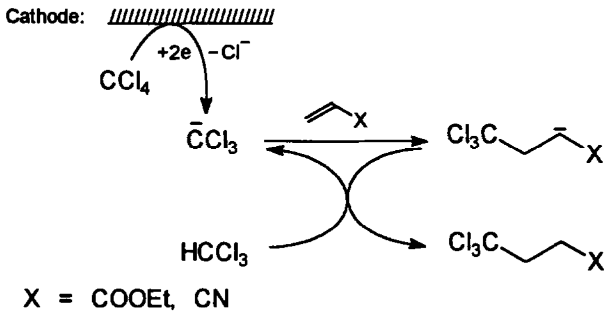
Scheme 36

As was mentioned above, the phosphonates can be synthesized electrochemically[37] (cf. Scheme 28). This allows one to prepare olefins in a "one-pot" reaction from dialkylphosphites, organic halides and carbonyl compounds.[38] Under the electrolysis conditions, the phosphonates that are formed from dialkylphosphite and organic halides react further with carbonyl compounds to form olefins in 48-57% isolated yield.



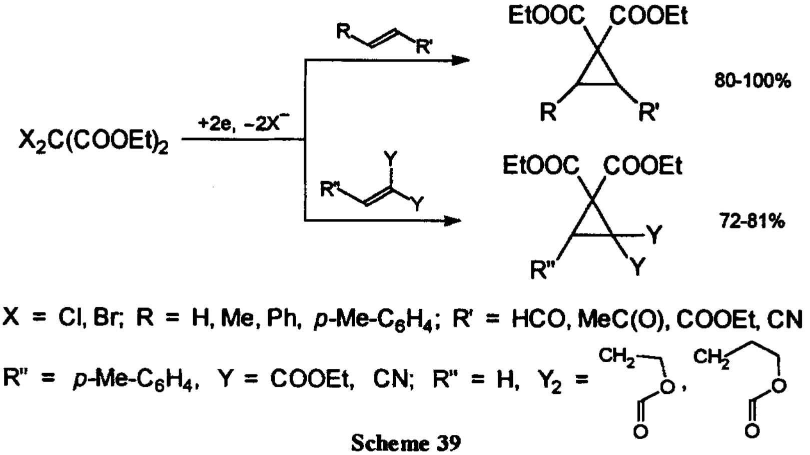
Scheme 37

The electrochemical method has proven to be very successful for promotion of Michael reactions. It has been shown[1] that electroreduction of carbon tetrachloride on a mercury cathode results in formation of the trichloromethyl anion, which will react with activated olefins. In the presence of chloroform, this reaction is electrocatalytic and the current efficiency for product formation exceeded 100%.



Scheme 38

In the case of trichloroacetate and tribromoacetate, the intermediate carbanion formed by Michael addition to the olefin cyclizes with expulsion of halide to form cyclopropane derivatives in high yields.[66,67]

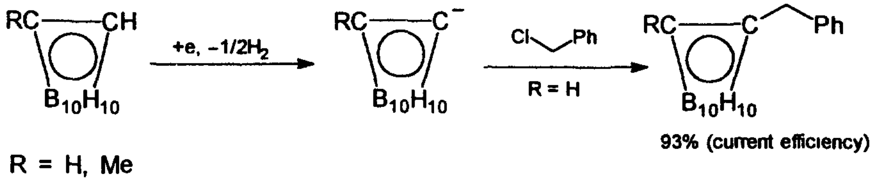


Scheme 39

This reaction may be a good way to prepare cyclopropane carboxylates In like manner, it has been shown[66,67] that the yields of *gem*-dicarboxylates are higher when the carbanion is generated by electroreduction of dihalomalonate than when prepared in a purely chemical way

Relatively strong C-H acids such as malonates, acetylacetonates and mononitroalkanes were easily introduced into Michael reactions by use of EGB.[3b,c,68] However, an obvious alternative route to the carbanions is by direct electrochemical reduction of the C-H acids Voltammetric investigations showed[69] that the aforementioned compounds are reduced on transition metal cathodes in MeCN with cleavage of a C-H bond The formation of carbanions was confirmed by the synthesis of some metal derivatives[68d,e] and reaction with alkyl halides.[69a,b] The same behavior was observed for weaker C-H acids such as phenylacetylene[70,71a] (pK_a = 23 3 in dimethoxyethane),[71a] cyclopentadiene (pK_a = 15), indene (18 5) and fluorene (22.9) [71b]

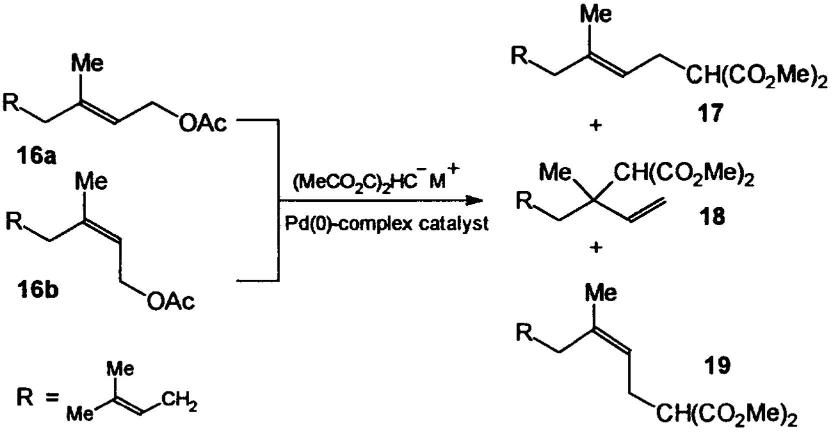
It has been shown[71c] that electroreduction of *o*-carborane and 1-methyl-*o*-carborane (pK_a = 23 3 and 23 1 in dimethoxyethane respectively) on transition metal cathodes in 0.1 M Et_4NCl/MeCN proceeds *via* cleavage of a C-H bond and formation of a carbanion which can subsequently be alkylated



Scheme 40

When the carbanions of dimethyl malonate, fluorene and nitromethane are formed by direct electrogeneration in the presence of a Pd(0)-catalyst, they react with allyl acetates to form the corresponding allylic derivatives (see Scheme 41).[72] The nucleophilicity, as well as the regio- and stereoselectivity of the carbanions in this reaction strongly depend upon the electrolysis conditions Reaction of the electrogenerated anion of dimethyl malonate with geranyl acetate **16a** and neryl acetate **16b** gave inner olefin (**17** or **19**), outer olefin (**18**) and some isomerized product (**19** or **17**), the ratios among these being sensitive to the electrolyte

Cathodic electrolysis of CH_2XY in the presence of 1,2-, 1,3- and 1,4-dihaloalkanes results in the formation of the corresponding cyclic derivatives (Scheme 42) [73] The reaction proceeds *via* cathodic cleavage

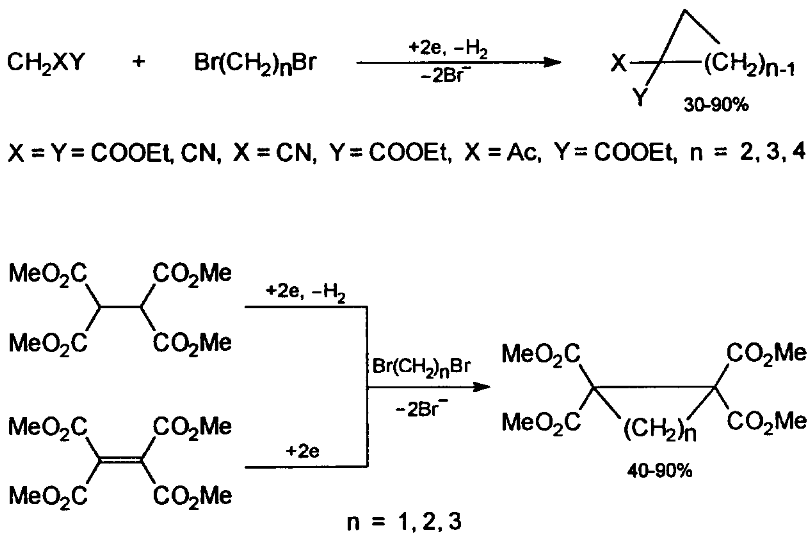


Allyl acetate **16**	Salt	Solvent	Reaction temp ,°C	Product distribution, % **17**	**18**	**19**	Total yield, %
a	$NaClO_4$	DMF	55-60	77	22	1	48
a	Et_4NClO_4	DMF	55-60	56	33	11	76
a	Bu_4NClO_4	DMF	55-60	63	28	9	57
a	Bu_4NClO_4	THF	reflux	75	20	5	77
a	Et_3SClO_4	DMF	55-60	87	12	1	27
a	Bu_4NClO_4	THF	r t	83	13	4	91
a	Bu_3SClO_4	THF	r t	86	6	8	78
b	$NaClO_4$	DMF	55-60	0	80	20	50
b	Et_4NClO_4	DMF	55-60	5	64	31	75
b	Bu_4NClO_4	THF	reflux	19	48	33	70
b	$NaClO_4$	THF	reflux	0	65	35	80
b	Bu_4NClO_4	THF	r t	15	19	66	98
b	Bu_3SClO_4	THF	r t	20	13	67	75

Catalyst Pd(0)[Ph_3P]$_4$, at r t bis(diphenylphosphino)ethane was used instead of Ph_3P

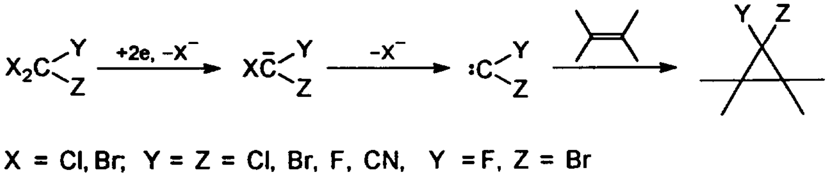
Scheme 41

of a C-H bond in CH_2XY, substitution of the first halide, cathodic cleavage of the second C-H bond and, finally, substitution of the second halide. Other cyclic compounds can be prepared from 1,1,2,2,-ethane- or ethylenetetracarboxylate esters and dihaloalkanes [74]



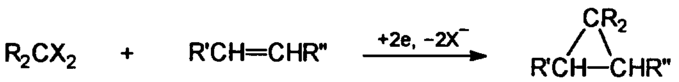
Scheme 42

Elimination of halide ion from electrogenerated α-halocarbanions results in formation of carbenes[75] such as CCl_2,[76] $\cdot CBr_2$,[77] $CBrCl$,[77] CF_2,[78] $CFBr$[79] and $C(CN)_2$[80] which form cyclopropanes with various substrates containing a double bond



Scheme 43

The electroreduction of dihalomethanes on an aluminum cathode[81] in the presence of $AlCl_3$ or reduction of dihalomethanes by electrogenerated solvated electrons[82] has been interpreted in terms of the intermediate formation of methylene, CH_2 In this connection, a very simple and convenient method for cyclopropanation has been reported recently [83] Electrolysis of dihalomethanes in an undivided cell with a carbon fiber or steel cathode and a sacrificial Zn anode in the presence of alkene results in the formation of the corresponding cyclopropanes, including those derived from methylene (Scheme 44) This approach was suitable for cyclopropanation of olefins even with 2,2-dibromopropane and α,α-dihalotoluenes It was proposed that cyclopropanation proceeds *via* intermediate formation of a zinc carbenoid

