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REVIEWS

Electroorganic Syntheses

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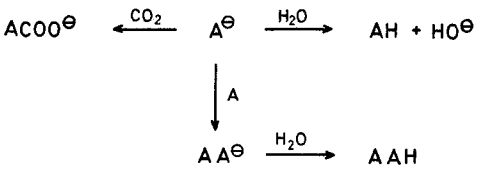
This review surveys the applications of electroorganic chemistry to the synthesis of organic compounds. Procedures are included for reactions which have been carried out for more than one example. Mention is also made of recent developments that have potential synthetic applicability.

Dieser Artikel gibt eine Übersicht über die Anwendungen der elektroorganischen Chemie auf die Synthese organischer Verbindungen. Die angegebenen Arbeitsvorschriften sind jeweils an mehreren Beispielen ausgeführt worden. Neuere Entwicklungen, die in der Zukunft synthetische Anwendung finden könnten, sind in der Abhandlung ebenfalls berücksichtigt.

Electrochemically one can prepare from organic compounds anions, anion radicals, radicals, cation radicals, and carbonium ions by direct electron transfer. All of these intermediates are reactive and are rarely isolated but they may undergo further reaction with the solvent, themselves, the electrode, added organic and inorganic compounds and form isolatable products. A selected example of this behavior is the reaction of generated carbanions (Scheme A).



Scheme A

In the present review, a brief resume of the general theory will be given, followed by a description of the equipment and its operation. There will then be a discussion, from a theoretical and practical viewpoint, of reactions at the cathode and anode and finally reactions in which inorganic intermediates

are formed and bring about chemical changes. The various techniques are illustrated by a number of procedures which were selected so that their yields are comparable to or may be better than those obtained by other methods. Mention is also made of other general reactions which have potential synthetic interest without specific details. Preparations carried out in connection with polarographic investigations in which products were usually identified by physical methods are not included.

1. Introduction

Electrolytic reactions are carried out by applying a suitable source of direct current to two electrodes dipping into an electrically conducting solution of the organic compounds. Since the great majority of organic compounds are non-conductors, acids, bases, or salts are used to provide electrical conductivity in the solution. These substances are chosen so that their reduction or oxidation occurs with more difficulty than that of the organic compound being studied. The decomposition potentials of various cations are shown in Figure 1.

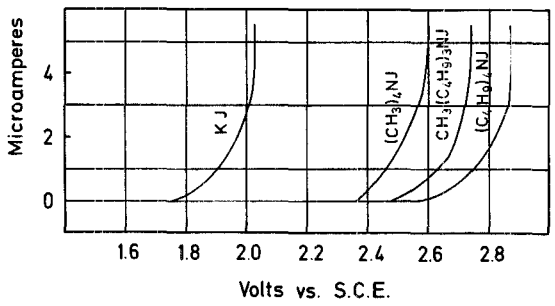


Figure 1. Discharge Potentials of Various Cations at a Mercury Cathode

For anodic processes in non-aqueous solvents, nitrates, tetrafluoroborates, hexafluorophosphates, and perchlorates are useful in attaining a maximum range of potential. The last named is hazardous for large-scale preparations.

Solvents used in electrolysis should have high dielectric constants in order to promote ionization of the electrolyte. Water, which is the best medium for doing this, has the disadvantage of not dissolving most organic compounds and therefore has to be used with miscible organic solvents such as alcohols, dioxane, acetone, acetonitrile, dimethylformamide, and cellosolves to effect solubilization.

Acetonitrile, dimethylformamide, propylene carbonate, dimethyl sulfoxide, acetone, hexamethylphosphortriamide, and dichloromethane have high enough dielectric constants to be used alone in electrolyses. Electrolytes in these possibilities are limited to lithium salts, alkali metal iodides, and tetraalkylammonium salts.

Solubilization of certain organic compounds without organic solvents can also be accomplished with concentrated solutions of alkali metal and tetraalkylammonium salts of arenesulfonic acids. These salts, which are known as McKee's salts[1], are used in concentrations of 30–56%, have the additional advantage of giving solutions with a low resistance and allow operations at high current densities. A saturated solution of sodium potassium (30%) xylenesulfonate (100 ml) at 50° will dissolve 52 g of nitrobenzene. Tetraethylammonium tosylate in a concentration of 56% will dissolve 40% acrylonitrile[2]. Such solutions can be varied in pH and can be used for oxidation and reduction reactions.

The feasibility of reducing or oxidizing an organic compound in the desired manner in a given system can be determined quickly in most examples by polarography. This technique can indicate the number of electrons involved and the type of intermediate formed. Exceptions are reductions which occur at or near that of hydrogen evolution. Polarographic measurements for such examples will show no polarographic wave but may show a shift of the residual or background current to more positive potentials.

The final products actually obtained in large-scale preparations will not always be the same as that predicted by polarography. The conditions used for the two methods are different; polarography is based on a diffusion-controlled process and the large-scale electrolysis uses vigorous stirring. Intermediates formed at the electrode in the latter method can therefore be removed from the electrode and transferred into the bulk of the solution where they undergo chemical reactions.

The half-wave potential obtained polarographically for the reduction or oxidation of the compound concerned can be used as the basis for the potential applied to the working electrode in large-scale electrolysis using controlled potentials. This technique is required if two or more reactive groups are present in the molecule and only one type of reduction or oxidation is desirable. For compounds in which the reduction potentials of the two groups differ greatly or if the reduction of the second group occurs at the same point as the hydrogen evolution, selectivity can be obtained by regulating the current density so that no hydrogen is evolved and using the theoretical amount of current necessary for the reduction of the more easily reducible group. For example, if 4-nitrobenzoic acid is reduced in sulfuric acid solution at a lead cathode with an unlimited amount of current, 4-aminobenzyl alcohol will be the main product. By using just 6 Faradays of electricity, 4-aminobenzoic acid is formed.

