Use of Sacrificial Anodes in Electrochemical Functionalization of Organic Halides

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This article reviews the new possibilities in organic synthesis offered by the electroreduction of organic halides in the presence of various electrophiles using sacrificial metallic anodes.

1. Introduction

Many studies have been devoted to the electrochemical reduction of organic halides in aprotic solvents in the presence of electrophiles with the aim of forming carbon–carbon or carbon–heteroatom bonds.[1,2] In many cases, however, either the organic halide is less easily reduced electrochemically than its coreactant, or the derived intermediate (radical or anion) reacts faster with a proton (or hydrogen) donating molecule (residual water, solvent, organic supporting electrolyte) than with the electrophile.

Some authors have attempted to overcome these drawbacks by using mediators or transition-metal-catalysts. Several recent reviews provide summaries on various reactions.[3,4,5,6] These approaches have greatly increased the selectivity of many reactions. However, even these improved methods suffer constraints imposed by the electrochemistry itself:

i.   Most frequently reductive electrolyses are carried out in divided cells to avoid the anodic oxidation of the species generated at the cathode. This requires membranes which would be stable in organic solvents.

ii. The use of organic aprotic solvents needs a supporting electrolyte, usually an expensive quaternary ammonium salt at a concentration as high as that of the substrate.

iii. Electrolyses are frequently performed at controlled potential which requires complex electrochemical apparatus.

Most of these restrictions, notably the anolyte–catholyte separation, can be suppressed by the use of consumable anodes made of readily oxidized metal. Anodic oxidation of metals has been previously described in many electrochemical processes leading to organometallic compounds from carbanions either preformed,[7] or formed simultaneously by cathodic reduction of organic halides.[8] A ligand is often added to form stable unreactive organometallic compounds.[9]

Applications of the process to electroorganic synthesis started in the early 80's with the electrocarboxylation of acenaphthylene.[10] Since 1984 important developments have been achieved with the electrocarboxylation of
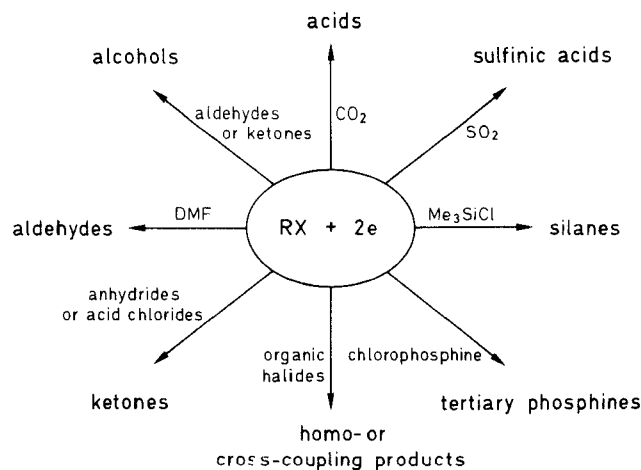
Scheme A

organic halides,[11,12] and more generally with the electro-reductive coupling of organic halides with a variety of electrophiles as outlined in Scheme **A**.

These reactions are closely related to organometallic syntheses, where the reduction would be made by the metal instead of electrically. They are of great synthetic utility as they offer valuable advantages over the corresponding organometallic routes and can be easily performed on a preparative scale.

The first part of this review article will focus on the general aspects of the process. The various reactions will then be described more thoroughly and their synthetic utility will be highlighted by comparison to the usual chemical methods.

2. General Aspects of the Sacrificial Anode Process

2.1. Methodology and General Conditions

A typical electrochemical cell commonly used for laboratory investigations[13] is presented in Figure 1.
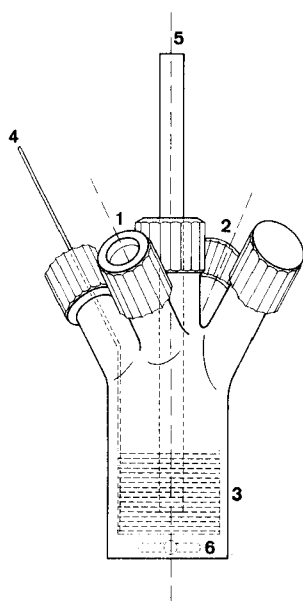
1,2 Input and output of gases (CO_2, CF_3Br,...)
3   Volume of the cell: 40 mL
4   Cathode (10 to 20 cm^2) stainless steel, nickel, carbon ...,
     and its connection
5   Anode: magnesium, aluminum, zinc
6   Magnetic stirrer

Figure 1. Typical Electrochemical Cell Used for Laboratory
Investigations

The anode is a rod of magnesium, aluminum or zinc, depending upon the type of reaction. The cathode is a concentric grid made of stainless steel, nickel foam or carbon fiber. Dimethylformamide (DMF) is mostly used as solvent. Other dipolar aprotic solvents such as acetonitrile, tetramethylurea (TMU), N-methylpyrrolidone (NMP), hexamethylphosphoric triamide (HMPT), tetrahydrofuran or mixtures thereof can be used. The solvent

is usually distilled before use according to common procedures. In most cases absolute dryness is not necessary.
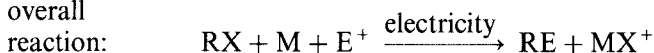
A tetrabutylammonium salt (bromide, iodide or tetrafluoroborate) is added at very low concentration (0.03 M) compared to that of the reagent (0.2 to 1 M). During the electrolysis the conductivity of the medium is ensured by the electrogenerated ions.

The electrolyses are run at room temperature or in some cases at about 0 °C under constant current corresponding to current densities from 0.5 to 5 A/dm^2 cathode. This allows the formation of 1 to 10 mmol of product per hour, given a cathode surface of 0.1 dm^2. Progress of the reaction is followed up by GC measurement of the amounts of organic halide and product. The product is isolated by standard workup procedures.

The mechanism can be schematically given as follows, for a divalent anode derived ion:

at the anode: $M \rightarrow M^{2+} + 2e$

at the cathode: $RX + 2e \rightarrow R^- + X^-$

in solution: $R^- + E^+ \rightarrow RE$

overall
reaction: $RX + M + E^+ \xrightarrow{\text{electricity}} RE + MX^+$

This transformation can be defined as an electroassisted organometallic reaction, though performed in unusual solvent for such a reaction and involving massive metal. Actually, it has been clearly demonstrated that the reaction does not proceed in the absence of electricity. In most cases at least 2F/mol of halide, i.e. the stoichiometric amount of electricity, is needed.

For a given reaction to work properly the relative reduction potentials of all components should be in the proper order, that is:

i. The metallic ion generated by the oxidation of the anode has to be reduced at more negative potential than the halide. This favors the use of magnesium or aluminum anodes since magnesium(II) and aluminum(III) are not reduced under the usual conditions, and allows the reduction of halides with potentials as low as -2.8 V/SCE (e.g. PhCl). Zinc anodes can be used only with easily reducible halides, Zn(II) species being reduced around -1.3 V/SCE.

ii. When the halide is reduced more easily than the electrophile E^+, homogeneous catalysis by transition metals can be used associated with the consumable anode.

Thus the process is mainly characterized by its simplicity. At the laboratory scale, at least, a very simple electrical power source is used, making the method accessible at moderate cost. Scaling-up has also been successfully performed, as will be described later.

The method has several advantages over the normal organometallic processes which will be demonstrated with selected examples:

i. it is a one-step reaction;

ii. the experimental conditions are mild as a result of using massive metals and nonflammable solvents and operating at or near room temperature;

iii. the selectivity of some reactions can be increased and new reactions have been published.

2.2. Nature of the Anode and Role of the Generated Metal Ions

The consumable anode was first used to suppress the need to use a separator between catholyte and anolyte. It has progressively appeared that the role of the anodically generated ions is often decisive.