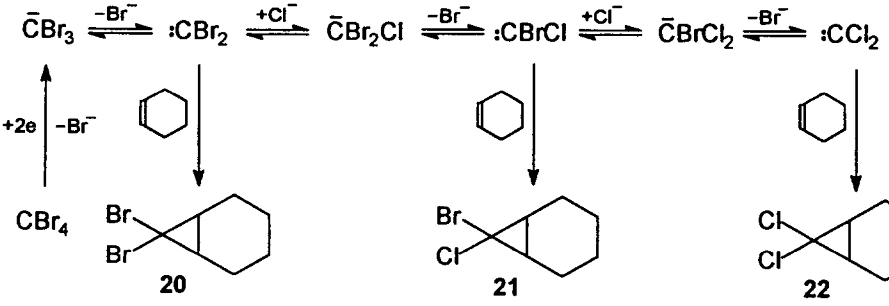


Alkene (Ref 83)	Dihalo compound	Cyclopropane, yield (isol), %
MeCH=CHCH$_2$OH	CH$_2$Br$_2$	56
MeCH=CHCH$_2$OH	CH$_2$BrCl	54
MeCH=CHCH$_2$OH	CH$_2$I$_2$	47
MeCH=CHCH$_2$OH	Me$_2$CBr$_2$	51
CH$_2$=CHCH$_2$OH	CH$_2$Br$_2$	42
PhCH=CHCH$_2$OH	CH$_2$BrCl	59
CH$_2$=CHCH$_2$OPh	CH$_2$Br$_2$	50

Alkene (Ref 83)	Dihalo compound	Cyclopropane, yield (isol), %
2-Cyclohexene-1-ol	CH$_2$BrCl	75
Geraniol	CH$_2$Br$_2$	70
Cyclooctene	CH$_2$I$_2$	75
Cyclooctene	Me$_2$CBr$_2$	46
Cyclooctene	PhCHBr$_2$	27
n-C$_6$H$_{13}$CH=CH	CH$_2$Br$_2$	66
PhCH=CH$_2$	CH$_2$I$_2$	33

Scheme 44

Very interesting results were obtained with CBr$_4$ [77] Reduction of this compound on a carbon (graphite) cathode in the presence of cyclohexene in MeCN containing Bu$_4$NBF$_4$ resulted in formation of only 7,7-dibromonorcarane (**20**) in 86% yield, while electrolysis in MeCN containing PhCH$_2$Et$_3$NCl gave a mixture of **20**, 7-bromo-7-chloro- (**21**) and 7,7-dichloronorcarane (**22**) in a ratio of 19/6/75 (total yield 85%) Under the electrolysis conditions, a number of reactions take place which are initiated by the interaction of dibromocarbene with chloride ion [77]

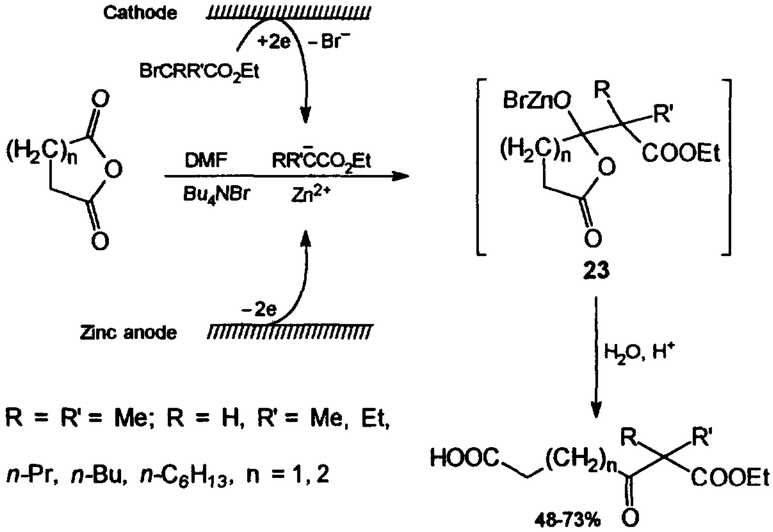


Scheme 45

Variation of the electrolyte allows one to obtain either of the symmetrical dihalides with a total yield of 86-90% It was found that electrolysis of CBr$_4$ in a solution of Bu$_4$NBF$_4$ in MeCN (or Bu$_4$NBr in CH$_2$Cl$_2$) containing a small amount of CHCl$_3$ (which serves as a source of dichlorocarbene and chloride ion), resulted in formation of a mixture containing mainly (60%) 7-bromo-7-chloronorcarane **21**.

Thus the above examples demonstrate that electrochemical generation of carbenes is a promising method that can become a good alternative for the synthesis of cyclopropane derivatives

The use of a sacrificial zinc anode was successful in promoting the Reformatsky reaction of α-halo esters with aldehydes or ketones.[84,85] One electrochemical version[84] of this reaction involves formation of the organozinc Reformatsky reagent through a metal-exchange reaction between electrogenerated Ni(0) complexes of α-chloroacetates and zinc chloride. In another version[85] the Reformatsky reagent is formed by direct reaction of the cathodically generated carbanion from α-bromoacetates and anodically generated zinc cation. The intermediate organozinc reagent further reacts with succinic or glutaric anhydride with formation of intermediate **23** Alternatively, the carbanion may react directly with the carbonyl compound with subsequent addition of zinc cation and formation of **23**

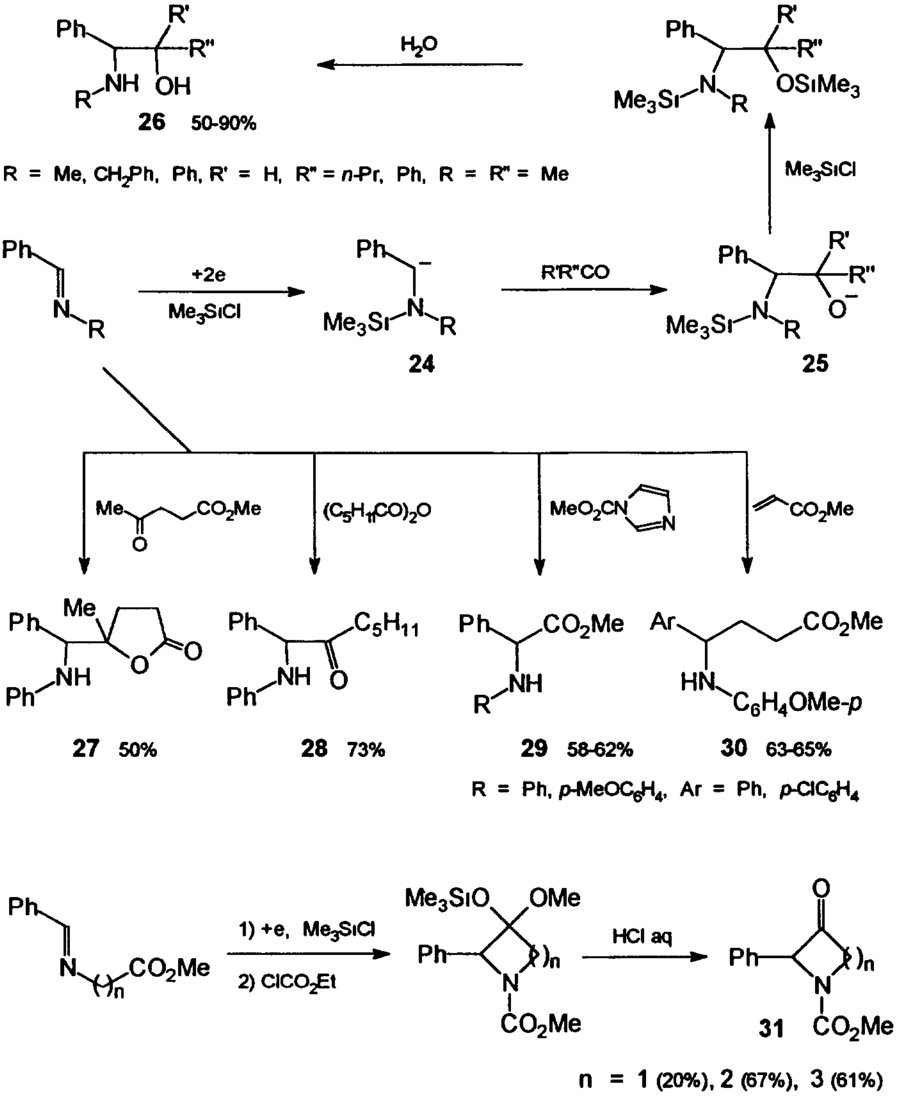


Scheme 46

The Reformatsky reaction is an important method for selective syntheses of a wide variety of organic compounds.[86] The electrochemical versions of this reaction look very promising due to the mild reaction conditions, the fact that activated zinc is not required, and the good yields that have been obtained

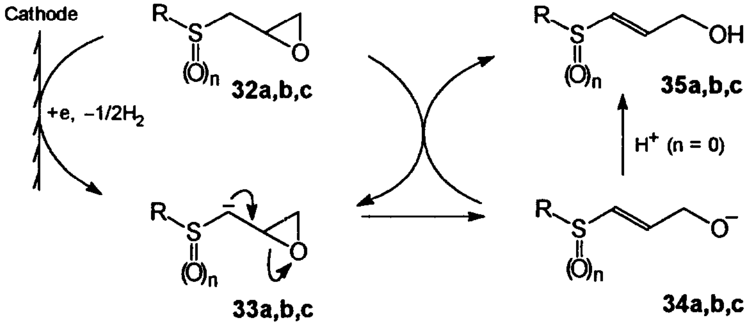
Electroreduction of aromatic imines in the presence of electrophiles results only in formation of amines.[87] However, when trimethylchlorosilane (TMClS) was also present, the coupling product was obtained in good yield. It was proposed that TMClS supports the reaction through formation of the intermediate carbanion **24**, which reacts with the electrophile The anion **25** that is formed is subsequently trapped by TMClS and, following hydrolysis, hydroxyamines **26** were isolated when the electrophile was an aldehyde or ketone

The electrolysis was carried out in a divided cell with a lead cathode in a solution of Et_4NOTs in DMF with controlled current It was demonstrated that a wide variety of functionalized amines (**27-30**) including cyclic compounds (**31**) can be prepared by the use of different starting materials and electrophiles.



Scheme 47

2,3-Epoxypropylalkylsulfoxides and the analogous sulfones, upon treatment with NaOMe in MeOH, undergo isomerization to the corresponding vinyl alcohols[88] The electrochemical approach permits this reaction to be carried out in the absence of added base under the conditions of cathodic electrolysis[11b,89] It should be noted that the electrochemical method successfully isomerizes 2,3-epoxypropylalkylsulfides for which a purely chemical reaction has not yet been described Thus, electrolysis of the epoxysulfide **32a** on a Pt or glassy carbon cathode in a solution of Et_4NBr in MeCN results in formation of mainly the *trans*-isomer of the corresponding allylic alcohol The key step of this reaction is cleavage of the α-C-H bond followed by intramolecular interaction of the α-carbanion **33a** with the epoxide ring

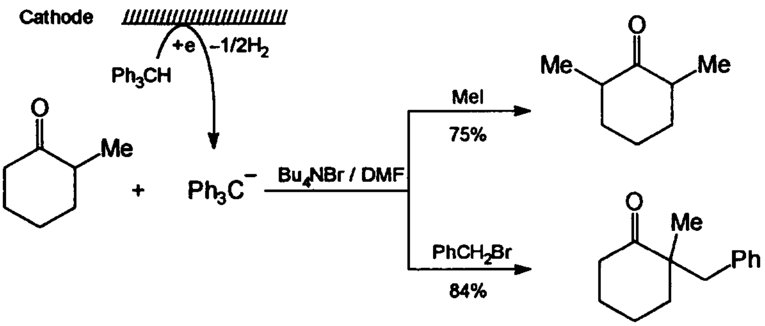


a n = 0, R = *n*-Bu, C_8H_{17} (yield 78-90%, trans/cis 4/1)
b n = 1, R = *n*-Bu, C_8H_{17}, $C_{10}H_{21}$ (yield 85-92%, trans/cis 100/3-5)
c n = 2, R = *n*-Bu, C_8H_{17}, $C_{10}H_{21}$ (yield 90-96%, trans)

Scheme 48

Epoxysulfoxides **32b** and epoxysulfones **32c** are isomerized under the same conditions [11b,89] However, in this case the reaction is catalytic since the basicity of alkoxide anions **34b,c** is high enough to deprotonate **32b,c** and regenerate the α-carbanions **33b,c** It should be noted that the electrocatalytic isomerization of epoxides **32b,c** is stereoselective even in the case of epoxysulfoxides, whose chemical isomerization is not stereoselective.