[1] R. H. McKee, Ind. Eng. Chem. **38**, 382 (1946).
[2] M. M. Baizer, J. Electrochem. Soc. **111**, 215 (1964).

Selectivity may be also attained by using solid electrodes with different hydrogen-overvoltage characteristics. Cathodes with a low hydrogen overvoltage would limit the reduction to easily reducible groups.

All electrochemical preparations are carried out with direct current. The voltages necessary to carry out the electrolysis will depend upon the resistance of the solution. For non-aqueous solutions where resistances of 1000 ohm or higher are encountered, voltages of 100 volt may be necessary to obtain a current flow with a workable magnitude.

The source of supply may be a direct-current generator, a storage battery, battery eliminator (Heath), or an electronic power supply. If a direct-current generator of 100 volt is available, a slidewire with suitable resistance should be satisfactory for maintaining the desired amperage. The wiring diagram is shown in Figure 2.

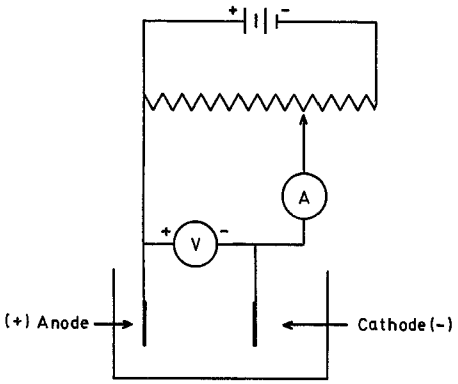


Figure 2. Simple Circuit for Electrolysis

The apparatus is modified for controlled-potential electrolysis by using a reference electrode in conjunction with the working electrode (Figure 3). The potential may be controlled manually by observing the potential between the working electrode and the reference electrode with a vacuum tube voltmeter, or more accurately with a potentiometer and regulating the applied voltage with a rheostat.

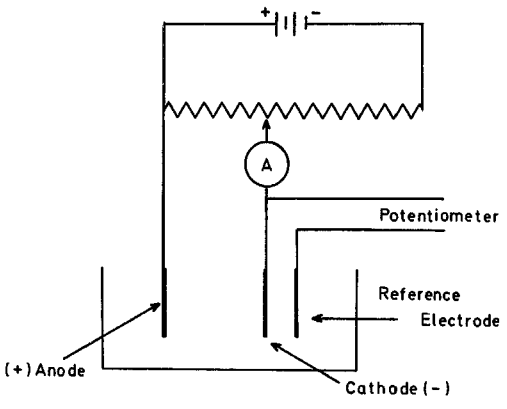


Figure 3. Simple Circuit for Controlled-Potential Electrolysis

To avoid the constant supervision in the above-described controlled-potential electrolysis, an automatic device known as a potentiostat may be substituted for the operator to control the potential during the electrolysis. Instruments of this type are available commercially or can be constructed.

In most of the electrolytic preparations, a divided cell must be used. The cathode is separated from the anode in order to prevent the reduced product from being reoxidized and vice versa. Separation of the electrolyte into anolyte and catholyte may be conveniently accomplished by use of a porous cup (Figure 4), a fine sintered glass disc, or an ion exchange membrane such as Amberplex[3] (Figure 5). The last one requires two separate cell compartments which are joined together by a large diameter tube containing the diaphragm.

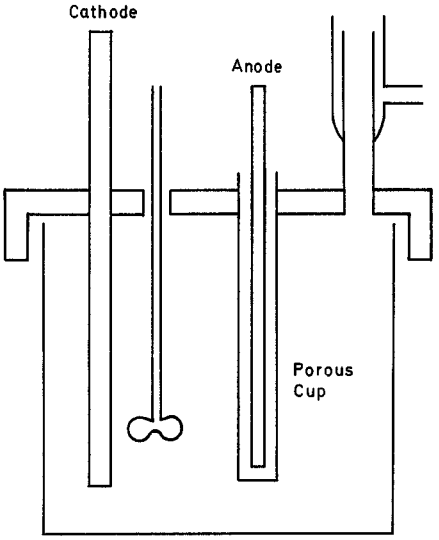


Figure 4. Electrolysis Cell with Porous Cup

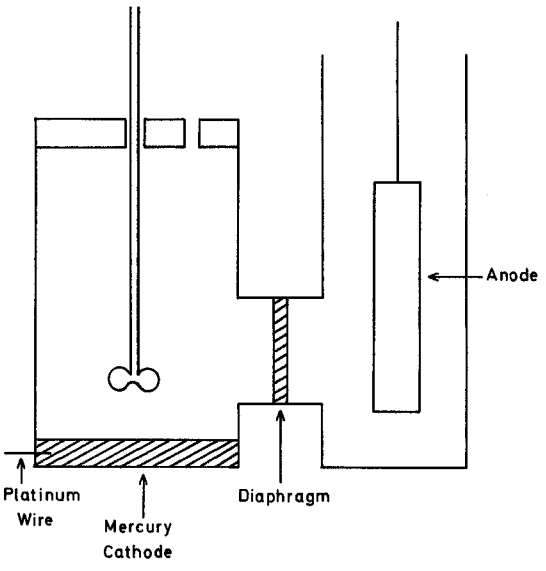


Figure 5. Diaphragm Cell for Electrolysis

[3] Rohm & Haas Co., Philadelphia, Pa.

