ELECTRO ORGANIC REACTIONS

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Electro organic Reactions

Electrosynthesis in organic chemistry is the synthesis of chemical compounds in an electrochemical cell. The main advantage of electrosynthesis over an ordinary redox reaction is avoidance of the potential wasteful other half-reaction and the ability to precisely tune the required potential. Electrosynthesis is actively studied as a science and also has many industrial applications.

Experimental setup

The basic setup in electrosynthesis is a galvanic cell, a potentiostat and two electrodes. Good electrosynthetic conditions use a solvent and electrolyte combination that minimizes electrical resistance. Protic conditions often use alcohol-water or dioxane-water solvent mixtures with an electrolyte such as a soluble salt, acid or base. Aprotic conditions often use an organic solvent such as acetonitrile or dichloromethane with electrolytes such as lithium perchlorate or tetrabutylammonium acetate.

Electrodes are selected which provide favorable electron transfer properties towards the substrate while maximizing the activation energy for side reactions. This activation energy is often related to an over potential of a competing reaction. For example, in aqueous conditions the competing reactions in the cell are the formation of oxygen at the anode and hydrogen at the cathode. In this case a graphite anode and lead cathode could be used effectively because of their high overpotentials for oxygen and hydrogen formation respectively.

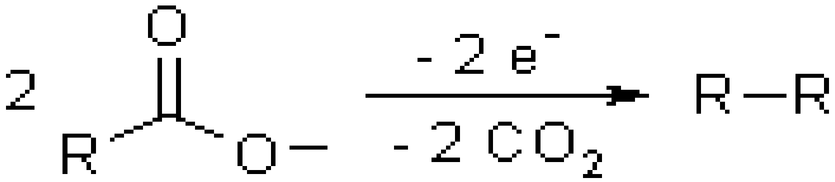
The two basic cell types are undivided cell or divided cell type. In divided cells the cathode and anode chambers are separated with a semiporous membrane. Common membrane materials include sintered glass, porous porcelain, polytetrafloroethane or polypropylene. The purpose of the divided cell is to permit the diffusion of ions while restricting the flow of the products and reactants. This is important when unwanted side reactions are possible. An example of a reaction requiring a divided cell is the reduction of nitrobenzene to phenylhydroxylamine, where the latter chemical is susceptible to oxidation at the anode.

- The yield of an electrosynthesis is expressed both in terms the chemical yield and current efficiency. Current efficiency is the ratio of Coulombs consumed in forming the products to the total number of Coulombs passed through the cell. Side reactions decrease the current efficiency.

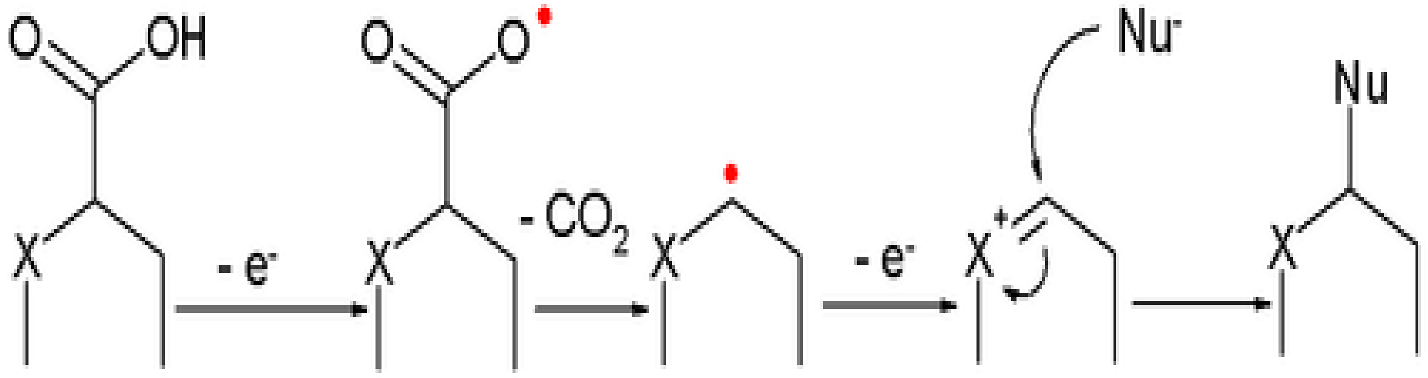
- The potential drop between the electrodes determines the rate constant of the reaction. Electrosynthesis is carried out with either constant potential or constant current. The reason one chooses one over the other is due to a trade off of ease of experimental conditions versus current efficiency. Constant potential uses current more efficiently because the current in the cell decreases with time due to the depletion of the substrate around the working electrode (stirring is usually necessary to decrease the diffusion layer around the electrode). This is not the case under constant current conditions however. Instead as the substrate's concentration decreases the potential across the cell increases in order to maintain the fixed reaction rate. This consumes current in side reactions produced outside the target voltage.