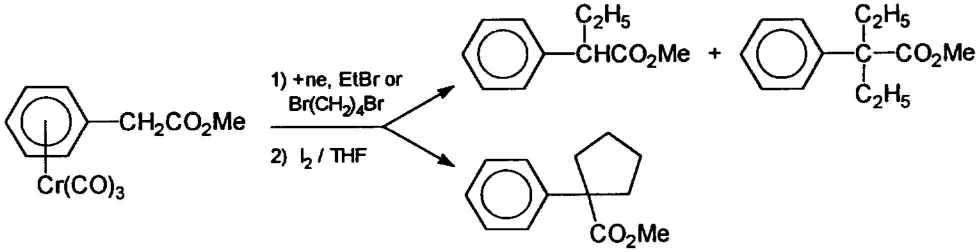
Recently it was shown[90a] that direct electroreduction of weak C-H acids such as triphenylmethane (pK_a 30) leads to generation of the corresponding carbanion which is rather stronger as a base than as a nucleophile This property of the anion was used with elegance to promote some useful base-catalyzed syntheses, including regioselective alkylation of an unsymmetrical cyclic ketone



Scheme 49

It should be noted that when reaction of 2-methylcyclohexanone with benzyl bromide was promoted with a widely used EGB, the anion of 2-pyrrolidone,[4,5d,25a] the yield of product was only 3% [90]

Alkyl esters or nitriles of phenylacetic acid usually have very low activity in the direct cathodic alkylation reaction with alkyl halides due to low acidity of the α-C-H bond [73] The efficiency of the reaction can be increased by enhancement of the acidity of the benzylic hydrogens by conversion of these compounds to tricarbonylchromium complexes [91a] For example, electrochemical reduction of (methyl phenylacetate)tricarbonylchromium on a Pt electrode in the presence of alkyl bromide followed by decomposition of the corresponding complexes by iodine results in formation of mono- and dialkylated or cyclic products in overall yields up to 80%

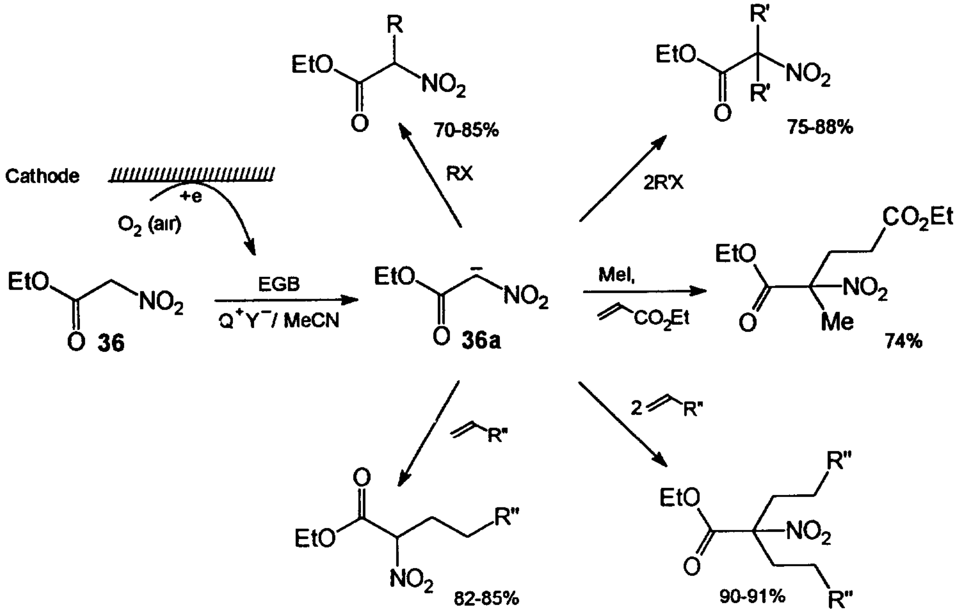


Scheme 50

On the other hand, the use of EGB was successful for derivatizing the aforementioned weak C-H acids For example, phenyl anion, electrogenerated from bromobenzene, promotes the reaction of compounds such as aceto- or propionitrile, and esters or nitriles of phenylacetic acid to produce coupling products with esters in 40-85% yield [91b]

It was found that aliphatic mononitrocompounds are reduced on transition metal cathodes with cleavage of an α-C-H bond and generation of the carbanion [69d,72] However, electroreduction of ethyl nitroacetate[7a] (36), which is a very useful starting material for synthesis of many classes of compounds,[92] is accompanied by cleavage of the C-N bond with elimination of the nitro group as has been found for reduction of tertiary nitro compounds[93] and dinitro compounds [93,94] This difficulty was easily overcome[7a] when electrogenerated superoxide[3c,4b,95,96] was used as an EGB for generation of carbanion **36a** By use of MeCN as solvent and tetraalkylammonium cations that do not tend to form ion pairs, very high nucleophilic reactivity of anion **36a** was realized (Scheme 51) Both mono- and dialkylation of **36** have been carried out with alkyl halides as well as Michael additions with higher yields than purely chemical versions of these reactions Moreover, monoalkylation with an alkyl halide followed by a Michael addition allows the preparation of an unsymmetrically dialkylated derivative of **36** by an attractive one-pot procedure [7a]

It should be noted that pure oxygen is usually used for generation of superoxide as an EGB so electrolyses are carried out under an oxygen atmosphere In the work cited,[7a] the viability of using oxygen



R = Me (X = I), CH_2Ph (X = Cl), $CH_2CH{=}CH_2$ (X = Br), $CH_2CH_2CO_2Et$ (X = Br, Cl)

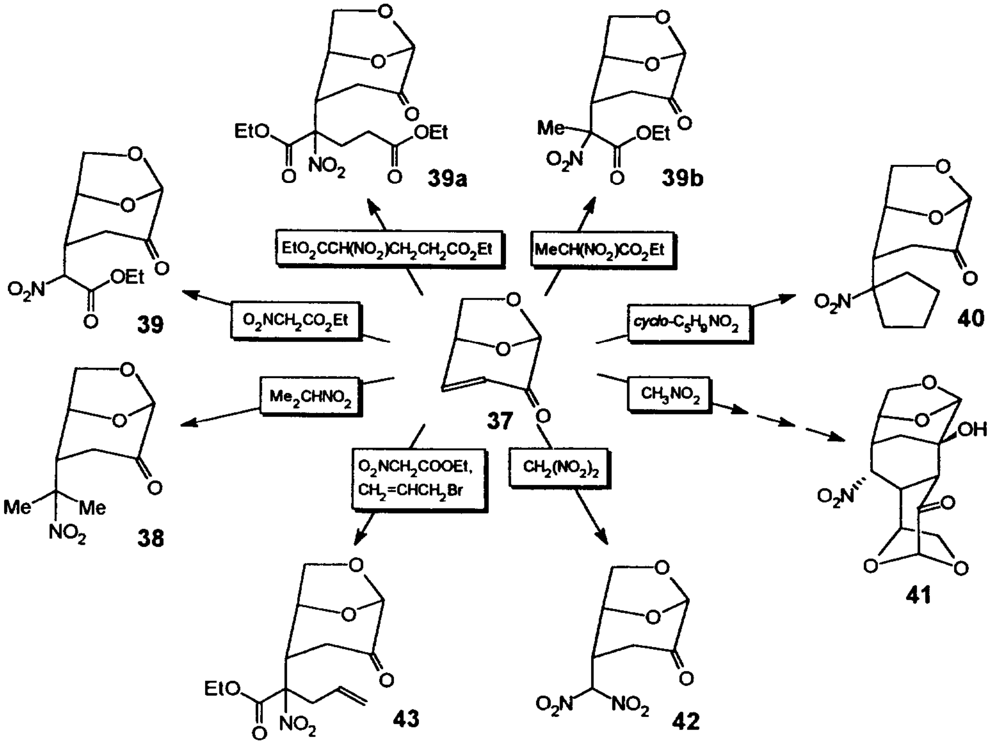
R' = Me (X = I), $CH_2CH_2CO_2Et$ (X = Br, Cl), R" = CO_2Et, CN

Scheme 51

from air was demonstrated whereby electrolyses were simply carried out in solutions exposed to the laboratory atmosphere

We hope that this approach, requiring as it does only a very simple cell and apparatus (see Section II of this review and Experimental section of ref 7a), will be very successful for organic synthesis, especially for synthesis with nitro compounds. The following examples support this proposition

Levoglucosenone (1,6-anhydro-3,4-dideoxy-β-D-glycero-hex-3-enopyranos-2-ulose,) **37**, is easily obtained by the pyrolysis of cellulose and serves as a useful chiral building block for synthesizing natural and unnatural products due to its highly functionalized structure One very important reaction of this substance is Michael reaction. However, the reaction is often accompanied by side reactions such as base-catalyzed oligomerization of **37** and the yield of desired products is not always high For example, Michael addition of 2-nitropropane to **37** in dry 1,4-dioxane using benzyltrimethylammonium hydroxide or triethylamine as catalyst, gave the coupling product **38** in only 15 % yield By using 2-nitropropane as solvent, the yield could be increased to 67% The analogous chemical addition of ethyl nitroacetate to levoglucosenone, under optimal conditions (MeCN-triethylamine), gives the Michael adduct **39** in 38% yield By contrast, the electrochemical version of the Michael addition of 2-nitropropane, ethyl nitroacetate and other nitro compounds to levoglucosenone, performed in air-saturated solutions of Bu_4NBr in MeCN, resulted in formation of the addition products **38-42** in 85-96% isolated yields [97]



Scheme 52

The aforementioned one-pot procedure[7a] was successfully used for synthesis of the ethyl 2-nitro-4-pentenoate derivative of levoglucosenone, **43**. Monoalkylation of **36** with allyl bromide was carried out on a Pt cathode in a solution of Bu_4NBr in MeCN followed by the addition of **37** and subsequent electrolysis to achieve Michael addition and the production of **43** in 67% isolated yield

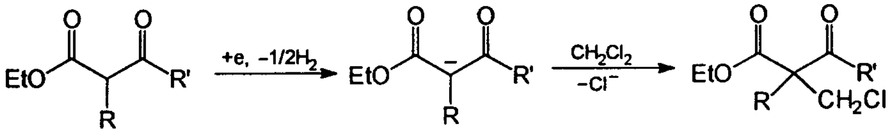
6 Alkylation by Methylene Chloride under Cathodic Electrolysis Conditions

Methylene chloride is widely used as a solvent for nucleophilic reactions and it is not particularly susceptible to nucleophilic attack It will react with typical nucleophiles at high temperature[98] or pressure [99] Strong nucleophilic reagents like sodium thiophenolate[100] can react with methylene chloride at room temperature Also, methylene chloride reacts under relatively mild conditions (refluxing/40 °C, 4 days) with tetrabutylammonium carboxylates resulting in methylene diesters [101] Under phase-transfer conditions, pyrrolyl anions react with methylene chloride (reflux, 5 h) with formation of 1,1'-methylenebispyrroles [102]

Recently the question of the reactivity of amines toward methylene chloride has been intensively discussed.[103] There are literature data indicating that the reaction of amines with methylene chloride proceeds only at high pressure.[104,105] However, it was found[103] that secondary amines react with methylene chloride at room temperature and atmospheric pressure (30% NaOH, 18 h) producing aminals. Nevertheless, methylene chloride is usually not very reactive under the conditions employed for nucleophilic substitution reactions.

As shown in previous sections, the conditions used for cathodic generation of anions (dipolar aprotic solvents, non ion pairing electrolytes) result in highly reactive nucleophiles. This suggests that methylene chloride may be quite reactive under these conditions and would be a good starting material for electrosynthesis. For example, it may be possible to prepare chloromethyl-, methyl- or methylene derivatives from methylene chloride and compounds with active element-hydrogen bonds.