The use of the porous cup involves placing one electrode within the cup and the other electrode on the outside. The porous cup should have thin walls so that it will absorb a minimum of the organic material and be resistant to acid or alkali. Alundum and unglazed porcelain cups have proved satisfactory but other materials may be used. Such cups when used should be equilibrated in the solvent being employed before the electrolysis.

Both of these cells can be modified for controlled-potential electrolysis by insertion of a reference electrode next to the working electrode. Connection to a mercury cathode may also be made by means of a platinum wire sealed into a glass tube which is filled with mercury as a conductor. The platinum wire is then submerged in the mercury.

In electrolytes where heat is generated, the cell may require external cooling or may be fitted with a condenser to prevent evaporation of the solvent. If elevated temperatures are required, the cell is heated by the most expeditious method.

A new technique which employs fluidized-bed electrodes offers the possibility of obtaining higher overall currents in relatively small cells than are ordinarily possible at a plane electrode[4].

In summary, the following conditions must be considered in carrying out electrolytic reactions:

- the type and concentration of the electrolyte,
- the concentration of the organic compound,
- the potential of the electrochemical reaction.

If the space occupied by the working electrode is large compared with that occupied by the electrolyte, stirring may not be necessary. In most examples, stirring is advantageous and is carried out mechanically with a separate stirrer or in the case of solid electrodes by rotating the electrode.

2. Reductions

Numerous electrolytic reductions of organic compounds have been carried out in yields which compare favorably with those by chemical methods. Listing of such reductions is given in a number of reviews[5,6].

[4] J. R. BACKHURST et al., J. Electrochem. Soc. **116**, 1600 (1969).

[5] S. SWANN, Trans. Electrochem. Soc. **69**, 287 (1936); **77**, 459 (1940); **88**, 103 (1945); **99**, 219 (1952).

[6] F. D. POPP, H. P. SCHULTZ, Chem. Rev. **62**, 19 (1962).

[7] L. GATTERMANN, H. WIELAND, *Die Praxis des organischen Chemikers*, 41th Edit., Walter de Gruyter & Co., Berlin, 1962, p. 273.
L. GATTERMANN, H. WIELAND, *Laboratory Methods of Organic Chemistry*, MacMillan, New York, 1937, p. 317.

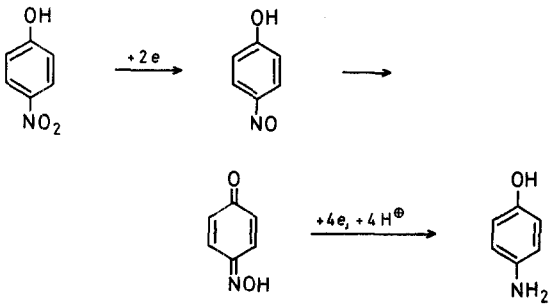
[8] P. H. RAVENSCROFT, R. W. LEWIS, O. W. BROWN, Trans. Electrochem. Soc. **84**, 145 (1943).

2.1. Reduction of Aromatic Nitro Compounds

Aromatic nitro compounds are readily reduced to amines, *p*-aminophenols, azoxy compounds, azo compounds, hydrazo compounds, and benzidines in aqueous or aqueous-alcoholic solution. The course of the reaction will depend upon the pH of the solution. The nitro group when attached to an aromatic ring is one of the easiest groups to reduce electrochemically; the potential required is low and allows the preferential reduction of this group in the presence of other groups by controlling the potential, current density, or using a metal with a low hydrogen overvoltage.

The reduction to the amine requires solutions of sulfuric acid or hydrochloric acid. The acid concentration should not be too high, or rearrangement of the intermediate phenylhydroxylamine to *p*-aminophenol or its derivatives is a competing reaction.

Exceptions are *o*- and *p*-nitrophenols, *o*- and *p*-nitroanilines and N-substituted anilines. The nitro group in these compounds is reduced to amines even in alkaline medium. The intermediate nitroso compound rearranges to the oximinoquinone or oximinoquinone imine which is reduced more easily to the corresponding aminophenol or phenylenediamine than the nitro compound.



Groups substituted in the *p*-position to the nitro group prevent the rearrangement of the intermediate hydroxylamine in acid medium; the yields of amine are therefore high.

The electrolytic method for the preparation of amines has the advantage over the chemical method when the resulting amine is difficult to recover from salts formed by the use of reducing agents such as stannous chloride. In the latter operation, separation of the amine from the stannic chloride may be accomplished electrochemically by placing in the mixture a carbon rod as a cathode and a small porous cup containing a carbon rod as an anode in a solution of 2 *N* sulfuric acid. Electrolysis is carried out until hydrogen evolution on the cathode is strong and the tin is deposited on the cathode[7].

[9] F. M. BRIGHAM, H. S. LUKENS, Trans. Electrochem. Soc. **61**, 281 (1932).

4-Aminobenzoic Acid[8]:
Anode: Platinum gauze (5 × 5 cm).
Anolyte: 35.6% sulfuric acid (30 ml) in a porous cup (60 ml capacity).
Cathode: Lead plated with a thin layer of spongy lead (area 0.833 dm^2 on one side).
Catholyte: 8.7% hydrochloric acid (500 ml) in a 1000-ml beaker.
Starting Material: 4-Nitrobenzoic acid (15 g).
The reaction is carried out at 70° with a current density of 6 amp/dm^2. The current density is calculated for one side of the cathode and the theoretical amount of current is used. Evaporation of the catholyte gives 4-aminobenzoic acid hydrochloride, which is purified by dissolving in a minimum amount of distilled water and filtering. Titration with alkali liberates 4-aminobenzoic acid; yield: 92%; m.p. 186°.