Anodic oxidations

The most well-known electrosynthesis is the Kolbe electrolysis, in which two carboxylic acids decarboxylate, and the remaining structures bond together:

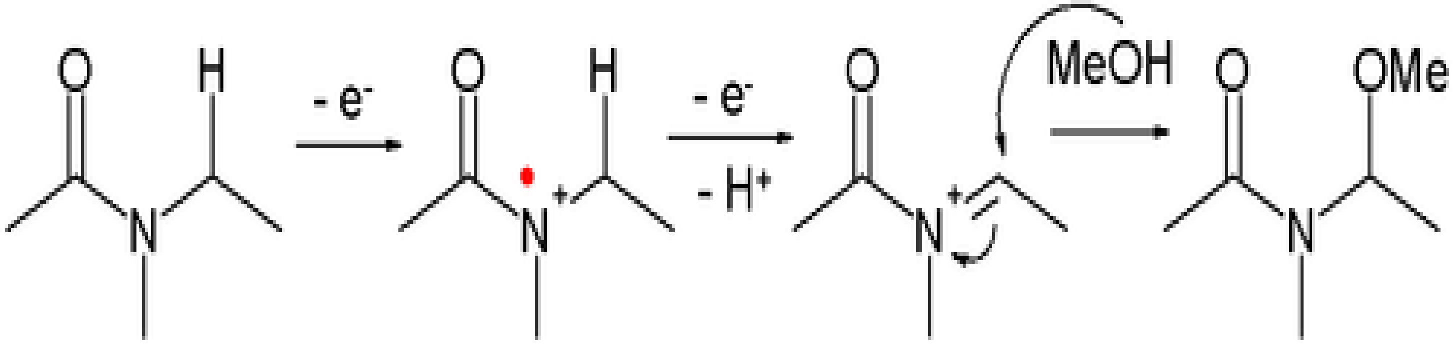


A variation is called the **non-Kolbe reaction** when a heteroatom (nitrogen or oxygen) is present at the α-position. The intermediate oxonium ion is trapped by a nucleophile usually solvent.



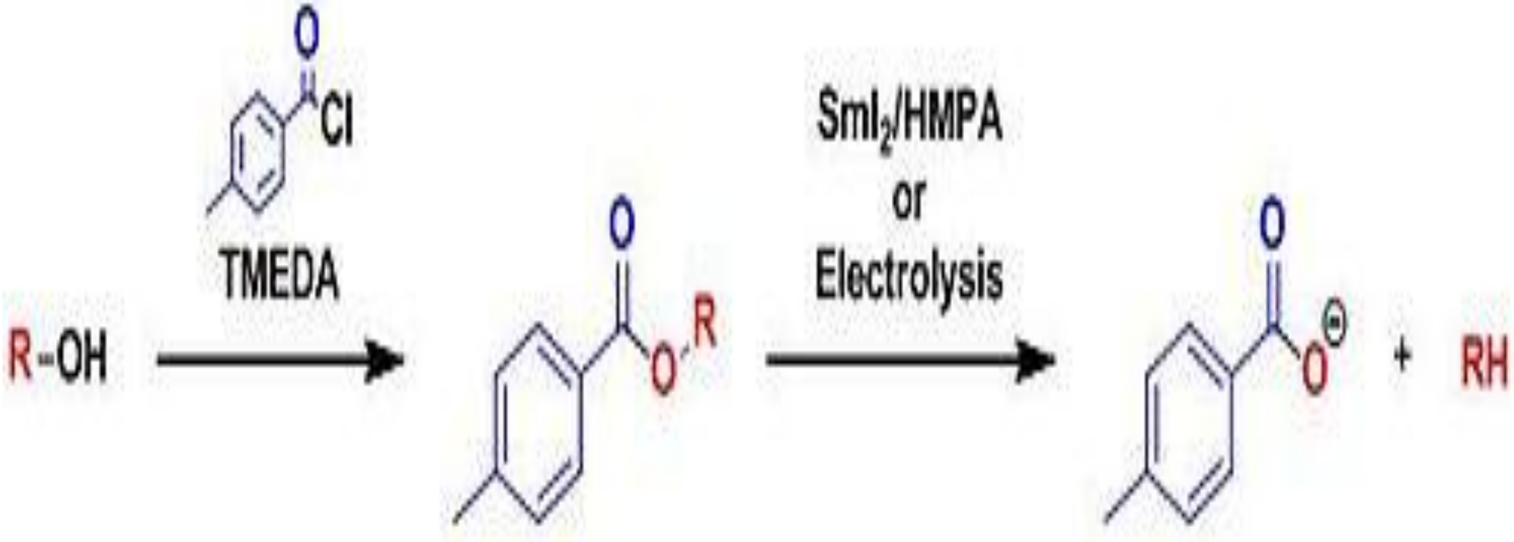
Amides can be oxidized to *N*-acyliminium ions, which can be captured by various nucleophiles, for example:

This reaction type is called a **Shono oxidation**.

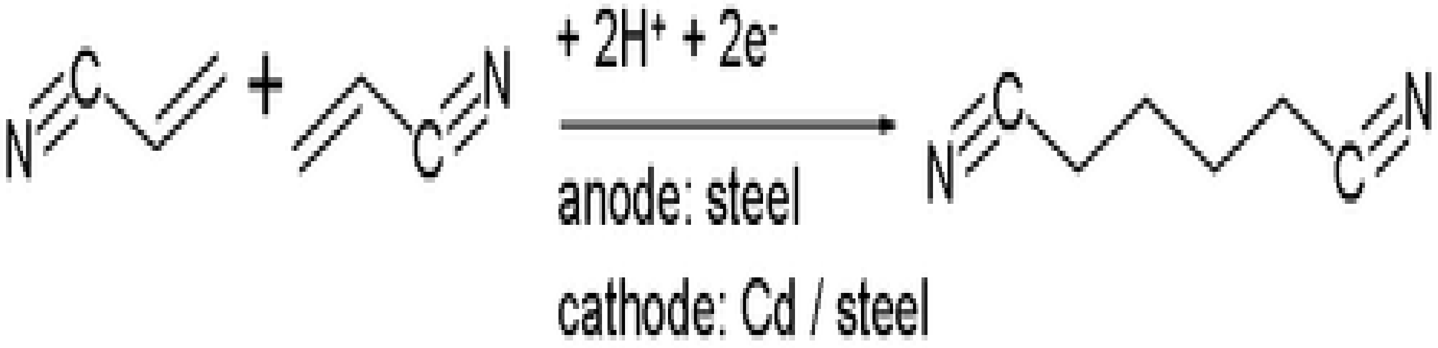


Cathodic reductions

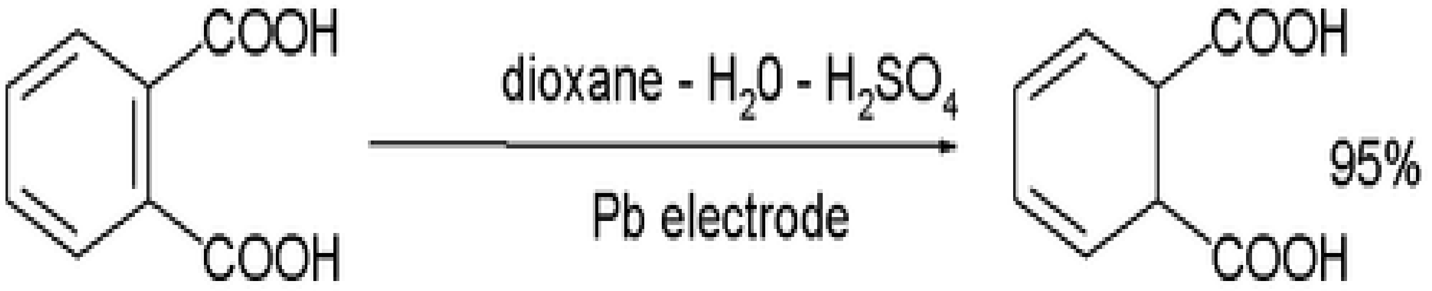
In the Markó–Lam deoxygenation, an alcohol could be almost instantaneously deoxygenated by electroreducing their toluate ester