This expectation has been fulfilled and several examples follow. Cathodic electrolysis of β-dicarbonyl compounds, containing an activated C-H bond, in a solution of Bu_4NBr in CH_2Cl_2, results in the formation of the corresponding chloromethyl derivatives in 40-60% isolated yield.[106]

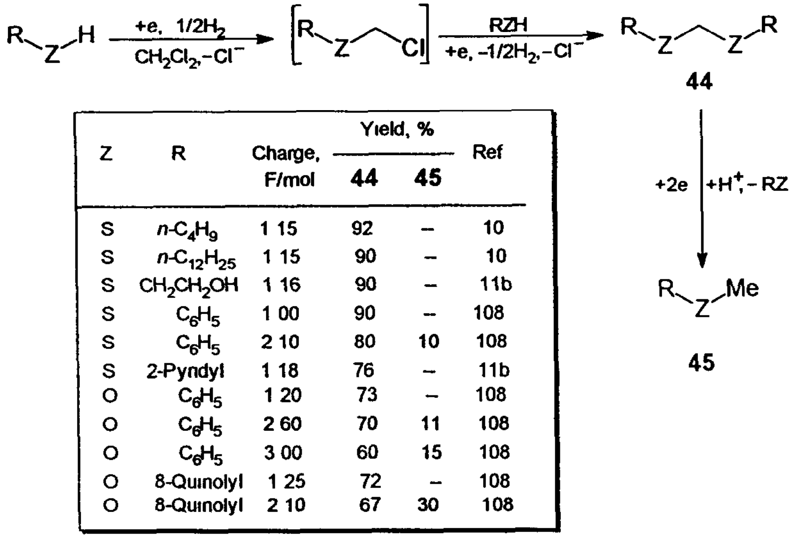


R = Me, R' = OEt, R = R' = Me, R = CH_2CH_2CN, R' = OEt

Scheme 53

In the case of electrogenerated thiolate anions, the intermediate chloromethyl compounds, which are formed by substitution of the first chloride, are very active and take part in a subsequent reaction with thiolate giving disubstituted products, the thioacetals (**44**).[2,10,107,108] In the same way, the reaction of electrogenerated alkoxide anions gives acetals of formaldehyde. It should be noted that passing 1.0-1.25 F/mol of electricity resulted only in formation of disubstituted products **44**. When 2.1-3.0 F/mole electricity was consumed, noticeable amounts of methylated products **45** were obtained,[108] obviously due to further electrochemical reduction of **44**.

The results suggest that the electrochemical method is a convenient way to prepare thioacetals and acetals by reaction of dichloromethane with thiols and alcohols without using any base. For comparison, in the reaction of thiols with dihalomethanes using a weak base (sodium carbonate) in acetone in the presence of platinum(II)*bis*(diphenylphosphino)methane, methane thioacetals were formed only from diiodomethane (yield up to 70%), while the reaction with dibromomethane was incomplete, and with dichloromethane no reaction occurred.[109]



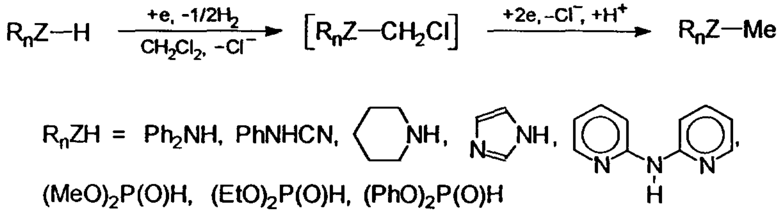
44

45

Z	R	Charge, F/mol	Yield, % 44	Yield, % 45	Ref
S	n-C_4H_9	1 15	92	–	10
S	n-$C_{12}H_{25}$	1 15	90	–	10
S	CH_2CH_2OH	1 16	90	–	11b
S	C_6H_5	1 00	90	–	108
S	C_6H_5	2 10	80	10	108
S	2-Pyridyl	1 18	76	–	11b
O	C_6H_5	1 20	73	–	108
O	C_6H_5	2 60	70	11	108
O	C_6H_5	3 00	60	15	108
O	8-Quinolyl	1 25	72	–	108
O	8-Quinolyl	2 10	67	30	108

Scheme 54

In the case of electrogenerated N- and P-anions, the intermediate chloromethyl adduct undergoes reductive dehalogenation rather than reacting with another anion. To illustrate, cathodic electrolysis of compounds containing N-H bonds on a Pt cathode in a solution of Bu_4NBr in CH_2Cl_2 gives the corresponding N-methyl derivatives with yields up to 80%[27b,c] Electrolysis of dialkyl or diaryl phosphites under the same conditions results in formation of methyl phosphonates in satisfactory yields (51-71%)[108]



Scheme 55

Interestingly, analogous behavior was displayed by phenylacetylene, which is a very weak C-H acid After electrolysis of this substance in methylene chloride, 1-phenyl-1-propyne was isolated in 40% yield.[108]

Thus, under cathodic electrolysis conditions, methylene chloride is a very active alkylating reagent Depending upon the structure of the starting materials, chloromethyl, methylene and methyl derivatives can be prepared The main advantage of this method is the surprisingly mild reaction conditions that are possible even with this weak alkylating reagent We believe that electrochemical alkylation with methylene chloride can be expanded to any kind of compound which has an activated element-hydrogen bond and that it can become a good alternative to existing chemical methods of methylation, chloromethylation or synthesis of acetals or thioacetals

IV. SYNTHETIC UTILITY OF HETEROATOM ANIONS AND CARBANIONS UNDER ANODIC ELECTROLYSIS CONDITIONS

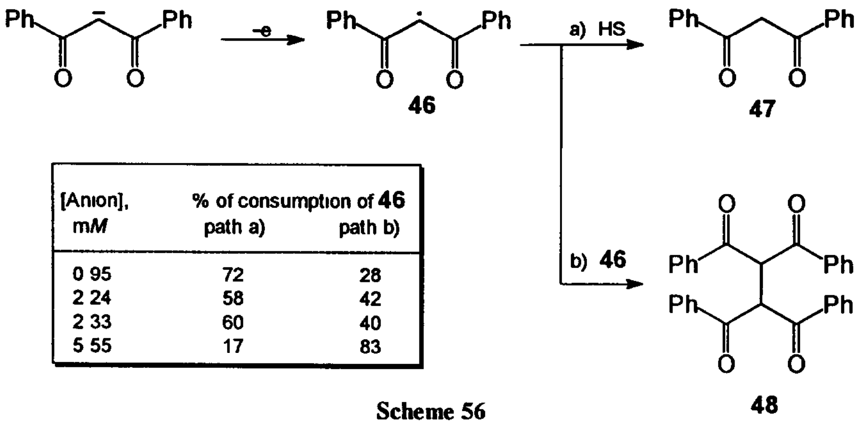
1 Electrooxidative Coupling Reactions of Anions.

One of the most well known and synthetically important electrochemical reactions, based on the utilization of organic anions, is the Kolbe synthesis which allows one to obtain the coupling product of alkyl radicals by electrooxidative decarboxylation of alkanoates This topic has been extensively reviewed (for a recent review see Ref.110a) Another well utilized reaction of radicals is the oxidative addition of anions to double bonds. This topic has been thoroughly reviewed by Schäfer.[110b,c]

Anodic one-electron oxidation of organic anions results in the generation of radicals which can combine to form dimeric products (see also Ref. 110b-e) Thus, for example electrochemical oxidation of thiolate anions produces disulfides[111] and dimeric products are also formed upon anodic oxidation of N-anions of amines,[112] amides[113] and imides.[114] Dimerization of the trichlorogermanium radical, generated by the electrooxidation of the corresponding anion, results in hexachlorogermane whose subsequent disproportionation gives tetrachlorogermane and dichlorogermylene [59a]

Electrochemical oxidation of O-anions from aldoximes and ketoximes proceeds via formation of unstable nitrosodimers.[115] But in the case of dialkyl- and diarylglyoximes (1,2-dioximes), the oxidation produces cyclic products, furoxans, in up to 96% yield [116,117] The key step of the reaction is oxidation of the anion to form the iminoxy radical Under the electrolysis conditions (Pt or graphite anode, NaOH electrolyte in MeOH or H_2O or LiOMe in MeOH), this radical undergoes further oxidation to an oxaimmonium cation, which reacts with the second oxime group to form the furoxan [116,117] In principle, furoxans can be prepared by electrooxidation of the unionized form of glyoximes.[117-119] However, in this case the yield of products[119] is lower and any furoxan with an easily oxidized substitutent, such as a dialkylamino group, does not survive [117]

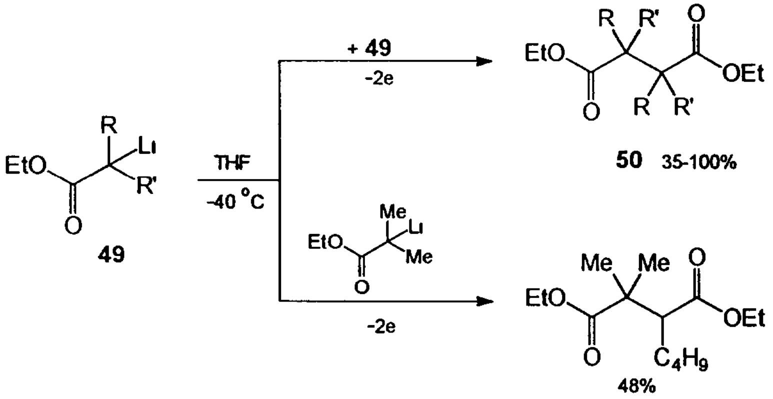
Voltammetric investigations and controlled potential coulometry showed[120] that the electrochemical oxidation of the anion of dibenzoylmethane proceeded *via* one-electron transfer and generation of radical **46** which can take part in two competitive reactions· hydrogen abstraction from the solvent to form dibenzoylmethane **47** and dimerization to give **48** The relative importance of the two reactions depends upon the concentration of the anion At low concentrations the main reaction is hydrogen abstraction while dimerization is dominant at the higher concentrations



[Anion], mM	% of consumption of **46** path a)	path b)
0 95	72	28
2 24	58	42
2 33	60	40
5 55	17	83

Scheme 56

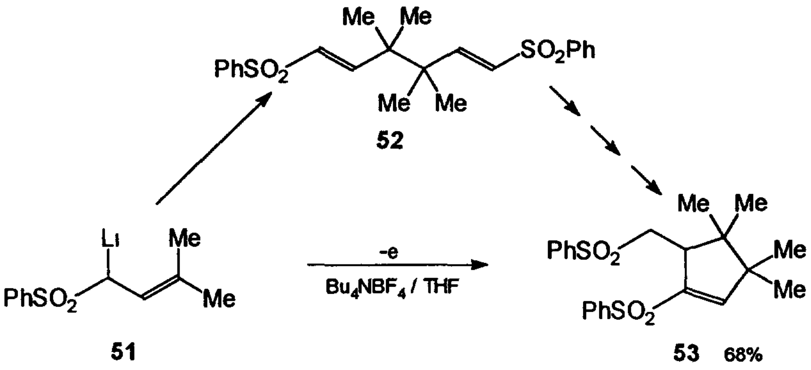
Electrooxidation of the sodium salts of alkyl malonates[121] and malononitrile[122] in nonaqueous media yields the corresponding dimeric products In an analogous fashion, anodic oxidation of the lithium enolates[123] of esters produced succinic esters **50** when the electrolysis was conducted in THF at low temperature in an undivided cell with Pt anode and mercury pool cathode When HMPA, in an amount equimolar with the enolate, was added to the THF, the yields of dimer were increased It should be noted that this method allows the preparation of unsymmetrically substituted succinate esters by the cooxidation of two different lithium enolates [123]