The reduction of aromatic nitro compounds to *p*-aminophenols, or the Gattermann reaction, proceeds at platinum, carbon, or a low hydrogen-overvoltage cathode in strong sulfuric acid. At these cathodes, the hydroxylamine produced is rearranged faster to *p*-aminophenol by the acid than it can be reduced to the aniline.

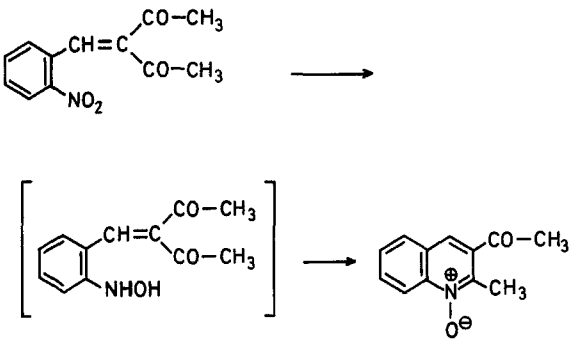
4-Aminophenol[9]:
Anode: Lead cylinder.
Anolyte: 50–75% sulfuric acid.
Cathode: Nickel, graphite, or platinum.
Catholyte: 50% sulfuric acid.
Starting Material: Nitrobenzene; the ratio of nitrobenzene to catholyte is 1.25:4.
Agitation is necessary to keep the nitrobenzene in uniform suspension. The current density is set at a value which is just below that which causes evolution of hydrogen; the temperature is maintained at 25–60°. About 90% of the theoretical current gives the best yields. At the conclusion of the electrolysis, the catholyte is poured into a distilling flask and the apparatus and electrode are thoroughly rinsed with distilled water and the washings are combined with the major portion of the electrolyte. Distillation at 100° at reduced pressure (10–20 mm) removes all the unchanged nitrobenzene and part of the water. On cooling, crystals of 4-aminophenol sulfate separate and are filtered. The crude sulfate is dissolved in a small amount of water, sodium hydrogensulfite is added to prevent oxidation, and the crude base is liberated with sodium hydrogencarbonate solution. Recrystallization from water containing sodium hydrogensulfite and using decolorizing carbon gives the 4-aminophenol in 50–60% yield.

Frequently, *p*-aminophenols are used for the preparation of quinones. In such preparations, the catholyte is diluted with water, treated with cooling with an aqueous solution of potassium dichromate and allowed to stand for 12 hours. Extraction with ether until the extracts become nearly colorless followed by steam distillation of the extracts gives the quinone. Yields of 3-chloro-2-methyl-*p*-benzoquinone[10] corresponding to 67–78% were obtained from the reduction of 6-chloro-2-nitrotoluene; yields of 58–63% of chloro-*p*-benzoquinone were obtained from *o*-chloronitrobenzene[11].

[10] J. Cason, C. F. Allen, S. Goodwin, J. Org. Chem. **13**, 403 (1948).
[11] R. E. Harman, Org. Syntheses, Coll. Vol. IV, 148 (1963).

The electrolytic reduction of aromatic nitro compounds to phenylhydroxylamines is difficult and would require controlled potential and very dilute acid in order to keep the rearrangement to the *p*-aminophenols at a minimum. This type of reduction is successful and useful if suitable reactive groups are present in the *o*-position. The hydroxylamino group reacts as soon as it is formed with the group and forms a heterocyclic compound.

Reduction of 3-nitrophthalic acid gives 3-oxobenzo-1,3-oxazoline-4-carboxylic acid[12] and reduction of suitably substituted aromatic nitro compounds gives heteroaromatic N-oxides[13], or benzotriazines[14].



Aromatic nitro compounds have been reduced electrolytically to azoxybenzenes, azobenzenes, and hydrazobenzenes in alkaline solution using cathodes with low hydrogen overvoltage. Since the reduction potentials at the same pH as determined by polarography are rather similar [nitrobenzene −0.54 volt, azoxybenzene −0.55 volt, and azobenzene −0.31 volt (S.C.E.)] the experimental conditions must be carefully manipulated in order to produce a specific product.

Reduction to azoxy compounds has in general been carried out by suspending or dissolving the nitro compound in an alkaline catholyte and reducing at a nickel cathode. Advantage has been taken of the insolubility of the azoxy compound which precipitates from the solution and out of contact with the cathode. The same technique can be applied for difficultly soluble nitro compounds, for which alcohol is added as a solvent. The amount of alcohol can be limited so that the azoxy compound will precipitate as it is formed.

In order to prepare the azo compounds the azoxy compound must be kept in solution for further reduction. The solubility of the latter can be increased by adding more alcohol to the catholyte or salts of aromatic sulfonic acids (McKee's salts). On the basis of reduction potentials, the hydrazobenzene would be expected to be formed but this compound can act as a reducing agent for the intermediate nitro, nitroso, or azoxy compound. When formed with the azo compound it can be oxidized to the azo compound by blowing air through the solution.

Hydrazobenzenes are formed from azo compounds by reduction using a lower current density (potential) than that necessary for the formation of the azo compound from the nitro derivative. They may also be prepared directly from the nitro compounds.

Reduction of azoxy and azo compounds in acid catholytes will form benzidines; the intermediate hydrazo compound is rearranged by acid to the benzidine.