This has been clearly demonstrated in comparative experiments as follows. A given reaction is performed: i. in the presence of the selected consumable anode; ii. in a divided cell in the presence of tetrabutylammonium salt as the only electrolyte; iii. in a divided cell in the presence of an ammonium salt plus a magnesium, zinc, or aluminum salt in the catholyte according to the anode used in the first experiment.

Typical results are given in Table 1.

In the carboxylation of benzyl chloride, the use of magnesium ions avoids the formation of the ester by trapping the carboxylate.

In the carboxylation of bromobenzene, the magnesium ions presumably prevent the reduction of carbon dioxide occurring instead of bromobenzene.

In the cross-coupling reaction, zinc ions afford the stabilization of trichloromethyl anion, possibly through an organozinc intermediate, thus avoiding its evolution into dichlorocarbene.

For a given reaction the nature of the anodic metal plays a decisive role. As already pointed out the ions formed in the anodic oxidation should not be reduced more readily than the organic halide. Thus in the electrocarboxylation reaction magnesium or aluminum can be used for benzyl halides, whereas magnesium is preferred with the less readily reduced aromatic halides.

In reactions involving easily reducible halides such as polyhalomethanes, chemical reduction at the anodically scoured metal can occur: thus magnesium should *not* be

used for reactions involving such compounds. Electroscoured magnesium can even chemically reduce the solvent, DMF.[17] Quite generally, zinc as the anode is convenient for reactions involving halides having reduction potential higher than -1.3 V/SCE. Interestingly also, the presence of electroreducible zinc ions in the reaction mixture can prevent the further reduction of electrosynthetized products.
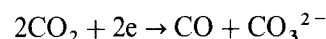
2.3. Low-Valent Transition-Metal-Catalysis

Many nickel-catalyzed electrochemical reactions can be conveniently achieved in the presence of a consumable anode. Thus, the homocoupling of aryl or vinyl halides previously performed in a divided cell,[18] occurs readily in a diaphragmless cell in the presence of a magnesium anode.[19]

The use of a zero-valent nickel complex as catalyst makes the reduction of the organic halide easier. This is of interest, for example, in the coupling reactions of allyl halides or α-halo esters with aromatic carbonyls,[20] which gives moderate results in the absence of catalyst.[21] With respect to this nickel-catalyzed reaction, the nature of the anode plays a role, inasmuch yields of coupling product are quantitative with zinc and very low with magnesium or aluminum. The suggested mechanism is via a nickel–zinc transmetalation reaction leading to an organozinc intermediate.[22]

$$RNiX + Zn(II) \rightarrow RZnX + Ni(II)$$
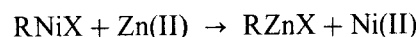
Another synergistic effect between nickel catalysis and the consumable anode has been found in the electroreduction of carbon dioxide into carbon monoxide catalyzed by nickel bipyridine complexes in the presence of a magnesium anode: the magnesium ions trap the produced carbonate ions, which would otherwise deactivate the catalyst by the formation of nickel carbonate.[23]

$$2CO_2 + 2e \rightarrow CO + CO_3^{2-}$$

Investigation of the features involving association between transition-metal-catalysis and a consumable anode

Table 1. Electrosyntheses from Organic Halides with Various Experimental Conditions

Reaction Type	Reaction Conditions			Ref.
	Divided Cell without Metallic Salt	Undivided Cell with a Sacrificial Anode	Divided Cell with Metallic Salts in the Catholyte	
carboxylation of $PhCH_2Cl$	formation of $PhCH_2CO_2CH_2Ph$	*anode: Mg* formation of $PhCH_2CO_2^-$	*ions: Mg(II)* formation of $PhCH_2CO_2^-$	12, 14
carboxylation of PhBr	formation of benzene. $PhCO_2^-$ is formed with low faradaic yield	*anode: Mg* formation of $PhCO_2^-$ with high faradaic yield	*ions: Mg(II)* formation of $PhCO_2^-$	12, 15
cross-coupling of $PhCH_2Br$ and CCl_4	formation of $PhCH_2Cl$, $CHCl_3$ and dichlorocarbene derived products	*anode: Zn* formation of $PhCH_2CCl_3$	*ions: Zn(II)* formation of $PhCH_2CCl_3$	16

have only recently begun. Current research will undoubtedly allow important progress in electroorganic synthesis.

3. Electrosyntheses Using the Sacrificial Anode Process

3.1. Carboxylic Acids from Organic Halides and Carbon Dioxide

For two decades much work has been devoted to the electrochemical carboxylation of organic substrates. Starting compounds generally have either unsaturation (olefins, carbonyls, imines, ...) or a good leaving group such as a halogen. This topic has been reviewed recently.[2,24]

For reactions involving organic halides, some successful results have been obtained from easily reducible compounds[25,26] (benzyl or allyl halides, alkyl bromides, aryl iodides, halo esters). Even aryl bromides or chlorides can be carboxylated in the presence of catalysts.[27,28] However, these methods show a lack of generality and handicaps inherent in the electrochemical technique, as discussed in the introduction.

The use of sacrificial anodes has allowed efficient carboxylation of a very large variety or organic mono- and polyhalides including: alkyl bromides, aryl, vinyl, allyl, benzyl, and heteroaryl bromides or chlorides (Table 2 and references therein).

$$RX + CO_2 + 2e \rightarrow RCO_2^- + X^-$$
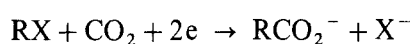
Even trifluoromethylarenes can be converted into 2-aryl-2,2-difluoroacetic acid.

Usually, the electrocarboxylation of halides (0.3–1.3 M) is carried out in DMF between a magnesium or aluminum anode and any cathode (nickel, carbon, stainless steel, ...). Carbon dioxide is supplied under atmospheric pressure at room temperature; at higher temperatures (40–60 °C) a slight pressure of carbon dioxide (3–5 bars) may be necessary to compensate the decrease in its solubility.

The reaction has been studied specially with benzyl and aryl halides which lead to valuable carboxylated products (e.g. antiinflammatory arylpropionic acids). Experimental conditions have more or less importance according to the nature of the starting material.

For example, with benzyl chloride several solvents (DMF, N-methylpyrrolidone, acetonitrile, THF, HMPT, etc.) or mixtures thereof are suitable. No difference is observed when using a magnesium or an aluminum anode. In this case the use of a sacrificial anode offers principally a convenient anodic reaction. In addition a complexation between the electrogenerated metal cations and carboxylate anions avoids the formation of esters by nucleophilic substitution of the carboxylate on the starting halide.

With aryl halides, the choice of experimental conditions are more restricted. DMF as solvent gives the best results; in other solvents the formation of arene is often observed to a larger extent. Faradaic and chemical yields of the carboxylation are very low in the absence of sacrificial anode, and depend on the nature of the anodic metal. In most cases best results are obtained with magnesium.