R = H, R' = Et, Bu, i-Pr, Ph, R = Me, R' = Me, RR' = -$(CH_2)_5$-

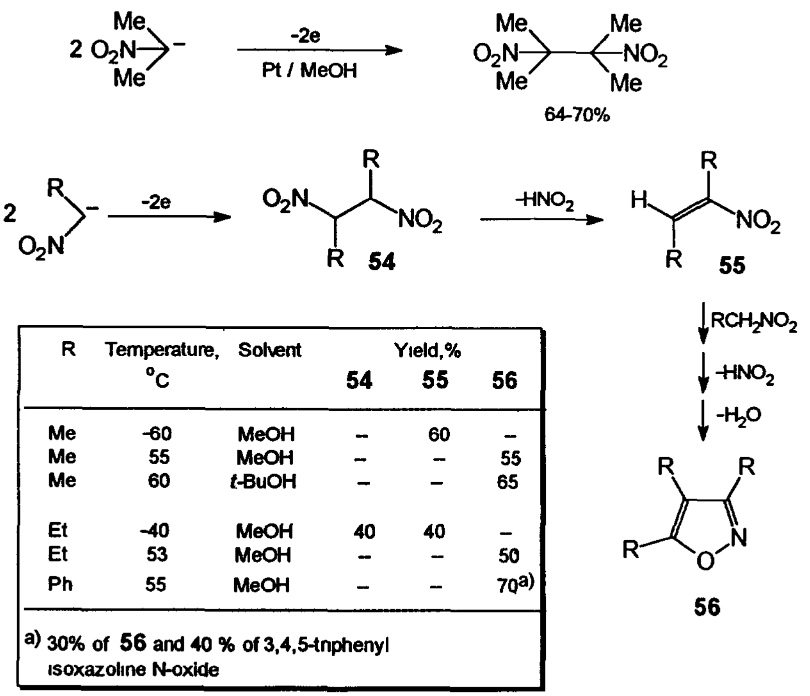
Scheme 57

The electrochemical oxidation of anions of 1,3-disulphones[124a] results in formation of the radical dimerization product while oxidation of α-sulfonyl carbanions[124b] **51** proceeds *via* coupling of the electrogenerated radical with starting carbanion and intermediate formation of dimeric product **52**, the subsequent transformation of which leads to the isolated cyclic product **53**



Scheme 58

The electrochemical oxidation of the sodium salt of 2-nitropropane in MeOH produces the corresponding *vic*-dinitro compound[125] but in the case of anions of primary nitroalkanes, the coupling products are unstable and eliminate HNO_2 giving the nitroolefin In turn, the nitroolefin undergoes further conversion to isoxazole under the electrolysis conditions [126] Control of the product composition can be achieved by manipulation of the electrolysis conditions at low temperature, the main product of the electrolysis is the nitroolefin, at higher temperatures the isoxazole is the major product



R	Temperature, °C	Solvent	Yield,% 54	55	56
Me	-60	MeOH	–	60	–
Me	55	MeOH	–	–	55
Me	60	*t*-BuOH	–	–	65
Et	-40	MeOH	40	40	–
Et	53	MeOH	–	–	50
Ph	55	MeOH	–	–	70[a]

[a] 30% of **56** and 40 % of 3,4,5-triphenyl isoxazoline N-oxide

Scheme 59

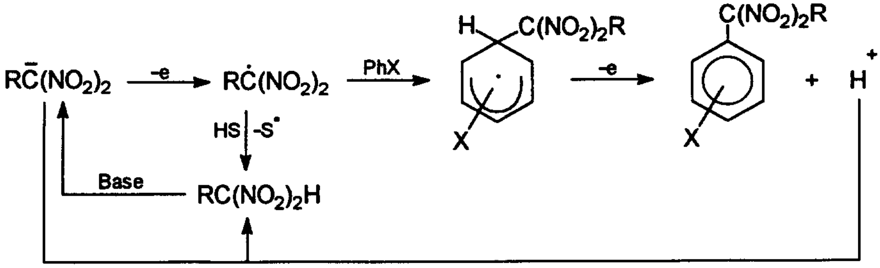
Thus, the electrochemical oxidation of salts of primary nitro compounds may be of some interest for the one-pot synthesis of isoxazoles, heterocyclic compounds which are important for their chemical, pharmaceutical, agricultural and other applications [127]

2 *Electroinduced Homolytic Aromatic Substitution Electrooxidation of Weak Anionic Nucleophiles to Generate Electrophilic Intermediates*

Reactions of radicals with aromatic substances would appear at first sight to be of no interest to synthesis because of the low selectivity that will arise from the intermediate cyclohexadienyl radicals which can disproportionate, dimerize or be oxidized to substituted product.[128] Under electrochemical conditions, it is possible that selectivity can be achieved by favoring further anodic oxidation of the cyclohexadienyl radical Another reaction which accompanies homolytic aromatic substitution is side-chain attack in the reactions of alkylbenzenes It is known that the amount of side-chain attack is greater with more nucleophilic radicals [128] Therefore, it can be expected that side-chain attack using electrophilic radicals will be significantly suppressed or eliminated

Radicals containing electron-withdrawing substitutents at the radical center, such as carbonyl, nitrile, alkoxycarbonyl or nitro, possess electrophilic properties[129-131] and they are easily generated by the electrochemical method Because the precursors of the radicals are organic anions which are nucleophiles, and the radicals formed by one-electron transfer are electrophilic, we have here an example of electrochemical "umpolung"[129c] of reactivity Of course, electrooxidation of thermodynamically stable and less reactive anions, those anions containing two or three electron-withdrawing groups at the carbanionic center, will lead to generation of radical intermediates that are very strong electrophiles It should be noted that these anions can be prepared simply by treatment of the corresponding organic acids with an ordinary base *in situ* or with prior isolation of the salts When anodic electrolysis of malonate anions,[132] as well as the anions of acetylacetone[133] and nitromethane[134] is conducted in the presence of aromatic substances, the corresponding substituted aryl derivatives are formed It was assumed that this reaction involves the anodic generation of the radicals which then react with the aromatic substances by the mechanism of homolytic aromatic substitution Under the electrolysis conditions, the formation of side-chain products was not observed but dimerization and trimerization of anions did occur The yield of aryl derivatives was higher with compounds having high electron density on the aromatic ring which clearly is related to the electrophilic properties of the radicals

Since the nitro group is one of the strongest electron-withdrawing groups, it can be expected that di- and trinitromethyl radicals should have strong electrophilic properties Detailed investigations of the anodic behavior of the anions of polynitromethanes, which are weak nucleophiles, showed[135] that the reaction proceeds *via* one-electron transfer Due to their electrophilic properties, the polynitromethyl radicals thus formed give no dimeric products[135b] but react with aromatic substances[136] exclusively on the aromatic ring by way of a σ-complex intermediate (cyclohexadienyl radical). Subsequent oxidation of this intermediate at the anode followed by deprotonation gives the final product, the arylpolynitroalkanes The yields based on aromatic substrates were 85-95% [136c] The reaction is accompanied by formation of the unionized polynitromethane since reaction of the radicals with solvent (hydrogen abstraction) and protonation of the starting anion occur However, in the case of trinitromethane, which is a strong acid ($pK_a = 0$), the addition of a weak base will deprotonate the neutral trinitromethane so formed, allowing the reintroduction of the anion into the reaction [136c]



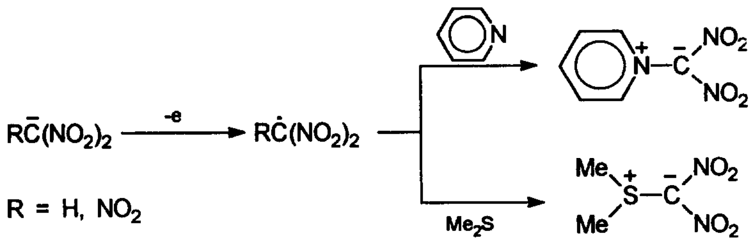
R = H, Ph, Cl, CN, NO_2, X = H, Me, OMe, Cl, NO_2

Scheme 60

The electrophilic properties of polynitromethyl radicals were confirmed by the method of competing reactions: the relative rates of the reaction of di- and trinitromethyl radicals with aromatic substances increased with increasing electronic density in the aromatic ring.[136b]

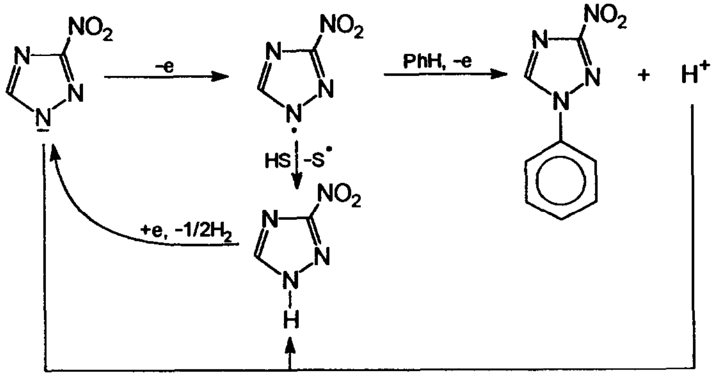
It should be noted that the electrochemical approach provides a short synthetic path to arylpolynitromethanes, which can serve as useful reagents in the chemistry of nitro and related compounds [137-139] The chemical synthesis of such compounds includes several steps using toxic N_2O_4 and the overall yields are low [140]

Due to their strong electrophilic properties, polynitromethyl radicals can react as normal electrophiles in reactions with compounds containing heteroatoms with unshared electron pairs So, for example, electrolysis of the anions of tri- and dinitromethane in the presence of pyridine or dimethylsulfide results in the formation of the corresponding dinitromethylides [141] The reaction was not optimized and the yields of the ylides were 12-20%



Scheme 61

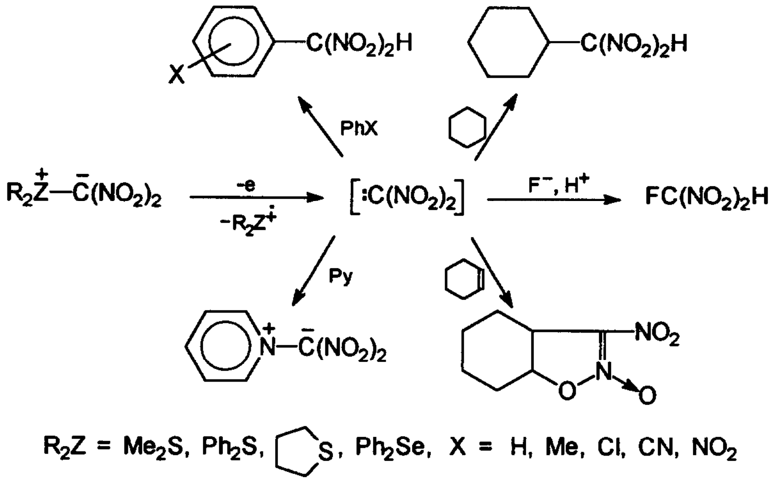
Electrochemical oxidation of the anions of nitro derivatives of imidazole, pyrazole, triazole and tetrazole in MeCN proceeds via one-electron transfer and generation of nitroazolyl radicals,[142] which, as explained above, can be expected to have electrophilic properties. Their principal reaction is abstraction of hydrogen from solvent No dimerization products were observed. However, electrolysis in the presence of aromatic substances results in formation of the corresponding aryl derivatives Anodic electrolysis of the tetramethylammonium salt of 3-nitro-1,2,4-triazole in the presence of benzene in MeCN results in formation of the N-phenyl derivatives in 20% yield [142b] However, additional unionized nitrotriazole was present and when the electrolysis was carried out in an undivided cell the isolated yield of product was 67% The improvement in yield is undoubtedly due to regeneration of the anion of nitrotriazole at the cathode



Scheme 62

Electrochemical oxidation of $(RO)_2P(O)Na$ in the presence of thiophene, furan, quinoline and naphthalene in MeCN results in formation of the corresponding arylphosphonates $(RO)_2P(O)Ar$.[143] It has been found[144] that this reaction proceeds by generation of the dialkylphosphonyl radical which enters into the homolytic aromatic substitution reaction