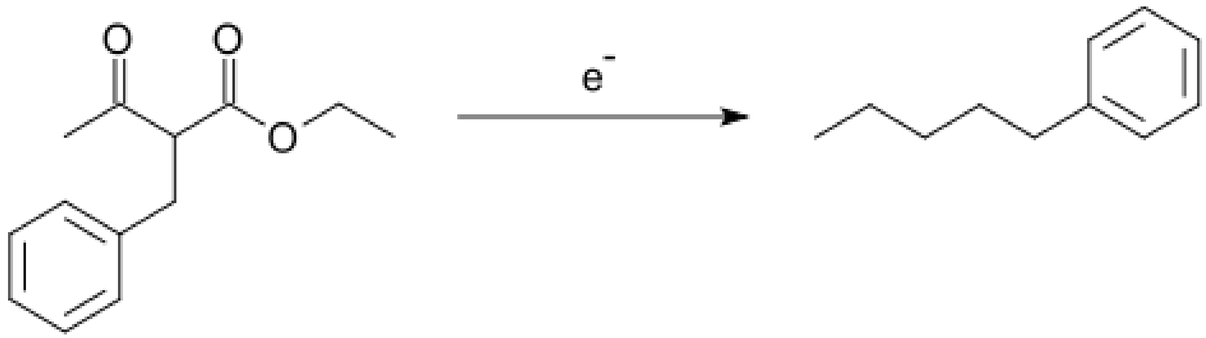
The cathodic hydroisomerization of activated olefins is applied industrially in the synthesis of adiponitrile from 2 equivalents of acrylonitrile:



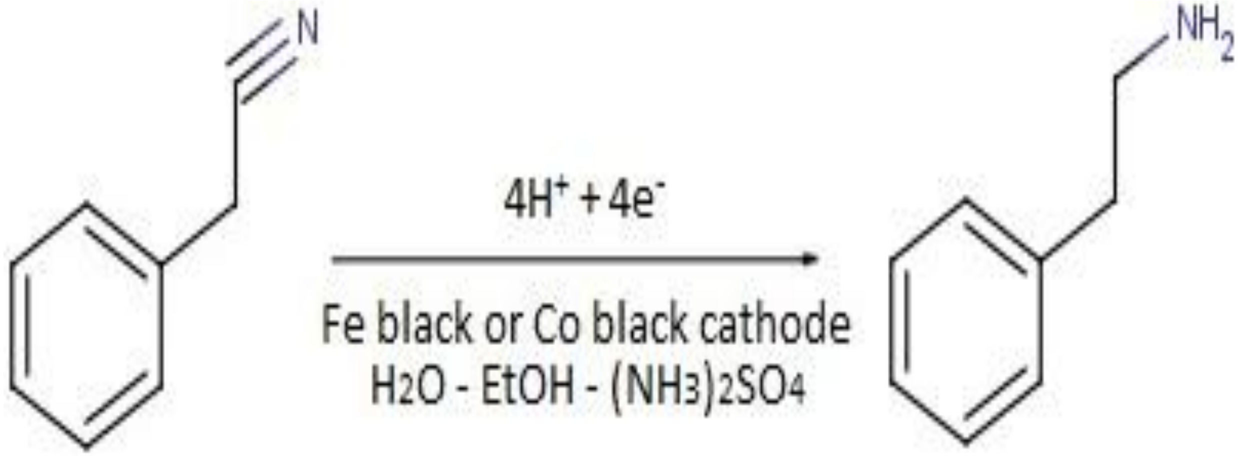
The cathodic reduction of arene compounds to the 1,4-dihydro derivatives is similar to a Birch reduction. Examples from industry are the reduction of phthalic acid



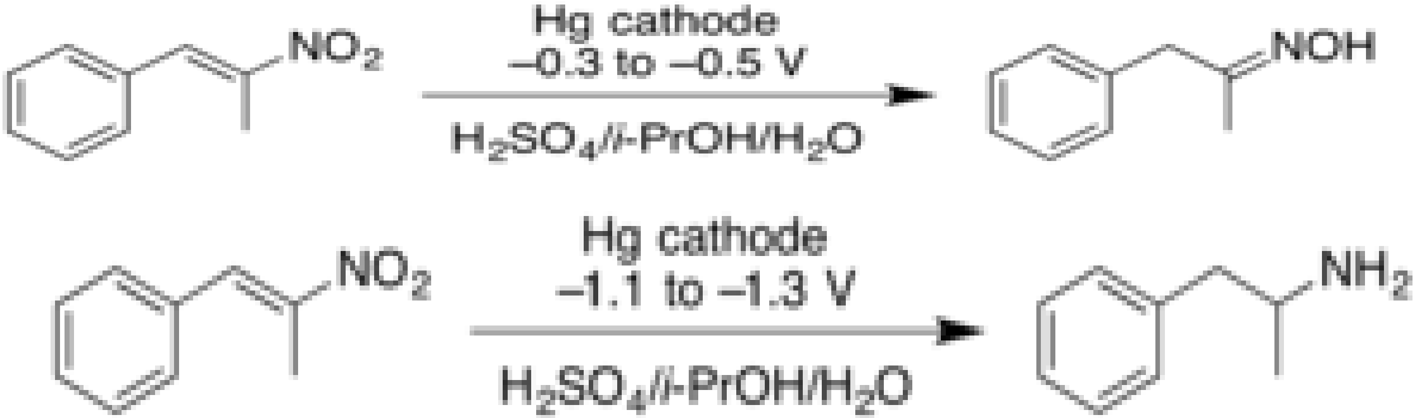
The Tafel rearrangement is important method for the synthesis of certain hydrocarbons from alkylated ethyl acetoacetate, a reaction accompanied by the rearrangement reaction of the alkyl group.