Nevertheless, some problems, which are not clearly understood, have been observed:

Table 2. Electrocarboxylation of Halides[a]

Substrate	Molar Concentration	Anode	Product	Yield (%)	Ref.
PhCH$_2$Cl[b]	0.14	Al	PhCH$_2$CO$_2$H	83	11
PhCH$_2$Cl	0.5	Mg	PhCH$_2$CO$_2$H	85	34
PhCHCl$_2$	0.16	Al	PhCH$_2$CO$_2$H	29	35
			PhCH(Cl)CO$_2$H	52	
PhBr	0.4	Mg	PhCO$_2$H	85	12
PhCl	0.5	Mg	PhCO$_2$H	85	12
1,4-dichlorobenzene[b]	0.34	Al	4-chlorobenzoic acid	78	11
1,2,3-trichlorobenzene	0.5	Mg	2,3-dichlorobenzoic acid	34	13
			2,6-dichlorobenzoic acid	34	
			2- or 3-chlorobenzoic acid	4	
2-chlorobenzonitrile	0.6	Mg	2-cyanobenzoic acid	65	13
4-bromoacetophenone	0.4	Mg	4-acetylbenzoic acid	82	12
2,4-Cl$_2$C$_6$H$_3$COCH$_3$	0.5	Mg	4-acetyl-3-chloro benzoic acid	56	13
			2-acetyl-5-chloro benzoic acid	24	
PhCH=CHBr	0.4	Mg	PhCH=CHCO$_2$H	80	12
2-chlorothiophene[c]	0.4	Mg	2-thiophenecarboxylic acid	80	12
3-bromofuran[c]		Mg	3-furancarboxylic acid	78	12
PhCH=CHCH$_2$Cl[c]	0.4	Mg	PhCH=CHCO$_2$H	80	12
3-chloropyridine	0.2	Mg	3-pyridinecarboxylic acid	75	36
3-chloromethylpyridine	0.2	Mg	3-pyridineacetic acid	85	36
PhCF$_3$	0.5	Mg	PhCF$_2$CO$_2$H	65	37

[a] These results were obtained under intentiostatic conditions (except where indicated) in solvent DMF (except where indicated) plus a tetrabutylammonium salt (0.03 M). Electrolyses were performed at room temperature, under atmospheric pressure of CO$_2$.
[b] Potentiostatic experiment.
[c] In THF/HMPT (1:1).

- It has been shown that the solvent DMF undergoes a reductive degradation by a chemical reaction with anodized magnesium.[17] This side-reaction can be limited by lowering the temperature to around 10 °C.
- A drastic passivation of the cathode sometimes may occur during the electrolysis of some aromatic compounds inhibiting the halide consumption. This drawback can be overcome either by using higher amounts of a tetrabutylammonium salt (0.1–0.2 M) or by employing a cathode freshly coated by an electrolytic deposit of a metal such as cadmium, zinc, lead or tin. In this connection, it has been shown that the electroreduction of halides then occurs at lower cathodic potentials than usual.[29]

Electrosynthesis of 2-Trifluoromethylbenzoic Acid from 2-Chloro-trifluoromethylbenzene; Typical Procedure:[13]
Freshly distilled DMF (30 mL), Bu$_4$NBr (0.3 g) and the halide (3 mL) are introduced in the cell (figure 1) fitted with a stainless steel grid and a magnesium rod. The cell is immersed in cold water and the solution is stirred magnetically. After bubbling CO$_2$ for a few minutes the current is set at 0.4 A during 3.2 hours, corresponding to a charge of 2.2 F/mol of halide. The electrolytic solution is evaporated to remove most of the solvent, 6 N HCl (10 mL) added, and the solution extracted with Et$_2$O (3 × 10 mL). The organic layer is treated with 2 N KOH (20 mL) and extracted with Et$_2$O (2 × 10 mL) to remove the neutral byproducts. After acidification of the aqueous layer, the organic acid is extracted with Et$_2$O (3 × 30 mL) and evaporated to dryness; yield: 3.4 g (80 %).

This electrochemical process is quite suitable for series of halides where the conventional carboxylation of a Grignard-type reagent is not feasible (e. g. presence of a carbonyl group), or even unknown (e. g. trifluoromethyl-arenes). For benzylic halides the one-step electrochemical reaction avoids the delicate preparation (e. g. low temperature, high dilution) of benzyl metal derivatives. Good to high yields of carboxylic acids are obtained. The results are so attractive that the reaction has been performed on a large scale.[30]

Limitations are, however, encountered:

- when the starting halide bears an easily reducible function (e. g. nitro compounds);
- when the carbon–halogen bond is reduced at very low cathodic potential (e. g. alkyl chlorides);
- in aromatic series where the presence of substituents such an ester group hinders the carboxylation of the carbon–halogen bond which is then converted into a carbon–hydrogen bond. Thus polyacids are never obtained from polyhaloarenes.

The same electrochemical method has been successfully applied to the carboxylation of unsaturated,[10] carbonyl,[31,32] and imino compounds.[33]
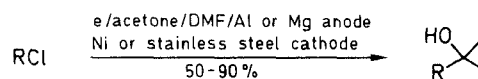
3.2. Alcohols from Organic Halides and Carbonyl Compounds

The use of a sacrificial anode enables also the electroreductive coupling of organic halides with ketones or aldehydes, yielding either tertiary or secondary alcohols.

$$ RX \ + \ 2e \ + \ R^1\!-\!\!\underset{O}{\overset{O}{C}}\!\!-\!R^2 \ \longrightarrow \ R\!-\!\!\underset{R^2}{\overset{R^1}{C}}\!\!-\!O^- \ + \ X^- $$
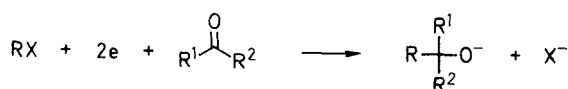
3.2.1. Coupling with Acetone

Acetone can be employed as an electrolysis cosolvent with DMF (80:20). Using these conditions various dimethyl substituted tertiary alcohols are obtained with good to excellent yields by electroreduction of benzyl or allyl halides, α-chloro esters and carbon tetrachloride[21] (Scheme **B**).
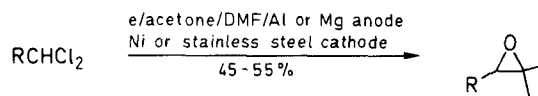
RCl $\xrightarrow[\text{50–90\%}]{\substack{\text{e/acetone/DMF/Al or Mg anode} \\ \text{Ni or stainless steel cathode}}}$ HO–C(CH$_3$)$_2$–R

R = CH$_2$Ph, CH$_2$C(CH$_3$)=CH$_2$, CH(CH$_3$)CO$_2$Et, CCl$_3$

Scheme **B**

The process allows the one-pot synthesis of 1,1-difluoro-2-methyl-1-phenyl-2-propanol from trifluoromethyl-benzene.[37]

PhCF$_3$ $\xrightarrow[\text{80\%}]{\substack{\text{e/acetone/DMF/Al anode} \\ \text{Ni or stainless steel cathode}}}$
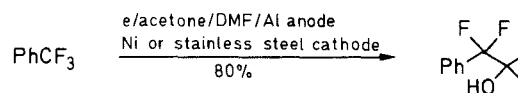
Using same conditions epoxides are obtained from gem-dihalides[38] (Scheme **C**).

RCHCl$_2$ $\xrightarrow[\text{45–55\%}]{\substack{\text{e/acetone/DMF/Al or Mg anode} \\ \text{Ni or stainless steel cathode}}}$
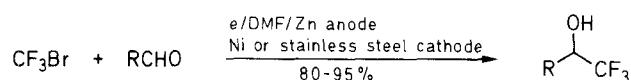
R = Ph, CO$_2$Et

Scheme **C**

Alkyl or aryl monohalides give only the corresponding hydrocarbons and enolization products of acetone.

Electrosynthesis of 2-Methyl-1-phenyl-2-propanol; Typical Procedure:[38]
A mixture of acetone (25 mL), DMF (5 mL), Bu$_4$NI (1 mmol), benzyl chloride (25 mmol) is introduced in the electrolysis cell fitted with an aluminum anode and a nickel cathode. 0.3 A is applied until 2.3 F/mol of benzyl chloride are passed (5 h). Acetone is evaporated, the residue is hydrolyzed with dilute HCl to pH = 2, and extracted with Et$_2$O (2 × 30 mL). The ethereal solution is washed with water, dried (MgSO$_4$) and evaporated. The crude product contains 2-methyl-1-phenyl-2-propanol, 4-hydroxy-4-methyl-2-pentanone and traces of DMF. Chromatography on silica gel (pentane/Et$_2$O, 90:10) gives the title alcohol; yield: 2.81 g (75%).