Azo Compounds:
Anode: Lead cylinder (sheet lead of 1 mm thickness).
Anolyte: Saturated sodium carbonate solution in a porous cup of 5 mm wall thickness, 18 cm high, and 6 cm in diameter.
Cathode: Nickel screen which is wound around the porous cylinder and extends a little below the edge of the cup and is folded underneath.
Catholyte: 70% ethanol (200 ml) containing sodium acetate (5 g).
Example; Azobenzene: Nitrobenzene (20 g) is dissolved in the catholyte (200 ml). The electrolysis is carried out at 70°. It is started with 16–20 amp and continued until hydrogen evolution at the cathode is observed. The heat generated will cause the solution to boil so that the ethanol lost must be replaced. When the electrolysis is finished, the catholyte is poured into a flask and the small amount of hydrazobenzene formed is oxidized by blowing air through the solution. Upon cooling, azobenzene crystallizes. The yields are almost quantitative.

Azoxy Compounds:
The conditions used are the same as those described for the preparation of azobenzene except that the cell is cooled in ice. A cold saturated sodium carbonate solution serves as the anolyte and ethanol saturated with sodium acetate as the catholyte.
Example; 4,4'-Dipropyloxyazoxybenzene: 4-nitrophenyl propyl ether (10 g) is dissolved in the catholyte (200 ml). The electrolysis is carried out with a 3 amp current. The greater part of the reaction product crystallizes from the catholyte and is filtered. The filtrate will yield more of the product upon the addition of water; yield: 3.4 g.

Hydrazobenzene:
The same method is used as is given for the preparation of azobenzene. The electrolysis is not stopped at the azo stage but is continued at a lower current density (one fourth) until the theoretical ampere hours are passed through the cell. Then another half-ampere hour is allowed to pass through at 2 amp, because in the second phase a small evolution of hydrogen at the cathode cannot be avoided. The yellowish catholyte is cooled during the last stage by setting the beaker in cold water. The main crop of the hydrazobenzene crystallizes and is filtered, and the crystals are washed with water containing sulfur dioxide, and then with ethanol and petroleum ether.

2.2. Reduction of Aliphatic Nitro Compounds

Aliphatic nitro compounds have been reduced to hydroxylamines in an acid catholyte at nickel or electroplated copper or mercury cathodes. The hydroxylamine formed is difficult to work with and is usually isolated as a derivative. The nitroso compound is apparently an intermediate in this reduction, and has been detected visually in the reduction of 2-nitro-2-methylpropane[15]. Isolation of this intermediate is difficult due to acid hydrolysis.

The nitroso compound or, if enolization is possible, the oxime, is the precursor for the amines formed in the electrolytic reduction of nitroparaffins in acid medium using lead or mercury cathodes. The hydroxylamine is not affected under these conditions.

Using controlled potentials, alkylhydroxylamines were obtained in yields of 59–81% from nitromethane, nitroethane, and 1- and 2-nitropropane[16]. *t*-Butylhydroxylamine is formed in 90–95% yield from 2-nitro-2-methylpropane.

2-Acetoxyamino-1-(3,4-dimethoxyphenyl)-1-hydroxypropane[17]:
Anode: Lead.
Anolyt: 20% Sulfuric Acid in a porous cup.
Cathode: Copper-plated copper.
Catholyte: Ethanol (160 ml), acetic acid (80 ml), and concentrated hydrochloric acid (12 ml).
Starting Material: 1-Acetoxy-1-(3,4-dimethoxyphenyl)-2-nitropropane (12 g).
The electrolysis is carried out at 30° using a current density of 0.04 amp/dm^2; 1.2–1.4 of the theoretical current is passed through the solution. The catholyte is treated with a concentrated aqueous solution of sodium acetate (12 g) and evaporated under reduced pressure. The residue is treated with water and the acetoxyamino derivative is isolated by filtration and washed with water; yield: 8.4 g. Recrystallization from methanol gives the pure compound; m.p. 176.

1-(Aminomethyl)-cyclohexanol[18]:
Anode: Lead plates.
Anolyte: 10% Sulfuric acid (700 ml) in a 2-l baker.
Cathode: Lead plate in a cylindrical porous cup 8 cm in diameter and 12.5 cm in height.
Catholyte: 10% Sulfuric acid (400 ml).
Starting Material: 1-(Nitromethyl)-cyclohexanol (53 g).
The nitro compound is added in 2 equal portions to the cathode compartment; the first portion is added at the beginning of the operation, the second 4 hr later. The material is kept in suspension by efficient mechanical stirring. The electrolysis is carried out at 30° with an 8 amp current and a density of 0.067 amp/cm^2 for 9 hr. The reaction mixture is adjusted to pH 4–5 and filtered. The filtrate is evaporated to dryness and the sulfate recrystallized several times from ethanol/water; yield: 77–83%; m.p. 266–267°.

α,β-Unsaturated nitro compounds are reduced to amines at lead or mercury cathodes.