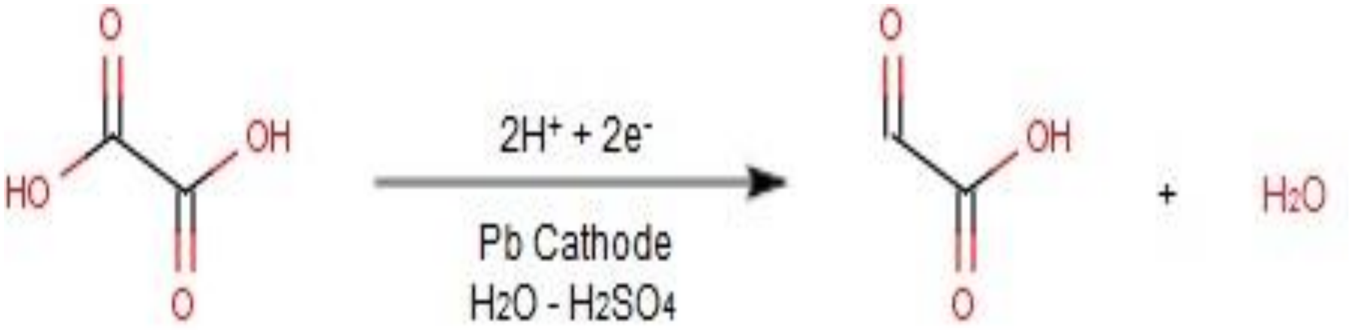
- The cathodic reduction of a nitrile to a primary amine in a divided cell



Cathodic reduction of a nitroalkene can give the oxime in good yield. At higher negative reduction potentials, the nitroalkene can be reduced further, giving the primary amine but with lower yield.



Cathodic reduction of a carboxylic acid (oxalic acid) to an aldehyde (glyoxylic acid) in a divided cell



Cathodic reduction of Nitro compounds

- It has been found that nitro methane can be reduced to methyl hydroxylamine in dilute HCl at constant current in a divided filter press cell with a Nickel, stainless steel or Monel 400 cathode. Unreacted nitromethane was distilled off and water removed to avoid decomposition.

Cathodic reduction of Halo group compounds

- The electrochemical reduction of mixture of R3SnCl in presence of organic chloride gives the corresponding coupling product. Since the reduction potential of R3SnCl is less negative than that of organic chloride, the reaction seems proceeds by the initial reduction of R3SnCl to generate stannyl ion which attacks the organic chloride nucleophilic R3SnCl.

Electrochemical Sensors

Electrochemical sensors have been used extensively either as a whole or an integral part of a chemical and biomedical sensing element. For instance, blood gas (PO_2, PCO_2, and pH) sensing can be accomplished entirely by electrochemical means. Many important biomedical enzymatic sensors, including glucose sensors, incorporate an enzymatic catalyst and an electrochemical sensing element. Electrochemical sensors are essentially an electrochemical cell which employs a two or three-electrode arrangement. Electrochemical sensor measurement can be made at steady-state or transient.

Industrial applications of photochemistry

The principal industrial applications of photochemistry have so far been in the fields of free-radical chlorination, sulfochlorination, sulfoxidation, and nitrosation. In addition, however, photochemical reactions are being utilized on an increasing scale for the synthesis of vitamins, drugs, and fragrances.

Photochemistry is an essential tool in both the manufacturing and the use of modern cars. Radiation curing is used as a very efficient, economically and ecologically attractive technology for the coating and bonding of many of the parts used in a car, and avoiding degradation of the coating due to photoinduced processes during the foreseen service time is a key issue.