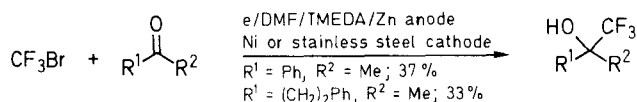## 3.2.2. Coupling with Other Carbonyl Compounds

Electroreductive coupling of organic halides with aldehydes or ketones other than acetone can be performed in DMF solution. Good results were obtained with polyhalomethanes such as carbon tetrachloride and bromo-trifluoromethane, using a zinc anode. A detailed study[39] of trifluoromethylation has shown that the coupling reaction proceeds via the reduction of zinc(II) salts, followed by a chemical reaction between the reduced metal, bromotrifluoromethane, and the carbonyl compound. Alcohols are obtained in nearly quantitative yields from aldehydes (Scheme **D**).

$$CF_3Br + RCHO \xrightarrow[\text{80-95\%}]{\substack{e/DMF/Zn \text{ anode} \\ \text{Ni or stainless steel cathode}}} R \overset{OH}{\underset{}{\diagup}} CF_3$$
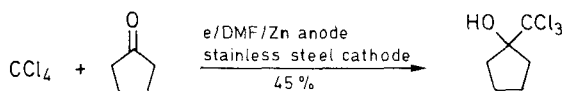
R = aryl, alkyl

Scheme D

With ketones, unreactive organozinc species CF_3ZnBr and $(CF_3)_2Zn$ are the main side-products. In this case the use of DMF/tetramethylethylenediamine (TMEDA) (70:30) as solvent was shown to repress the formation of the organozinc species and promote carbonyl attack, affording tertiary alcohols in moderate yields (Scheme E).

$$CF_3Br + R^1 \overset{O}{\underset{}{\overset{\|}{C}}} R^2 \xrightarrow[\substack{R^1 = Ph,\ R^2 = Me;\ 37\% \\ R^1 = (CH_2)_2Ph,\ R^2 = Me;\ 33\%}]{\substack{e/DMF/TMEDA/Zn \text{ anode} \\ \text{Ni or stainless steel cathode}}} \overset{HO}{\underset{R^1}{\diagup}} \overset{CF_3}{\underset{R^2}{}}$$

Scheme E

From carbon tetrachloride and aldehydes, secondary alcohols were obtained almost quantitatively using a sacrificial anode of zinc,[21] as well as by other electrochemical procedures.[40] Coupling with cyclopentanone gives the alcohol in moderate yield (Scheme F).

$$CCl_4 + \overset{O}{\underset{\text{(cyclopentanone)}}{\bigcirc}} \xrightarrow[\text{45\%}]{\substack{e/DMF/Zn \text{ anode} \\ \text{stainless steel cathode}}} \overset{HO \quad CCl_3}{\underset{}{\bigcirc}}$$

Scheme F

Allyl chlorides and α-chloro esters give moderate yields of coupling product with aldehydes or ketones other than acetone. As will be shown hereafter nickel catalysis greatly improves these reactions.

Benzyl chloride reacts in moderate yield (50%) with benzophenone but through a different mechanism involving the reduction of the carbonyl compound followed by electron-transfer to the halide.[41]

### 3.2.3. Electrosynthesis of Alcohols Using a Nickel Catalyst

Homogeneous catalysis has been shown to be useful when used in conjunction with a sacrificial anode: it has been shown[20,22] that the electroreductive coupling of allyl chlorides (or acetates) or α-chloro esters with carbonyl compounds is almost quantitative in the presence of a catalytic amount of nickel 2,2'-bipyridine complexes. DMF was found to be a more suitable solvent than, for example, acetonitrile. The use of a zinc anode is imperative and the coupling reaction can even be improved by adding zinc salts to the electrolysis solution. Nickel-2,2'-bipyridine complexes are better catalyst precursors than nickel-phosphine, or even other nickel–nitrogen containing complexes.[22]

Electroanalytical investigations have shown that the nickel complex catalyzes the electroreduction of allyl chlorides, via the formation of allylnickel species. These organonickel complexes slowly attack the carbonyl compound, but in the presence of zinc salts, either arising from

the anodic reaction or added to the solution, a nickel(II) regeneration is observed and interpreted as a previously undescribed transmetalation reaction:
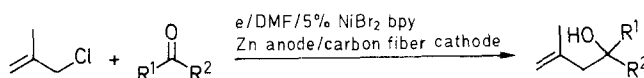
$$RNiX + Zn(II) \rightarrow RZnX + Ni(II)$$
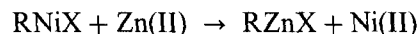
Chemical evidence has been obtained for this mechanism (Scheme G). The reactivity patterns, based on steric factors or allylic transposition, are those of allylzinc and not of allylnickel species.[22]
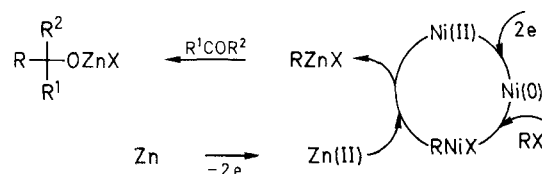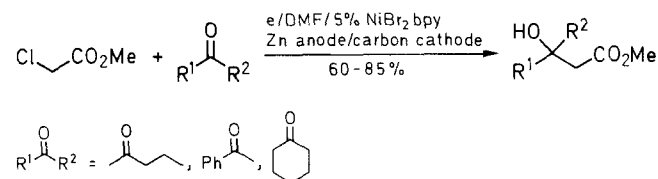
Scheme G

Due to the relatively high reduction potential of nickel(II) (− 1.1 V/SCE), coupling of allyl chlorides with easily reducible carbonyls such as aryl or α,β-unsaturated aldehydes and ketones was successfully attempted (Scheme H). With compounds containing a vinyl ketone subunit, no conjugate addition product was detected, although nickel salts are claimed to promote such reactions.

$$\overset{}{\underset{}{\diagdown}}\!\!\diagdown\! Cl + R^1 \overset{O}{\underset{}{\overset{\|}{C}}} R^2 \xrightarrow[]{\substack{e/DMF/5\% \text{ NiBr}_2 \text{ bpy} \\ \text{Zn anode/carbon fiber cathode}}} \overset{}{\underset{}{\diagdown}}\!\!\diagdown\!\!\overset{HO \quad R^1}{\underset{R^2}{\diagup}}$$

R^1	R^2	Yield (%)	R^1	R^2	Yield (%)
Ph	H	85	(furyl)	H	48
Ph	Ph	86			
t-Bu	Me	60	$-(CH_2)_5-$		85

Scheme H

The main constraint of this electrosynthetic procedure seems to be due to steric factors: hindered ketones such as 2,6-dimethylcyclohexanone or even pinacolone give poor results. Concerning α-chloro esters good results have been obtained for the coupling of alkyl chloroacetate with various ketones[20] (Scheme I).

$$Cl\!\!\diagdown\!\!\diagup CO_2Me + R^1 \overset{O}{\underset{}{\overset{\|}{C}}} R^2 \xrightarrow[\text{60-85\%}]{\substack{e/DMF/5\% \text{ NiBr}_2 \text{ bpy} \\ \text{Zn anode/carbon cathode}}} \overset{HO \quad R^2}{\underset{R^1}{\diagup}}\!\!\diagdown\! CO_2Me$$

$$R^1 \overset{O}{\underset{}{\overset{\|}{C}}} R^2 = \overset{O}{\underset{}{\diagdown\!\!\diagup\!\!\diagdown\!\!\diagup}}, \ Ph\overset{O}{\underset{}{\overset{\|}{C}}}, \ \overset{O}{\underset{}{\bigcirc}}$$

Scheme I

3.2.4. Conclusion

The electrosynthesis of alcohols from organic halides and carbonyl compounds, using sacrificial anodes, gives good results essentially with easily reducible halides:

allyl or benzyl chlorides, polyhalomethanes, α-chloro esters. The reaction conditions (choice of the anodic material, use of a cosolvent in addition to DMF and concentration of the reagents) have to be defined in each case and a number of the described reactions have yet to be optimized. This electrosynthetic process appears to be a useful tool in organic synthesis, inasmuch as valuable alcohols could be obtained in high yield, mainly in the cases where the organometallic synthesis does not apply well: benzylic organometallic derivatives are difficult to prepare, and in the case of trifluoromethylbenzene, organometallics are even unknown. Good results were obtained from bromotrifluoromethane: alcohols are obtained quantitatively from aldehydes and in moderate yield from ketones, whereas no chemical procedure could give comparable yields.[42]

Concerning the synthesis of homoallylic alcohols or β-hydroxy esters, the sacrificial anode process combined with the use of a nickel catalyst is very efficient. It offers an alternative to the well-known Barbier synthesis, which generally uses activated zinc as the reducing agent, and advantageously the starting materials are chlorine derivatives (or even acetates in the case of allyl derivatives) instead of bromides.