2-Amino-1-(3,4,5-trimethoxyphenyl)-ethane[19]:
Anode: Lead or carbon.
Anolyte: 20% Sulfuric acid (200 ml) in a porous cup (75 × 160 mm).
Cathode: Lead sheet (220 × 90 × 2 mm).
Catholyte: Ethanol (100 ml), acetic acid (100 ml), and concentrated hydrochloric acid (50 ml).
Starting Material: ω-Nitro-3,4,5-trimethoxystyrene (30 g).
The electrolysis is carried out at 20° for 12 hr at 5–6 amp. The

[12] K. Gleu, K. Pfannstiel, J. prakt. Chem. [2] **146**, 129 (1936).
[13] H. Lund, L. G. Feoktistov, Acta Chem. Scand. **23**, 3482 (1969).
[14] S. Kwee, H. Lund, Acta Chem. Scand. **23**, 2711 (1969).
[15] P. E. Iversen, H. Lund, Tetrahedron Lett. **1967**, 4027.
[16] P. E. Iversen, H. Lund, Acta Chem. Scand. **19**, 2303 (1965).
[17] V. Bruckner, Liebigs Ann. Chem. **518**, 226 (1935).
[18] F. F. Blicke, N. J. Doorenbos, R. H. Cox, J. Amer. Chem. Soc. **74**, 2924 (1952).
[19] K. H. Slotta, G. Szyszka, J. prakt. Chem. [2] **137**, 339 (1933).

solvent is removed under reduced pressure and the residue is dissolved in water and extracted with ethyl acetate and ether. The amine is liberated from the aqueous layer with sodium hydroxide; yield: 77%.

Nitro- and nitrosoamines are reduced to hydrazines in acid medium at lead, mercury, cadmium, copper, and galvanized copper cathodes.

For the reduction of a nitroamine, see the directions for the reduction of nitrourea to semicarbazide[20].

N-Aminoisoindoline[21]:
Anode: Platinum.
Anolyte: 15% Sulfuric acid (20 ml).
Cathode: Lead or cadmium (4.5 × 5 cm).
Catholyte: 10% Sulfuric acid (108 ml).
Starting Material: N-Nitrosoisoindoline (5.0 g).
The electrolysis is carried out with a current of 3 amp and a current density of 4.45 amp/cm² for 3.75 hr. The catholyte after extraction with ether is made alkaline and steam-distilled. The product in the distillate is obtained in 72% yield using a lead cathode and 91.7% yield using a cadmium cathode.

2.3. Reduction of Aldehydes and Ketones and their Derivatives

Aldehydes and ketones are reduced electrolytically to glycols, pinacols, and alcohols. Aliphatic ketones with no branched chains on the carbon atoms adjacent to the carbonyl group have been reduced to the corresponding hydrocarbons. A similar reaction is observed with ketone groups attached to aromatic rings.

The formation of glycols electrolytically from aldehydes has been limited mainly to aromatic aldehydes and has been carried out in both acid and alkaline media with the latter medium being used more frequently. Under acid conditions, the ratios of *dl*- to *meso*-hydrobenzoin formed are in the same range (1.0–1.3) as those reported for photochemical reduction. In the presence of adsorbed ions such as iodide and tetraethylammonium ions, more *meso*-hydrobenzoin is formed; ratios of *dl* to *meso* as low as 0.5 are observed[22].

1,2-Bis-[4-dimethylaminophenyl]-1,2-dihydroxyethane[23]:
Anode: A smooth sheet of platinum bent to encircle the inner surface of a porous cup 8 cm high by 3 cm in diameter.
Anolyte: 5% Potassium hydroxide in 50% ethanol.
Cathode: Mercury in an amount sufficient to cover the bottom of a 150-ml beaker. The saturated-calomel reference electrode is placed adjacent to the cathode.
Catholyte: 5% Potassium hydroxide in 50% ethanol (75 ml).
Starting Material: 4-Dimethylaminobenzaldehyde (5 g).
The electrolysis was carried out at 35° at a controlled potential of −1.9 volt, the initial current was 3.3 amp. Eight minutes after initiation of the reduction, crystals appeared and at the end of 21 min., a current plateau of 0.5 amp was reached which indicated completion of the reaction. The crystals were filtered and recrystallized from ethanol and were the higher melting isomer; yield: 1.95 g; m.p. 178–179°. Addition of an equal volume of water to the filtrate gave the lower melting isomer; which was recrystallized from ethanol/petroleum ether (b.p. 65–85°; 1:9); yield: 2.9 g; m.p. 112–113°.

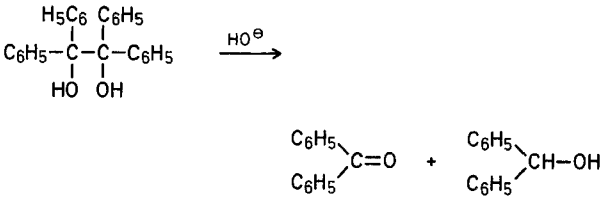
Aliphatic aldehydes are reduced to glycols at a electrodeposited tin cathode at pH 9. The maximum yield is obtained by the reduction of solutions containing 25 vol.% of aldehyde with a current density of 6 amp/dm². The yield of glycol increased with increasing length of the carbon chain[24].

The formation of pinacols from ketones has been limited mainly to alkyl aryl ketones. Exceptions are acetone and a variety of steroidal ketones[25].

2,3-Bis-[4-aminophenyl]-2,3-dihydroxybutane[26]:
Anode: Smooth platinum.
Anolyte: 1.6 *N* hydrochloric acid.
Cathode: Cast tin (99.9% purity or better) with a surface area of 100 cm².
Catholyte: 1.6 *N* hydrochloric acid (100 ml).
Starting Material: 4-Aminoacetophenone (13.5 g).
The electrolysis is carried out at 24–30°. A current of 1 amp is allowed to flow through the solution with an initial current density of 0.01 amp/cm². During the course of the reduction, the current diminishes to 0.84 amp (after 4 hr). Approximately 1.5 l of hydrogen is evolved, the rate of evolution increasing toward the end of the reaction. After 5.3 hr (twice the time theoretically required), the catholyte is evaporated under reduced pressure. The resultant residue (10.2 g) is treated with a saturated aqueous solution of potassium carbonate until the mixture is strongly alkaline. The pinacol liberated is recrystallized from acetone; yield: 40%; m.p. 248–249°.