Dinitromethylides have a carbanionic structure[145] and can be oxidized at relatively high potentials (1 2-1 98 V vs Ag/Ag^+ in MeCN) [146a] Anodic oxidation in the presence of benzene and its derivatives gives the corresponding dinitromethylaryl compounds.[75,146b] On the basis of voltammetric investigations and the identity of electrolysis products, it was proposed that oxidation of dinitromethylides proceeds via formation of an unstable cation-radical which decomposes by cleavage of the heteroatom-carbon bond forming electrophilic dinitrocarbene [75,146c,d] Like other electrophilic carbenes, dinitrocarbene reacts with aromatic substances exclusively on the aromatic ring with formation of the products of insertion into a C-H bond No cyclopropanation products were observed It should be noted that the reaction proceeds even in the case of aromatic substances with strong electron-withdrawing groups such as CN and NO_2 The carbene mechanism accounts for products which are formed in low yields during electrolysis of dinitromethylides in the presence of cyclohexane, cyclohexene, pyridine and fluoride ion [75,146b]



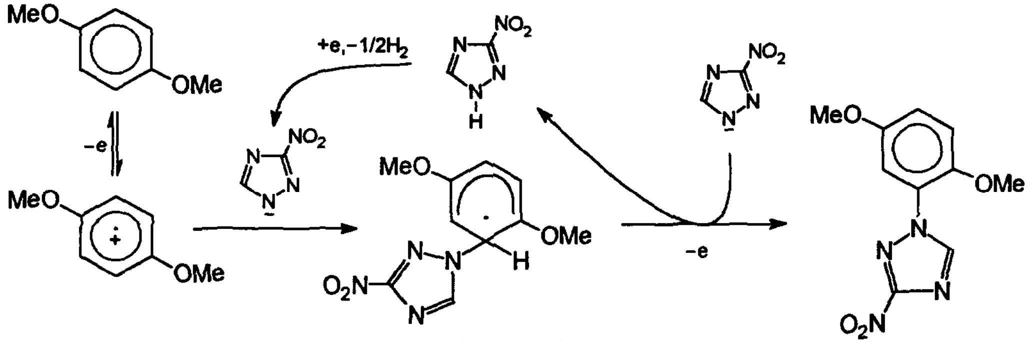
Scheme 63

3 *Anions as Acceptors of Anodically-Generated Electrophilic Intermediates*

A wide variety of organic substances such as aromatic compounds, condensed aromatic compounds, aromatic and nonaromatic heterocycles, amines, olefins, thiols, sulfides, alcohols etc., under anodic electrolysis conditions in nonaqueous media, can be oxidized to cation-radical or cation intermediates Due to the strong electrophilic character of these intermediates, they are able to couple with nucleophiles, especially anionic nucleophiles, that are present in the solution. Well known examples of this type of reaction are anodic alkoxylation, acyloxylation, cyanation and thiocyanation and these reactions have been recently reviewed [147]

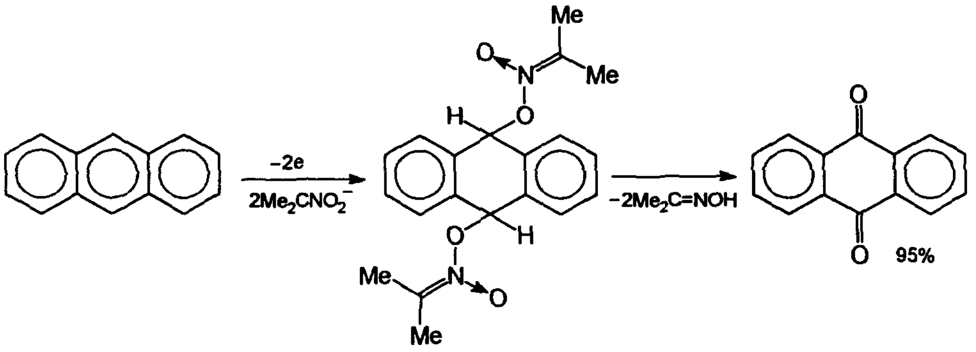
This approach opens excellent possibilities for the synthetic utility of thermodynamically stable organic anions which are usually very weak nucleophiles Due to the high oxidation potentials of these anions, the electrolysis proceeds by selective oxidation of the organic substrate rather than the anion However, the cation-radicals or cations so formed can react with unoxidized anions at the surface of electrode or in the bulk of solution

Aromatic compounds with electron-donating substitutents or condensed aromatic substances are oxidized at relatively low potentials and can serve as a good source for electrogenerated electrophilic intermediates For example, electrooxidation of 1,4-dimethoxybenzene proceeds *via* one-electron transfer and formation of a relatively stable cation radical, which has been detected by the electrogenerated chemiluminescence method and by ring-disc voltammetry [148] In the presence of the anion of 3-nitro-1,2,4-triazole, which is oxidized at a higher potential ($E_{1/2}$ = 1.77 V vs Ag/Ag^+ in MeCN[142a]) than 1,4-dimethoxybenzene ($E_{1/2}$ = 1 0 V vs Ag/Ag^+ in MeCN[148]), the cation-radical of the aromatic substance is not detected but complete two-electron oxidation occurs forming the aryl derivative of nitrotriazole [149] The cation radical that is generated at the anode is thought to react with the anion of nitrotriazole to produce a cyclohexadienyl radical that in turn undergoes oxidation and deprotonation The reaction was carried out in an undivided cell and the product was obtained in 75-85% isolated yields[149] The undivided cell again allows for cathodic regeneration of the anion from the neutral nitrotriazole that is produced from the protons generated at the anode



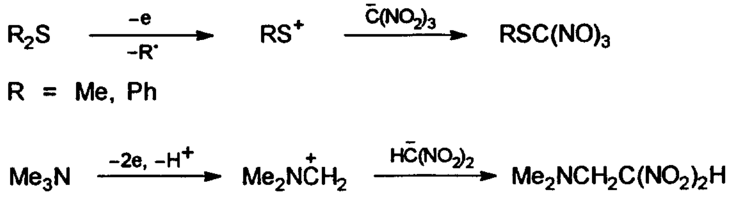
Scheme 64

Under the same conditions, the anion of 3-nitro-1,2,4-triazole reacts with the electrogenerated cation radical of naphthalene at the α-position of the aromatic system.[149b] The formation of α-trinitromethyl- and α-dinitromethylnaphthalenes was observed when naphthalene was oxidized in the presence of the salts of dinitromethane and trinitromethane.[136c] Interesting results were obtained with anthracene and the anion of 2-nitropropane[136c] The electrochemical oxidation of anthracene in MeCN in the presence of a suspension of the sodium salt of 2-nitropropane, resulted in a high yield (95%) of anthraquinone. An unstable nitronic ester is an intermediate in this reaction These compounds are known[150] to decompose to carbonyl compounds and oximes



Scheme 65

The electrochemical oxidation of sulfides[136c, 141b] in the presence of the anion of trinitromethane and oxidation of trimethylamine[151] in the presence of the anion of dinitromethane resulted in formation of the corresponding polynitromethyl derivatives. These reactions proceed through intermediate formation of cationic intermediates which subsequently react with the anions.



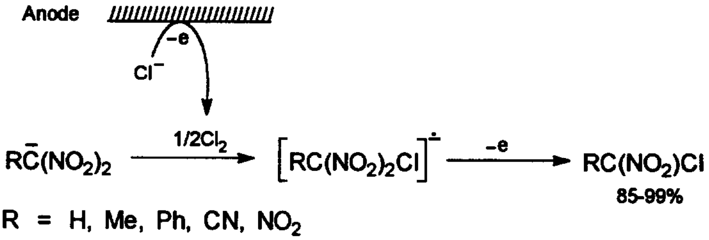
$$R_2S \xrightarrow[-R^{\cdot}]{-e} RS^+ \xrightarrow{\bar{C}(NO_2)_3} RSC(NO)_3$$

R = Me, Ph

$$Me_3N \xrightarrow{-2e,\ -H^+} Me_2N\overset{+}{C}H_2 \xrightarrow{H\bar{C}(NO_2)_2} Me_2NCH_2C(NO_2)_2H$$

Scheme 66

Thermodynamically stable anions, which have relatively high oxidation potentials, are very good acceptors of electrogenerated halogens.[152] It has been found that polynitrocarbanions, the oxidation potentials of which are higher than the oxidation potential of chloride anion ($E_{1/2}$ = 0.8 V vs Ag/Ag$^+$ in MeCN), are chlorinated in quantitative yields in both aqueous and nonaqueous media on Pt, graphite, ruthenium dioxide or titanium anodes. the formation of chlorinated products of carbanions with oxidation potentials lower than chloride can be achieved in high yield with ruthenium dioxide or titanium anodes, high concentrations of chloride and high current densities.[152]



Scheme 67

It should be noted that electrochemical chlorination allows selective preparation of either monochloro or dichloro derivatives of these strongly acidic organic acids. Electrolysis of a solution of 0.2 M Et_4NCl in MeCN in the presence of the anion of dinitromethane with charge consumption of 1 F/mol results in the exclusive formation of monochlorinated product in 99% yield. When under the same conditions 5 F/mol charge was passed or the electrolysis was carried out in a solution of 3-5 M NaCl in H_2O containing 0.5 g/l $NaHCO_3$, the dichlorinated product was formed in 80-93% yield. For comparison it should be noted that the known chemical chlorination of the anion of dinitromethane[153] results in formation of dichlorodinitromethane in 70% yield and chlorodinitromethane can be prepared in 56% yield (total yield 39%) only by dechlorination of dichlorodinitromethane

V. SYNCHRONOUS UTILIZATION OF ANODIC AND CATHODIC REACTIONS IN SYNTHESIS. PAIRED ELECTROSYNTHESIS

The performance of any electrochemical synthesis involves the simultaneous occurrence of both reduction and oxidation reactions. By using a diaphragm, these reactions can be separated and synthesis of useful products is possible with either cathodic or anodic electrolysis. However, in this case the reaction product in the counter electrode compartment is wasted. Therefore, the synchronous utilization of anodic and cathodic reactions for synthesis of two useful products would be very interesting and might instigate the wider use of electrosynthesis in the field of organic synthesis. Baizer, who first formulated and demonstrated approaches to solve this problem, introduced the term "Paired Electrosynthesis" in the sense that both cathodic and anodic reactions are used in formation of final products [154] Paired electrosynthesis can be carried out with either divided or undivided cells

As a rule, paired electrosynthesis with undivided cells leads to one product as a result of interaction of cathodically and anodically generated intermediates Some examples of this type of paired electrosynthesis were included in previous sections of this review The use of sacrificial anodes (for reviews on sacrificial anodes in electrosynthesis see Ref 155) allows the preparation of metal-organic compounds (Section **III.1**, Ref 9, **III.2**, Ref 18; **III.3**, Refs 26, 31, **III.4**, Refs 35, 39, **III.5**, Refs 69d,e) by cathodic generation of organic anions and anodic generation of metal cations Clearly, the metal-organic compounds formed in this way can take part in subsequent reactions such as addition of thiols to activated olefins (Section **III.1**, Ref 11) and epichlorohydrin (**III.1**, Refs 11b, 12, 13), formation of organosilicon compounds (**III.4**, Refs 54, 57, 58,) cyclopropanation of olefins (**III.5**, Ref 83) and the Reformatsky reaction (**III.5**, Refs 84, 85) Electrosynthesis of N-aryl derivatives of 3-nitro-1,2,4-triazole (Sections **IV.2**, **IV.3**, Refs 142b, 149) is an example of a paired electrosynthesis where the heterocyclic anion is generated on the cathode and the heterocyclic radical or the cation-radical of an aromatic substance is generated at the anode The further reaction of these intermediates results in formation of the final product

The synchronous cathodic generation of organic anions and anodic generation of halogens opens up excellent synthetic possibilities It has been found that electrooxidation of malonates in an undivided cell in the presence of iodide ions results in increased yields of dimeric products [156] This approach was used as a basis for creation of paired electrosynthesis of tetraethyl ethane-1,1,2,2-tetracarboxylate and diethyl adipate (starting from diethyl malonate and ethyl acrylate) in 95% chromatographic yields (Scheme 68).[154a,157] The reaction was carried out in an undivided cell with graphite anode and lead cathode in a solution of Bu_4NI in MeCN. The main limitation of this method is the required separation of the products after electrolysis as they are formed in the same vessel.