3.3. Acylation and Formylation of Organic Halides: Ketones from Anhydrides or Acid Chlorides, Aldehydes from Dimethylformamide

3.3.1. Ketones

Electroreductive acylation is potentially an extremely useful tool for the synthesis of ketones:

$$RX + 2e + (R'CO)_2O \rightarrow RCOR' + X^- + R'CO_2^-$$
or
$$RX + 2e + R'COCl \rightarrow RCOR' + X^- + Cl^-$$
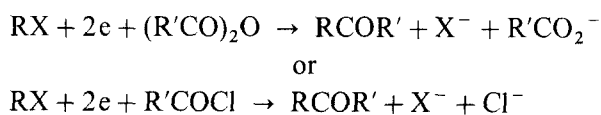
It was found that the reduction of benzyl and allyl chlorides in DMF containing anhydrides and using a magnesium sacrificial anode produces the expected ketones with good yields[43] (Scheme J).
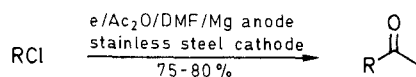

R = PhCH₂, Ph(Me)CH, CH₂=C(Me)CH₂

Scheme J

The anhydride has to be in large excess with respect to the halide; acetic or propionic anhydrides can be used as cosolvent with DMF, in the ratio 80:20. Lower yields were obtained from benzoic or succinic anhydrides, which were not, however, used in very large excess.

Direct electroreduction of a mixture of alkyl halide and acid halide in acetonitrile either in a divided cell,[44] or using a consumable anode,[45] gives the cross-product when the alkyl halide can be reduced, even in the presence of easily reducible acid halides.

The nickel-catalyzed electrochemical cross-coupling of acid chlorides and alkyl or aryl halides with a consumable

anode affords ketones in good yields.[46] Preliminary results involving a wide range of reagents are indicative of the potential of the method (Scheme K).
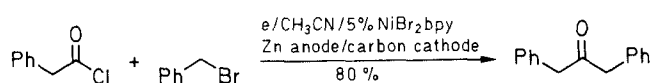

Scheme K

The nature of the anode is quite important, but its role remains unexplained: the highest yields of product are obtained with a zinc anode using a 1:1 reagent mixture, whereas a fivefold excess of the acid halide over the alkyl halide is required when magnesium is used.
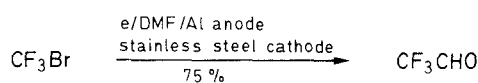
3.3.2. Aldehydes

Since the first report by Bouveault at the beginning of the century, it has been well established that organometallic species such as Grignard reagents may be formylated by DMF to yield aldehydes.[47]

The generation of carbanionic species by electroreduction of organic halides in DMF should be an attractive alternative route according to the sequence:
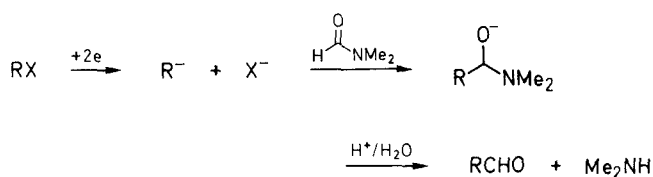

Unfortunately only poor yields were obtained.[48,49]

It has been reported[29] that use of a sacrificial anode affords aldehydes in moderate yields. Arenes from aryl halides or dimers from benzyl derivatives are the main products. However in the case of bromotrifluoromethane electroreduction using an aluminum anode gives trifluoroacetaldehyde[50] in high yield.


The yields of aldehydes from aryl or benzyl halides are good provided that the cathode has been freshly coated with an electrolytic deposit of zinc, cadmium or tin[29] (Scheme L) enabling the one-pot synthesis of valuable compounds.
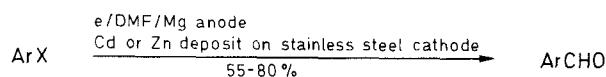
ArX = PhBr, 4-ClC₆H₄CF₃, 3-BrC₆H₄OMe

Scheme L

The process gives also a new original simple route for the synthesis of 2,2-difluoro-2-phenylethanal from trifluoromethylbenzene.[37]
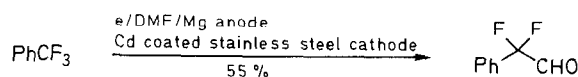
Electrosynthesis of 4-Trifluoromethylbenzaldehyde from 1-Chloro-4-trifluoromethylbenzene; Typical Procedure:[29]

The cell is fitted with a nickel grid (cathode) and a zinc rod. A solution of DMF (40 mL), Bu_4NBF_4 (2 mmol) and $ZnBr_2$ (2 mmol) is electrolyzed at constant current (0.2 A) during twenty minutes to coat the cathode with a black deposit of zinc. This solution is replaced by DMF (40 mL), containing Bu_4NBr (1.6 mmol), the halide (20 mmol) and the zinc rod replaced by a magnesium one. The solution is electrolyzed (0.2 A) until complete consumption of the halide (2.2 F/mol). The electrolytic solution is cooled, 1 N aq HCl (100 mL) is added and the mixture extracted with Et_2O (3 × 40 mL). The organic layer is concentrated, then chromatographed on silica gel eluting with pentane/Et_2O (90:10) to give 4-trifluoromethylbenzaldehyde; yield: 1.95 g (56%).

### 3.4. Electrochemical Homo- and Cross-Coupling of Organic Halides

New carbon–carbon bond formation can be made by coupling of organic halides, according to the Wurtz reaction (dialkyl compound formation) or the Ullman reaction (diaryl compound formation). Improvements of these methods are constantly searched for, to avoid side reactions, especially by using preformed organometallic species and transition-metal-catalysts. If homocoupling reactions can usually be performed efficiently, cross-coupling reactions are less feasible and can rarely be carried out in a one-pot procedure.

The direct electroreduction of alkyl halides (RX) in a classical divided cell generally gives RH as the main product and little or no dimer. In contrast the use of transition-metal-catalysts, notably nickel complexes, in divided cell has enabled the homocoupling of alkyl,[51] vinyl and aryl halides.[18]

In a preliminary examination it has been found that these reactions involving nickel complex as catalyst can also be performed with identical or even better efficiency in an undivided cell in the presence of a magnesium anode.[19] Furthermore cross-coupling involving aryl or vinyl halides can be carried out under the same conditions. As for the alkyl halides, some homo- and cross-coupling was obtained without a catalyst.

3.4.1. Electrochemical Coupling of Alkyl Halides

The homocoupling of alkyl halides was one of the first demonstrations of the specificity of the electroreduction of organic halides in the presence of a sacrificial anode. Thus 1-bromoheptane is near quantitatively dimerized in THF/HMPT using a magnesium anode, whereas heptane is the main product in a divided cell.[52]
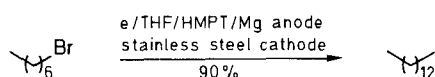

This reaction has not been optimized, nor studied in full. It appears that THF/HMPT gives the best results, but other aprotic solvents can be used such as DMF, diethylcarbonate or THF/tetramethylurea (1:1). Thus, benzyl chloride can be efficiently reduced to 1,2-diphenylethane in DMF. Phenylethanal is a minor product[29] under these experimental conditions where a high concentration of organic halide is used.