The same preparation at a mercury cathode using controlled potentials gave yields varying from 26.3 to 62.6%. Chemical methods gave only the carbinol[27].

Aromatic ketones involving two aromatic groups are reduced to the pinacol in acid medium and in alkaline medium to the alcohol. The expected pinacol under the latter conditions is cleaved to the alcohol and ketone; the net result is the formation of high yields of the alcohol[28].



Aliphatic ketones are reduced to alcohols at mercury, lead, and cadmium electrodes in alkaline medium.

[20] A. W. INGERSOLL, L. J. BIRCHER, M. M. BRUBAKER, Org. Syntheses, Coll. Vol. I, 485 (1941).
[21] E. W. COOK, W. G. FRANCE, J. Phys. Chem. **36**, 2383 (1932).
[22] V. J. PUGLISI, G. L. CLAPPER, D. H. EVANS, Anal. Chem. **41**, 279 (1969).
[23] M. J. ALLEN, J. Org. Chem. **15**, 435 (1950).
[24] V. G. KHOMYAKOV, A. P. TOMILOV, B. G. SOLDATOV, Elektrokhimya **5**, 850, 853 (1969).
[25] H. LUND, Acta Chem. Scand. **11**, 283 (1957).
P. BLADON, J. W. CORNFORTH, R. H. JAEGER, J. Chem. Soc. **1958**, 863.

3-Methylpentane-2,4-diol[29]:
Anode: Nickel sheet.
Anolyte: Saturated solution of potassium carbonate.
Cathode: Mercury (400 cm^2).
Catholyte: 10% potassium hydrogencarbonate solution (2000 ml).
Starting Material: 4-Hydroxy-2-oxo-3-methylpentane (406 g).
The electrolysis is carried out with stirring at 20° and with a good stream of carbon dioxide passing through to buffer the solution. A current of 11 amp at 23 volt is used for 22 hr. The catholyte upon concentration under reduced pressure gives a solid mixed with an oil which is separated and fractionated under reduced pressure; yield: 273 g (66%); b.p. 124–126°/36 mm.

In the presence of conductive chiral salts such as (−)-ephedrine hydrochloride, the reduction of acetophenone gave a 44% yield of (*R*)-(+)-C_6H_5—$CH(CH_3)$-OH with an optical purity of 4.2%[30].

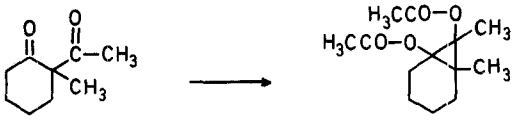
Nitrogen derivatives of carbonyl compounds have been reduced to amines. Both aldoximes and ketoximes have been reduced to amines in sulfuric acid solution at lead, mercury, tin, and carbon cathodes[31].

Schiff's bases of benzophenone have been reduced to amines in alkaline solution at lead cathodes[32].

Acetophenone-N-benzylimine in the presence of conductive chiral salts is reduced to N-benzyl-α-phenethylamine with optical purity varying from 5.3–7.3%[33].

2-Chlorocyclohexanone in an ammonia buffer of pH 9.5 was reduced at a mercury cathode to cyclohexylamine[34]. Schiff's bases of aldehydes (R—CH=N—R') when reduced in ethanol/methyl acetate/water (5:3:1) containing tetrabutylammonium bromide as an electrolyte at a mercury cathode gave vicinal diamines in yields of 22–66% with a *meso*:*dl* ratio of 1:1[35].

Suitably substituted 1,3-diketones when electrolyzed in tetrahydrofuran containing acetic anhydride as a trapping agent and tributylethylammonium tetrafluoroborate as an electrolyte give diacetates of cyclopropane diols[36].



[26] N. J. Leonard, S. Swann, G. Fuller, J. Amer. Chem. Soc. **75**, 5127 (1953).
[27] M. J. Allen, A. H. Corwin, J. Amer. Chem. Soc. **72**, 114 (1950).
[28] S. Swann, S. W. Briggs, V. C. Neplutin, A. J. Jerome, Trans. Electrochem. Soc. **80**, 163 (1941).
[29] L. P. Kyrides, J. Amer. Chem. Soc. **55**, 3431 (1933).
[30] L. Horner, D. Degner, Tetrahedron Lett. **1968**, 5889.
[31] J. Tafel, E. Pfeffermann, Chem. Ber. **35**, 1510 (1902).
S. Swann, C. Y. Chen, H. D. Kerfman, J. Electrochem. Soc. **99**, 460 (1952).
For other references see H. Lund, *Electrochemistry of the Carbon-Nitrogen Double Bond*, in S. Patai, *The Chemistry of the Carbon-Nitrogen Double Bond*, Interscience Publishers, New York, 1970, p. 505.
[32] W. Hoffmann, Dissertation, Universität Giessen, 1914.
[33] L. Horner, D. H. Skaletz, Tetrahedron Lett. **1970**, 3679.

2.4. Reduction of Acids and Acid Derivatives

Many aromatic acids have been reduced in sulfuric acid solution to alcohols at a rolled lead-sheet cathode or lead electroplated from a perchlorate bath. Aliphatic acids are not reduced under these conditions.

Salicylic acid and substituted salicylic acids are unique and in the presence of boric acid at a pH of 5.4–5.7[37] have been reduced to salicylaldehydes. The reduction of salicylic acid has been carried out in 2.5 kilogram amounts at an amalgamated copper or brass rotating cathode and gave 1 kg of the aldehyde.