The electrolysis of trialkylboranes R_3B in an undivided cell in MeCN containing tetraalkylammonium bromide or iodide afforded aliphatic nitriles RCH_2CN in good yields [158] The cathodic reaction is cleavage

$$\text{Anode}\quad 2I^- - 2e \longrightarrow I_2$$

$$\text{Cathode}\quad 2CH_2{=}CHCO_2R \xrightarrow{+2e} \underset{\mathbf{57}}{[RO_2CCH(CH_2)_2CHCO_2R]^{2-}}$$

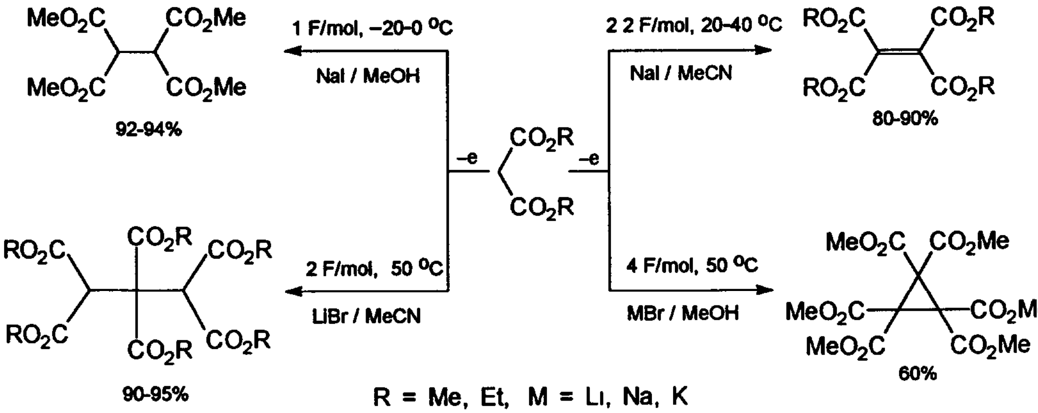
$$\text{Solution}\quad \mathbf{57} + 2CH_2(CO_2R)_2 \longrightarrow RO_2C(CH_2)_4CO_2R + 2\bar{C}H(CO_2R)_2$$

$$2\bar{C}H(CO_2R)_2 + I_2 \longrightarrow (RO_2C)_2CHCH(CO_2R)_2$$

Scheme 68

of a C-H bond of acetonitrile generating $NCCH_2^-$ while halogen formed at the anode reacts with R_3B to produce RHal, the reaction of which with the carbanion forms RCH_2CN

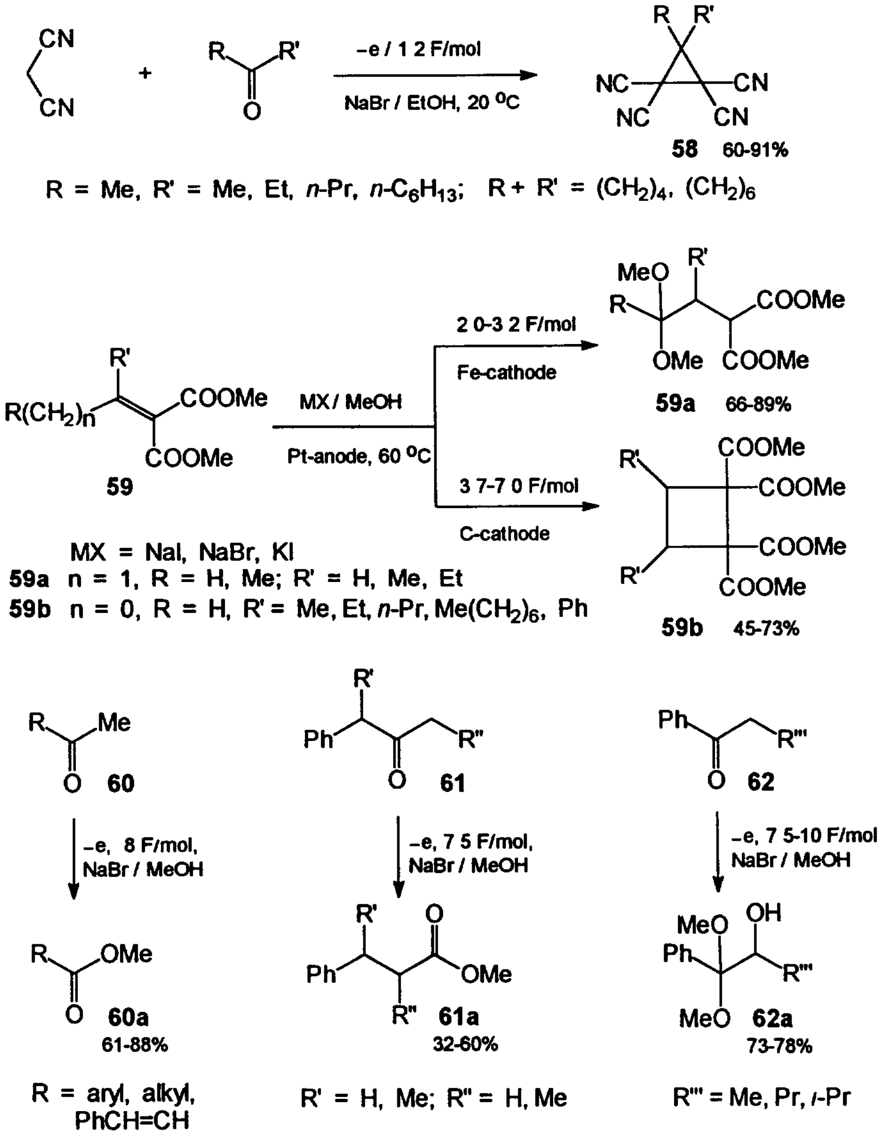
Detailed investigations of the indirect oxidation of malonates in the presence of halide ions in an undivided cell showed that the yields and structures of products are strongly dependent on the experimental conditions By changing the amount of charge passed, the solvent, temperature and the halide ion, esters of ethane-[159,160] and ethylenetetracarboxylic[160] acids, as well as linear and cyclic trimers[160] of malonates can be prepared



Scheme 69

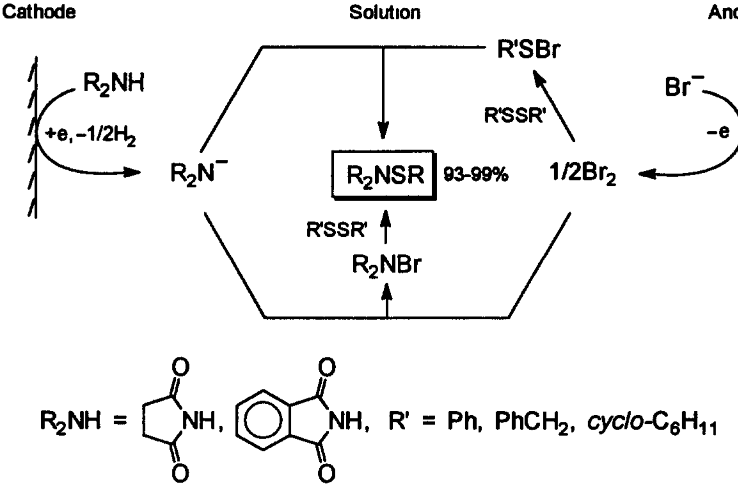
In the case of malonodinitrile, the dimeric product was not obtained due to its further oligomerization under the electrolysis conditions However, electrolysis of this substance in the presence of carbonyl compounds results in the formation of 3,3-disubstituted 1,1,2,2-tetracyanocyclopropanes[161] (**58**). Undivided electrolysis of alkylidenemalonates (**59**) in MeOH in the presence of halide ions results in the formation of 2-alkyl-3,3-dimethoxyalkane-1,1-dicarboxylates[162a] (**59a**) and 3,4-disubstituted cyclobutane-1,1,2,2-

tetracarboxylates (**59b**),[162b] while under conditions of cathodic generation of methoxide ion and anodic formation of bromoketones, ketones **60-62** have been converted into methyl carboxylates **60a** and **61a** and α-hydroxyketals **62a**.[163] The formation of **61a** is an example of an electrochemically-induced Favorskii rearrangement.



Scheme 70

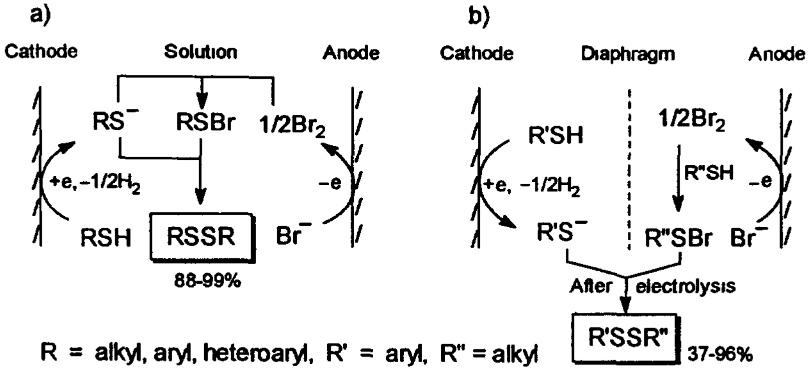
An undivided electrolysis in which the anodic reaction is oxidation of halide ions, was successfully used for formation of hetero atom-hetero atom bonds Thus, electrolysis of a mixture of succinimide or phthalimide and a disulfide in MeCN containing sodium bromide or iodide, leads to the corresponding sulfenimides in high yields[164] A possible mechanism of this reaction is given in Scheme 71



Scheme 71

In an analogous fashion, electrolysis of a mixture of dialkyl (or diaryl) phosphites and disulfides in the presence of sodium bromide or amines in the presence of sodium iodide, results in formation of phosphorothiolates[165] $(RO)_2P(O)SR'$ or phosphoramidates[166] $(RO)_2P(O)NR'R''$ in good yields. α-Aminoalkanoates $RCH(NH_2)COOR'$ and disulfides $R''SSR''$ have been converted to sulfenimines[167] $R(R'OOC)C{=}NSR''$ by electrolysis in a two-phase system comprising CH_2Cl_2 and aqueous $MgBr_2$.

Undivided electrolysis of thiols in the presence of halide ions is a facile general method for the synthesis of aliphatic, aromatic and heteroaromatic disulfides in practically quantitative yields (Scheme 72a)[168] The electrolysis can be carried out in a dilute solution of sodium bromide or chloride in MeOH, but it is preferable to use a two-phase system of benzene/H_2O which results in increased current efficiency, especially in the case of heteroaromatic thiols The reason for this improvement is that partial reduction of the disulfides on the cathode is eliminated Moreover, the two-phase electrolyte is convenient preparatively isolation of product requires only separation of the organic layer and removal of the solvent under vacuum It should be noted that the main disadvantage of other electrochemical methods for the preparation of disulfides is that they do not provide uniformly high yields of disulfides for different thiols as starting materials[111,169] In addition, these procedures are not as preparatively convenient because they require the use of concentrated salts of perchloric acids in MeCN[170] or MeONa in MeOH,[111] carrying out the electrolysis with controlled potential[169,171] or using modified electrodes[172]



Scheme 72

When electrolysis is conducted in divided cells, paired electrosynthesis can achieve the parallel formation of two useful products A way of exploiting this approach is to take the product formed in one compartment (*e g.* the anode compartment) and add it to the other compartment (cathode) where it can react to produce the identical product being formed in the cathode reaction. For example, in the cathodic compartment sulfur dioxide can be reductively alkylated by propyl bromide to dipropyl sulfone. At the same time, in the anodic compartment propyl alcohol will be converted to propyl bromide, which then can be used in the cathodic compartment as the alkylating reagent [173]

The preparation of unsymmetrically substituted disulfides is an example where two active reagents are formed and their post-electrolysis mixing results in formation of the final product (Scheme 72b) Generation of thiolate anions from thiols or disulfides takes place in the cathode compartment while at the anode, sulphenyl halides are formed from thiols and anodically generated halogen Mixing of the cathodic and anodic solutions after electrolysis produces unsymmetrical disulfides [168]

Another reason for using divided paired electrosynthesis is to achieve simultaneous synthesis of two different desired products, one in the cathodic and one in the anodic compartment. For example, 2-mercaptobenzoxazole has been cathodically alkylated by p-chlorobenzyl chloride forming the corresponding sulfide in 97% isolated yield while in the anodic compartment 2-mercaptobenzoxazole was converted to disulfide in 71% isolated yield [168]

Thus, the examples cited above demonstrate that a number of interesting syntheses can be carried out by paired electrosynthesis One of the advantages of undivided electrolysis is the simplicity of the cell and the fact that electrolysis can be carried out under controlled-current conditions. Divided cells with a very simple design have also made divided paired electrosynthesis quite attractive owing to the expanded range of syntheses that is possible

VI. A GUIDE TO CHOICE OF THE PREFERRED TYPE OF ELECTROLYSIS, CATHODIC OR ANODIC.

As we can see from previous sections of this review, the literature contains numerous examples of the electrosynthetic utility of carbanions and heteroatom-anions Different types of anions have been used both in cathodic and anodic syntheses as well as in undivided electrolyses However, there are no guidelines for choosing the type of electrolysis that will be most effective for selective electroorganic synthesis using a given kind of carbanion or heteroatom-anion. In this section, we will show that classification of organic anions according to their nucleophilic properties can be used successfully to guide the choice of the type of electrolysis.