The sacrificial anode process is also a convenient method for the coupling of gem-trichloro substituted compounds with alkyl bromides or activated chlorides.[16,53]

$$RCl_3 + R'X + 2e \rightarrow RCl_2R' + Cl^- + X^-$$
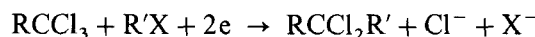
The selective reduction of the easily electroreducible gem-trichloro derivatives ($RCCl_3$) in THF/tetramethylurea produces α-halogenated anions which are stable in the presence of zinc or aluminum ions, thus avoiding the transformation to carbenes frequently observed under other reaction conditions (Scheme M).
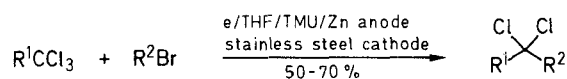
Scheme M

It is important to point out that these reactions were performed at room temperature, whereas α-halogenated organometallics have low-thermal stability:[54] thus CCl_3MgX decomposes at $-65°C$. Zinc is preferably used as the anode to prevent further reduction of the product.

Aluminum is used especially when the starting halide (RX) is a chloride: the reaction requires then tetrabutylammonium bromide as the supporting electrolyte to favor chlorine–bromine exchange.
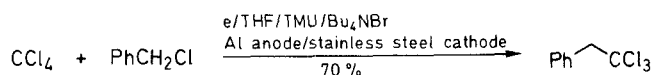
Mixtures of polar solvents, e.g. THF/tetramethylurea or THF/N-methylpyrrolidone, were found more effective than pure solvents.

**Trichloromethylation of Benzyl Bromide; Typical Procedure:[16]**

To a cell fitted with a zinc-rod anode, and a cylindrical stainless steel grid cathode is added THF/TMU (1:1, 40 mL), Bu_4NBF_4 (0.165 g, 0.5 mmol) and Bu_4NI (0.185 g, 0.5 mmol) as supporting electrolyte, CCl_4 (4 mL, 40 mmol) and benzyl bromide (2.4 mL, 20 mmol). 3 F/mol of benzyl bromide are passed under argon at constant current with a current density of 2 A/dm^2. The reaction mixture is then poured into a cold mixture of 1 N HCl (50 mL) and Et_2O (50 mL). The layers are separated and the aqueous layer is extracted with Et_2O (25 mL). The combined ethereal extracts are washed with water, dried ($MgSO_4$) and evaporated. Flash chromatography on silica gel eluting with pentane gives 2,2,2-trichloroethylbenzene; yield: 2.9 g (70%).

3.4.2. Electrochemical Homocoupling of Aryl and Vinyl Halides

There are a number of studies that demonstrate the usefulness of zero-valent nickel complexes as catalyst for the reductive dimerization of aryl and vinyl halides.[55] The preparation and regeneration of the catalyst can be conveniently carried out electrochemically and the reaction can be advantageously performed in an undivided cell equipped with a magnesium anode in N-methyl-

pyrrolidone or DMF, with a nickel complex of 2,2'-bipyridine as the catalyst.[19]

Yields of dimerized biaryls are good to high, and comparable to or higher than those obtained chemically,[55] especially for reactions involving chlorides (Scheme N).


R = Ph, naphthyl, 3-CH₃C₆H₄, PhCH=CH
X = Cl, Br
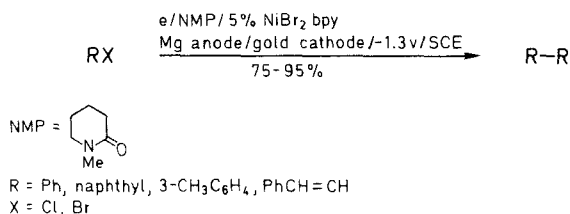
Scheme N

This electrochemical coupling can be used with a wide variety of organic halides, with the exception of compounds which have protonic (e.g. OH, CO_2H) or other easily reduced substituents (e.g. NO_2).

The coupling of *ortho*-substituted haloarenes requires a special procedure, because of the formation of a stable diaryl nickel Ar_2Ni. Oxidation of this intermediate gives quantitatively biaryl and regenerates nickel(II): thus by alternatively passing electricity and bubbling O_2 into the solution, a variety of 2,2'-disubstituted biaryls have been prepared,[56] for example Scheme O.
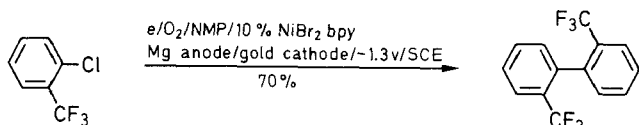

Scheme O

The cross-coupling of two different aryl halides cannot be performed efficiently in this way.[56] If one of the halides is much more reactive than the other, it is dimerized in the early stage of the reaction and then the other; little or no cross-coupling product is formed. With halides ArX and Ar'X having similar reactivity, three products are obtained in approximate statistical ratio[56] (Scheme P).
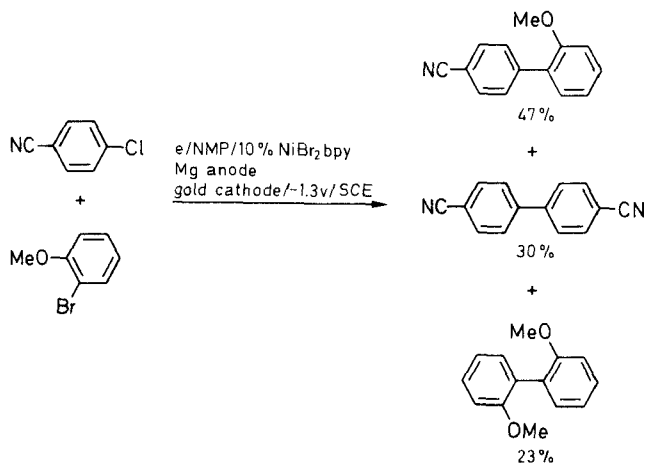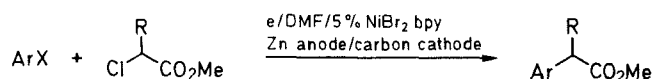

Scheme P

3.4.3. Electrochemical Cross-Coupling of α-Halo Esters with Aryl and Vinyl Halides

The coupling of aryl halides and α-halo esters catalyzed by nickel complexes, is not particularly favored, because chloro esters are much more reactive towards zerovalent nickel than aryl halides. An electrochemical two-step procedure had to be adopted[57] using stoichiometric amounts of nickel complex:

$$ArX + Ni(II) + 2e \longrightarrow ArNiX$$

$$ArNiX + RCHXCO_2R' \rightarrow ArCH(R)CO_2R' + Ni(II)$$
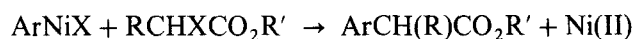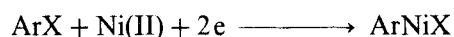
Recently it has been shown that the electrochemical cross-coupling reaction can be conducted in one-step using a sacrificial anode and a nickel(II) 2,2'-bipyridine complex as catalyst precursor.[58]

Methyl chloroacetate was found to couple with iodobenzene in DMF using a zinc anode to give phenylacetate in 60% yield. With bromobenzene the yield was only 10%. Replacing the zinc anode by aluminum improved the yield especially in the case of poorly reactive aryl bromides. Some valuable arylacetic and arylpropionic esters were thus obtained from cheap aryl bromides (Scheme Q).