1 The Oxidation Potential as a Criterion for Estimating Nucleophilic Reactivity of Hetero- and Carbanions

The reactivity of different types of nucleophiles is known to depend strongly on both the solvent and the counter ion The advantages of the electrochemical method of producing nucleophiles include the fact that stoichiometric quantities of strong chemical bases are not needed and the reactive anions can be generated in almost any solvent with free choice of counter ion It has long been recognized[174] that nucleophilicity is likely to be related to the oxidation potential of the nucleophile with high (positive) oxidation potentials associated with low reactivity The relevant oxidation potential is the reversible potential of the reaction

$$A^- \rightarrow A + e^- \qquad (1)$$

However, direct experimental determination of the reversible potentials of these one-electron oxidation reactions is difficult for most nucleophiles used in organic chemistry. Therefore, it would be useful to identify an easily measurable quantity that is related in a simple manner to the reversible potential of reaction (1) Recently it has been shown that the observed potential for the overall irreversible oxidation of A^- is well-correlated with nucleophilicity.

For example, it was found[175] that the literature values of the nucleophilicity parameter N showed a good correlation ($r = 0.983$) with irreversible oxidation half-wave potentials $E_{1/2}$ measured for twelve anionic nucleophiles in acetonitrile at a platinum electrode The correlation spanned a very wide range of potential (2.22 V) and nucleophilicity ($N = 1.5$-10) and included nucleophiles whose charge was centered at several different kinds of atoms Thus the irreversible oxidation potentials (obtained from hydrodynamic voltammetry as a half-wave potential, or from cyclic voltammetry as an anodic peak potential or half-peak potential) can be used for estimating the nucleophilic reactivity of anionic nucleophiles the more easily the anion is oxidized, the more nucleophilic it is

Not only do the oxidation potentials for a series of nucleophiles in the same solvent correlate well with nucleophilicity, it is also true that the oxidation potentials of a single nucleophile measured in various solvents with various electrolytes, also show the same trend, *i e* , the conditions for greatest reactivity are those that cause the nucleophile to be most easily oxidized [176] These correlations included anionic nucleophiles with different reaction centers as well as different types of reactions. S_N2 and S_NAr reactions as well as addition to Michael acceptors.

Solvent plays an important role in determining both the oxidation potential and nucleophilicity, hence the observed correlation of the two Thus, solvents that stabilize anions by strong solvation cause the oxidation potential of the nucleophile to be more positive and the nucleophilicity to be suppressed The role of the electrolyte is less clear; one should simply note that when ion pairing occurs between the nucleophile and the cation of the electrolyte, the oxidation potential is shifted in the positive direction and the anion is less reactive as a nucleophile

Thus it is usually found that those solvents that solvate anions poorly (acetonitrile, DMF, etc) are also those in which anionic nucleophiles are most reactive Similarly, the identity of the electrolyte cation is relatively unimportant in strongly ionizing solvents but can become crucial in solvents like acetonitrile where reactions may proceed at less than one-tenth the rate in the presence of lithium counter ions as opposed to tetraalkylammonium cations

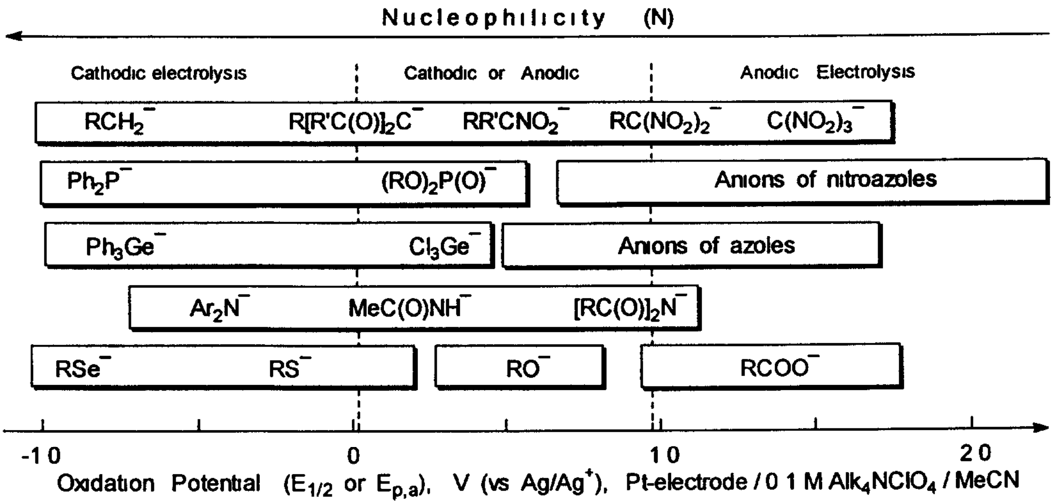
In view of the fact that simple voltammetric instrumentation is widely available, the measurement of oxidation potential holds considerable promise as a rapid means of establishing the reaction conditions that should give greatest reactivity of anionic nucleophiles

2 *Nucleophilicity as an Organizing Principle for Choice of Cathodic or Anodic Electrolysis Using Hetero- and Carbanions*

Now that we have established that a correlation exists between oxidation potential and nucleophilicity, it is useful to consider how this information can illuminate the problem of finding the most useful type of electrochemical procedure involving hetero- and carbanions The various synthetic applications that have been cited in earlier sections of this review make it clear that anions can be successfully used under conditions of cathodic or anodic electrolysis but it remains to be determined how one would choose the type of reaction to carry out

The relationship between nucleophilic reactivity and oxidation potential is pictorially presented in Scheme 73 where the inverse correlation of nucleophilicity and potential is represented by the opposing horizontal scales Within the graph, approximate ranges of oxidation potential for various classes of anions are shown It should be emphasized that the boundaries of the region of a given class are not exactly defined and there will be examples in each class that fall outside the boundaries

At the left side of the diagram one finds, for example, thiolate anions which have very low oxidation potentials and are known to be among the most nucleophilic anions The anions of aliphatic, aromatic and heteroaromatic thiols are oxidized in the range of -0 58 to +0 10 V (vs Ag/Ag^+)[175,177] which corresponds to a nucleophilicity (N) of 7-10 (estimated from the regression equation from Ref 175). The least nucleophilic of the sulfur-based anions is NCS^- which has an oxidation potential of +0.20 V and N = 6 6



Scheme 73

Among N-anions, the lowest oxidation potentials are observed with amides For example, the oxidation potential of the anion of 2,2'-dipyridylamine is -0 4 V[27c] The anions of acetamides,[26d] succinimide[5c] and azoles[178] are less nucleophilic and have more positive oxidation potentials The weakest N-nucleophiles are the anions of derivatives (especially nitro derivatives) of the nitrogen-containing heterocycles such as triazoles and tetrazoles.[142a,178] The oxidation potentials of 5-nitro-1,2,3-triazole,[142a] tetrazole[27a] and 5-nitrotetrazole[142a] are 1.87, 1 47 and 2 3 V which correspond to N = 0.02, 1 61 and -1 68 respectively

The nucleophilicity and oxidation potentials of carbanions that can be used in electrosynthesis also show great variability For example, the anions of cyclopentadienes and fluorenes[179] are oxidized in the range of -0 8 to -1.1 V while the anions of polynitroalkanes[135b] are oxidized between +1 0 and +1 5 V

The left-hand side of the diagram (good nucleophiles, easily oxidized) is designated as a region that is conducive to successful electrosynthesis by cathodic electrolysis It will be recognized that this designation is fully consistent with the examples given earlier in the review Thus, to use thiolates or R_2N^- anions successfully in electrosynthesis, it is best to generate them by cathodic electrolysis of RSH or R_2NH and allow the anions so formed to react, for example, with alkyl halides or Michael acceptors The advantages of the electrochemical approach are mainly that no strong chemical bases are needed and the anions can be generated in a state of high reactivity by simple control of solvent and electrolyte

The middle region of the diagram is labeled as a region where either cathodic or anodic electrolysis may be most advantageous Here are included a variety of anions such as RO^-, carboxamide anions and mononitroalkane anions that also undergo useful reactions when generated at the cathode

On the far right are found anions that are poor nucleophiles and are quite difficult to oxidize There is little point in employing cathodic electrogeneration of these anions because their reactivity is often too low to be useful and, in any case, they can be easily prepared with quite weak chemical bases.

However, it is possible to reverse the role of the anion in this region. Instead of forming the anion as the product of a cathodic reaction, the anion can serve as a reactant from which an electrophilic radical or carbene can be generated by anodic electrolysis. It is obvious that the radicals produced from anions that are very difficult to oxidize will themselves be strongly electrophilic and because of this trait, the radicals can be trapped by suitable nucleophiles. Examples have been given in Section IV.2.

Another way to use weakly nucleophilic anions that are extremely difficult to oxidize is to generate an electrophilic cation or cation radical by anodic oxidation of a precursor that is more easily oxidized than the anion itself. Though a weak nucleophile, the anion will nonetheless react effectively with the electrogenerated cation and through subsequent reactions, desirable final products can be obtained. Examples of this strategy have been described in Section IV.3.

Thus, the classification of anions according to their nucleophilic properties (Scheme 73) can be a useful guide to choosing the type of electrolysis to use. Furthermore, the nucleophilicity can be conveniently estimated by the simple measurement of oxidation potential of the anion. Naturally, the boundaries between regions where cathodic, cathodic or anodic, and anodic electrolyses are preferred are indistinct and somewhat arbitrary. Nevertheless, the diagram embodies a valid generalization and can be useful for planning electroorganic syntheses.

VII. CONCLUSIONS

Carbanions and heteroanions have been widely used in electroorganic synthesis. Cathodic electrolysis of C-H, S-H, O-H, N-H acids etc. (or other precursors) results in generation of the anions *in situ*. The anions will undergo subsequent reactions with added electrophiles to produce useful products. Those anions that are difficult to oxidize are best used as starting materials in anodic electrolyses. The anodic reaction produces electrophilic radicals or carbenes that undergo further reaction to produce the desired product. A variant of this method, used with anions that are very difficult to oxidize, involves anodic oxidation of a precursor to form an electrophilic cation or cation radical that subsequently reacts with the weakly nucleophilic anion.

The oxidation potential of anionic nucleophiles is a useful measure of their nucleophilicity which, in turn, provides a guide to the type of electrolysis that can most profitably be developed. In general, strongly nucleophilic anions are conducive to electrogeneration by cathodic electrolysis while weak anionic nucleophiles are best used in anodic electrolysis.

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