R = H, CH₃

ArX	PhI	PhBr	4-IC₆H₄OMe	4-BrC₆H₄CN	4-BrC₆H₄CF₃
Yield (%)	70	40	85	70	66

Scheme Q

The procedure was extended to vinyl and heteroaryl bromides.
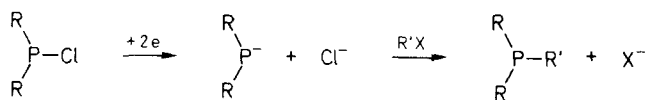
3.5. Formation of Carbon–Heteroatom Bond

The consumable anode process has been shown to be very effective for coupling of organic halides with chlorophosphines, chlorotrimethylsilane and sulfur dioxide forming carbon–phosphorus, carbon–silicon and carbon–sulfur bonds.

3.5.1. Electrosynthesis of Carbon-Phosphorus Bond

Trisubstituted phosphines are interesting ligands of low-valent metal complexes, used in homogeneous catalysis. They are usually prepared in several steps[59] by reaction of an organometallic compound with mono- or dihalophosphines,[60-62] or of a metallophosphide with an organic halide.[63] These methods cannot be used when the reagent contains sensitive functionalities. The electrochemical method, however, enables the one-pot synthesis of a variety of functionalized phosphines in good to high yield.[64]
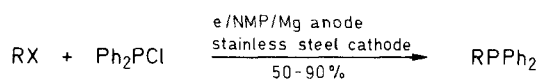
The electroreduction of a mixture of the organic halide and the chlorophosphine using a sacrificial anode is performed in DMF or *N*-methylpyrrolidone at constant

current. Chlorophenylphosphines (Ph_2PCl, $PhPCl_2$) are electroreduced in aprotic solvent at more positive potential than all the studied organic halides (about-1 V/vs. SCE),[65,66] giving the phenylphosphide anion which reacts efficiently with the organic halide, according to Scheme R.

$$\underset{R}{\overset{R}{\diagup}}P-Cl \quad \xrightarrow{+2e} \quad \underset{R}{\overset{R}{\diagup}}P^- \;+\; Cl^- \quad \xrightarrow{R'X} \quad \underset{R}{\overset{R}{\diagup}}P-R' \;+\; X^-$$

Scheme R

The best yields are obtained with a magnesium anode in N-methylpyrrolidone (Scheme S).

$$RX \;+\; Ph_2PCl \quad \xrightarrow[\substack{50-90\%}]{\substack{e/NMP/Mg \text{ anode} \\ \text{stainless steel cathode}}} \quad RPPh_2$$

R = CH_2Ph, Pr, CH_2CO_2Et
X = Cl, Br

Scheme S

Electrosynthesis of Ethylenebis(diphenylphosphine), (diphos); Typical Procedure:[64]

In the electrochemical cell, fitted with a magnesium rod as anode and a cylindrical stainless steel grid as cathode, are mixed 1,2-dichloroethane (10 mmol), Ph_2PCl (20 mmol), Bu_4NBF_4 (0.5 mmol), Bu_4NI (0.5 mmol) in NMP (25 mL). The electrolysis is carried out with a current density of $2 A/dm^2$, at r.t., until 2.2 F/mol of Ph_2PCl is passed. The reaction mixture is poured into aq HCl to pH 4, stirred for five minutes. Diphos precipitates. Recrystallization from butanol gives diphos; yield: 2.6 g (65%).

Alkyl bromides and some alkyl chlorides can be phosphinated by this new method. Interestingly functionalized phosphines for example ethyl diphenylphosphinoacetate ($Ph_2PCH_2CO_2Et$) can be easily obtained compared with the chemical method.[61] The process does not apply, however, to aryl and vinyl halides.

3.5.2. Electrosynthesis of Carbon-Silicon Bond

Alkyl- and arylsilanes are valuable molecules of increasing interest in organic synthesis and also as new materials.
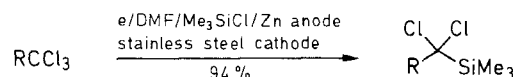
Many methods of carbon–silicon bond formation have been described, which are either not highly selective (mono- vs polysilylation) or are of limited applicability. Electrochemical monosilylation of benzyl (and allyl) chlorides or bromides, aryl and vinyl iodides has recently been reported:[67,68] both studies have been carried out in a divided cell and good yields of silylated products have been obtained. However, aryl chlorides or bromides are not converted under these conditions.

Chlorotrimethylsilane is reduced at more negative potential than alkyl or aryl halides hence the mechanism proposed is:

$$RX + 2e \rightarrow R^- + X^-$$

$$R^- + Me_3SiCl \rightarrow RSiMe_3 + Cl^-$$
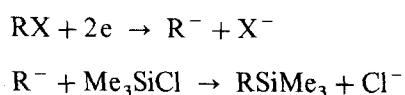
To perform such reactions with high efficiency and high selectivity, the use of a consumable anode appears more convenient.

Aryl chlorides and bromides are silylated in moderate to good yields.[69] It is also interesting to note that a convenient choice of the experimental conditions, notably the nature of the anode and the solvent, allows the controlled partial silylation of polychloromethanes. Monosilylation of carbon tetrachloride and chloroform[70] with a zinc anode in DMF is a highly selective process (Scheme T), compared to the best chemical method (magnesium in HMPT).

$$RCCl_3 \quad \xrightarrow[\substack{94\%}]{\substack{e/DMF/Me_3SiCl/Zn \text{ anode} \\ \text{stainless steel cathode}}} \quad \underset{R}{\overset{Cl}{\diagup}}\underset{SiMe_3}{\overset{Cl}{\diagdown}}$$

R = H, Cl

Scheme T

Further reduction of these products is possible if aluminum is used instead of zinc, DMF being replaced by a more complexing solvent, like tetramethylurea/HMPT.

The reaction requires a very dry and degassed medium. It is also necessary to remove hydrochloric acid by a preliminary electrolysis and large excess of chlorotrimethylsilane is usually necessary to obtain high yield of cross-coupling product.
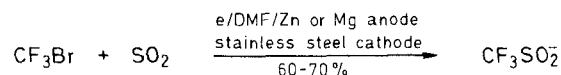
Electromonosilylation of Carbon Tetrachloride; Typical Procedure:[70]

The cell is fitted with a zinc rod and a stainless steel grid. DMF (50 mL) containing Et_4NBF_4 (1 mmol) is degassed in an ultrasonic cleaning bath for 20 min. Freshly distilled Me_3SiCl (15 mL, 118 mmol) is then introduced and the solution is electrolyzed for 2 h at constant current intensity (I = 0.1 A). CCl_4 (20 mmol) is then added and the electrolysis is conducted at constant intensity (I = 0.3 A) for 4 h. The crude mixture is extracted with Et_2O (3 × 50 mL) and washed with brine. The solution is dried (Na_2SO_4) and the solvent removed to give a mixture of Me_3SiCCl_3 (94%) and $(Me_3Si)_2Cl_2$ (6%).

3.5.3. Electrosynthesis of Trifluoromethanesulfinic Acid

Electrolysis of a mixture of sulfur dioxide and trifluorobromomethane at normal pressure and room temperature in DMF affords trifluoromethanesulfinate with good faradaic yields.[71]

The reaction is conducted at constant potential or constant current between a zinc or magnesium anode and a stainless steel cathode.

$$CF_3Br \;+\; SO_2 \quad \xrightarrow[\substack{60-70\%}]{\substack{e/DMF/Zn \text{ or } Mg \text{ anode} \\ \text{stainless steel cathode}}} \quad CF_3SO_2^-$$

Results are better than those obtained by the new Barbier procedure using zinc powder as reductant.[72] It is interesting to note that magnesium, prohibited in the chemical process, can be used as the anode in the electrochemical one and gives yields comparable to those obtained using zinc.

3.6. Miscellaneous

The consumable anode process has recently been used successfully in various other electrochemical transformations of organic halides.

3.6.1. Electrochemical Alkylation of the Carbon–Hydrogen Bond

The electroreduction in DMF of a alkyl bromide, or benzyl chloride in the presence of an activated $C-H$ bond such as those in ethyl phenylacetate or phenylacetone leads to selective monoalkylation of these substrates with good yields when a consumable anode process (magnesium anode) is used.[73]

It is thought that a carbanion R^- obtained by electroreduction of RX acts as probase (Scheme U).

$$RX + 2e \rightarrow R^- + X^-$$

$$R^- + PhCH_2Y \rightarrow RH + Ph\bar{C}HY$$

$$Ph\bar{C}HY + RX \rightarrow PhCH(R)Y + X^-$$
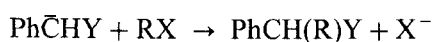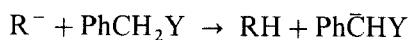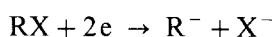
| RX	Y	Yield (%)
EtBr	CO_2Et	80
EtBr	CN	85
EtBr	$COCH_3$	65
$PhCH_2Cl$	CN	75

Scheme U

In contrast to other methods,[74] this monoalkylation is easily achieved.

3.6.2. Electrosynthesis of Symmetrical Ketones from Carbon Dioxide and Organic Halides

Catalytic electroreduction of carbon dioxide using nickel-2,2′-bipyridine complexes can be achieved in *N*-methylpyrrolidone or DMF with a sacrificial magnesium anode.[23]

$$2CO_2 + 2e \longrightarrow CO_3^= + CO$$

The formation of magnesium salts from oxidation of the anode are necessary as this avoids deactivation of the catalyst by formation of nickel carbonate. Under these conditions, electrolysis at constant current or constant potential of a mixture of carbon dioxide and alkyl bromide, benzyl or allyl halides afford the corresponding symmetrical ketone in good yields (60–90%).[75]

$$2RX + 2CO_2 + 4e \rightarrow RCOR + 2X^- + CO_3^=$$
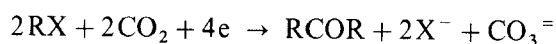
The reaction fails with aryl or vinyl halides which give mainly carboxylic acids.

To our knowledge no equivalent chemical reaction has been described.

3.6.3. Electrosynthesis of Cyclic Compounds from Activated Olefins and Organic dihalides

Electroreduction of a mixture of organic dihalides and activated olefins is a good method for the preparation of cyclic compounds.[76] The reaction can be easily performed in *N*-methylpyrrolidone, in the presence of an aluminum anode, to prepare three-, five- and six-membered cyclic products in good yields[77] (Scheme V).

$$n = 1, 3, 4$$
$$X = Br, Cl$$
$$Z = CO_2R, COR$$
$$Y = H, Ph, CO_2R$$
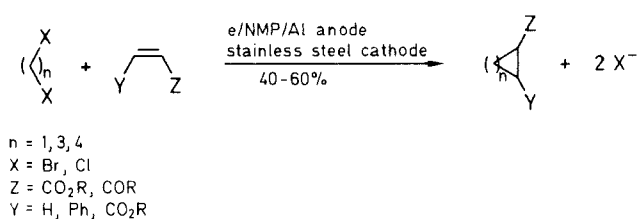
Scheme V

4. Future Prospects, Conclusions

4.1. Application of the Consumable Anode Process to the Synthesis of Complex Molecules

Section three has emphasized the wide range of synthetic applications of the electroreductive coupling of organic halides with various electrophiles. The electrochemical reaction can replace organometallic procedures such as the Grignard, Reformatsky, Ulmann, and Wurtz reactions with some practical advantages especially for industrial syntheses.

For example, 2-methyl-1-phenyl-2-propanol, an important intermediate for rose perfumes can be prepared in good yield in a single-step reaction[21,38] from benzyl chloride and acetone, without the handling of any dangerous organometallic intermediate, ethereal solvents or divided magnesium. Furthermore the electrochemical preparation avoids the formation of 1,2-diphenylethane as a byproduct.

Even organic halides which do not usually afford stable organometallics, such as bromoacetophenone,[13] *ortho*-dichlorobenzene,[13,35] and trifluoromethyltoluene[37] were readily carboxylated by electrolysis using a sacrificial anode.

Moreover this electrochemical method is by no means limited to organometallic reactions. For instance, electrocarboxylation of benzyl halides avoids the use of hazardous sodium cyanide for the synthesis of valuable arylacetic acids such as chlorophenyl-, fluorophenyl-, methoxylphenyl-, and naphthylacetic acids. The products are intermediates in the synthesis of pharmaceuticals and pesticides. The electrochemical route is even more attractive when one electrochemical step can replace several chemical ones. For example arylacetones which are starting materials for the synthesis of amphetamine-like drugs, are usually prepared from benzyl halides by a cyanation, acetylation, hydrolysis–decarboxylation reaction sequence. This three-step synthesis can be replaced by electroreduction of the benzyl halide in the presence of acetic anhydride.[43]

In other cases, completely new synthetic routes have been described, using an electrochemical reaction as the key step, thus avoiding dangerous reactions or expensive starting materials. For instance α-arylalkanoic acids (naproxen, ibuprofen, fenoprofen) can be obtained by electrocarboxylation of benzylic halides substituted in the α-positions,[11,12] instead of α-alkylation of an arylacetonitrile followed by hydrolysis to the carboxylic acid.

The synthesis of trifluoromethylbenzaldehyde, a pesticide intermediate, is another example where the electrochemical route[29] is much simpler than the chemical. It takes

advantage of the industrial availability of cheap parachlorotrifluoromethylbenzene (Scheme X). This compound is manufactured from chlorotoluene via chlorination and halide exchange as an important starting material for dinitroaniline herbicide, very large quantities of para-chlorotrifluoromethylbenzene are manufactured with sale prices as low as four dollars per kg.

CF₃—⟨⟩—Cl   →e/DMF→   CF₃—⟨⟩—CHO
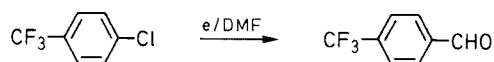
Scheme X

In the synthesis of 4,4'-difluoro-1,1'-diphenyl, the electrochemical process[19] avoids the use of benzidine which is carcinogenic (Scheme Y).

⟨⟩—F → F—⟨⟩—Br →e/Ni catalyst→ F—⟨⟩—⟨⟩—F
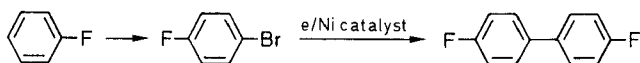
Scheme Y

4.2. Industrial Developments:

The above examples clearly demonstrate the preparative interest of the electroreduction of organic halides in aprotic solvents using consumable anodes. The main disadvantages of these electroreductions are the need for electrolytic cells specially adapted to the use of aprotic solvents, and the need for consumable electrodes. These cells must fulfill the following requirements:

- have an interelectrode gap narrow and constant, as well in time as in space;
- have consumable electrodes that are easy to replace;
- be run in explosive atmosphere;
- be operated under pressure (for gas handling).

Several such scale cells have recently been deviced for these reactions by CGE,[78]SNPE[79] and Silvestri.[80] SNPE has been operating a pilot unit for a few years. It is currently used for the manufacture of various fine chemicals such as diphenylacetic acid from chlorodiphenylmethane, ortho- and para-trifluoromethylbenzoic acid from chlorotrifluorotoluenes, arylpropionic acids from chloroethylarenes, and meta-trifluoromethylbenzylacetone from trifluoromethylbenzyl chloride.

Industrial grade magnesium is of sufficient purity for these reactions (PECHINEY manufacturer, 99.7%, costing about four dollars per kg). For most syntheses only about 0.2 kg of magnesium are consumed per kg of product which means about 0.8 dollar per kg. Magnesium salts are disposed of by standard procedures or can be transformed into valuable magnesium stearate.

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