Benzyl Alcohol[38]:
Anode: Lead sheet.
Anolyte: 10% sulfuric acid in a 400-ml beaker.
Cathode: Commercial lead sheet (99.9%) 7.7 × 3 × 0.3 cm; total area 51.7 cm.
Catholyte: In porous cup a solution (~85 ml) consisting of water (20 ml), ethanol (50 ml), and sulfuric acid (40 g). Dimensions of porous cup: 100 mm in height, 47 mm inside diameter, 3 mm in thickness.
Starting Material: Benzoic acid (20 g).

The lead cathode is activated prior to the electrolysis by placing it in a 20% solution of sulfuric acid and surrounding it by a sheet of lead. The cathode is used as an anode with a current of 2 amp for 5 min. and becomes coated with lead oxide. Reversal of the polarity will form sponge metallic lead on the surface. The cycle is repeated two more times and at the end of the last one, the cathode is left in the oxidized condition. It is washed thoroughly with distilled water before being used in the reduction.

The electrolysis is carried out with external cooling using a current of 5 amp for 10.5 hr. The cathode current density is 0.1 amp/cm^2.

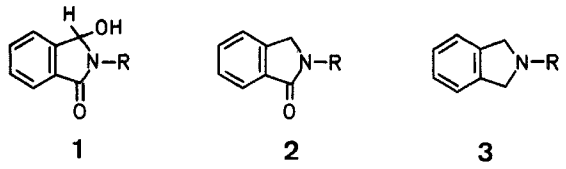
At the end of the electrolysis, the contents of the porous cup are poured into an 800-ml beaker. The cup is washed with water and the washings added to the catholyte in the beaker. The catholyte is neutralized with solid sodium carbonate and the resulting organic layer of benzyl alcohol in ethanol is separated and refluxed with sodium hydroxide (15 g) for 1 hr to saponify any esters. After saponification, the alcoholic liquid is subjected to steam distillation until the distillate is no longer turbid. The distillate is then salted out with potassium carbonate until dry and is then distilled until the temperature of the thermometer reaches 120°. The neutralized catholyte and residue of steam distillation are both extracted with ether and the extract added to the crude benzyl alcohol in the distilling flask, after drying overnight with anhydrous magnesium sulfate. Removal of the ether affords almost pure benzyl alcohol; yield: 14 g (79%); b.p. 200–202° (uncorr.).

Anthranilic acid is reduced under similar conditions to 2-aminobenzyl alcohol[38].

N- and N,N-substituted aliphatic amides and all three types of aromatic amides have been reduced in sulfuric acid at a lead cathode to the corresponding amines[39,40].

[34] P. J. Elving, R. E. VanAtta, J. Electrochem. Soc. **103**, 676 (1956).
[35] L. Horner, D. H. Skaletz, Tetrahedron Lett. **1970**, 1103.
[36] T. J. Curphey, C. W. Amelotti, T. P. Layloff, R. L. McCartney, J. H. Williams, J. Amer. Chem. Soc. **91**, 2817 (1969).
[37] K. S. Udupa, G. S. Subramonian, H. V. K. Udupa, Ind. Chemist **39**, 238 (1963).

Phthalimides are reduced in sulfuric acid solution at a lead cathode to 3-hydroxyphthalimidines (**1**), phthalimidines (**2**), and isoindolines (**3**):



1 **2** **3**

2-(2-Dimethylaminoethyl)-1-hydroxy-3-oxo-4,5,6,7-tetrachloro-isoindoline and 2-(2-Dimethylaminoethyl)-4,5,6,7-tetrachloro-indoline[41]:

Anode: Platinum.

Anolyte: conc. sulfuric acid (9 ml) in distilled water (66 ml).

Cathode: Lead sheet (78 cm^2), pretreated as described under benzyl alcohol.

Catholyte: Glacial acetic acid (30 ml), water (36 ml), and conc. sulfuric acid (9 ml).

Reference Electrode: S.C.E.

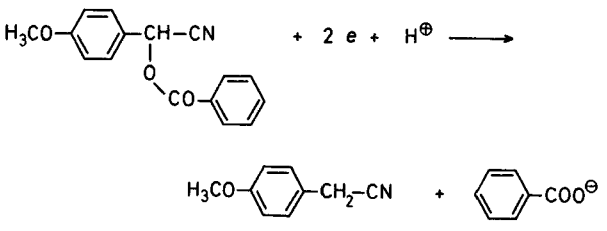
Starting Material: 2-(2-Dimethylaminoethyl)-4,5,6,7-tetrachlorophthalimide (6.5 g).

The electrolysis was carried out at 50–55° at a reference potential of −0.68 volt *vs.* S.C.E. The initial current density was 0.0189 amp/cm^2. After 70 min., the current plateaued at 0.0107 amp/cm^2. The catholyte was made basic and the *2-(2-dimethylaminoethyl)-1-hydroxy-3-oxo-4,5,6,7-tetrachloroisoindoline* was filtered; yield: 4.31 g; m.p. 158–162°. Recrystallization from aqueous ethanol gave colorless crystals; m.p. 164–165°.

If a reference potential of −1.10 volt *vs.* S.C.E. was used, the initial current density of 0.0589 amp/cm^2 plateaued after 80 min. to 0.0143 amp/cm^2. The catholyte was treated as above and gave *2-(2-dimethylaminoethyl)-4,5,6,7-tetrachloroisoindoline;* yield: 5.0 g.

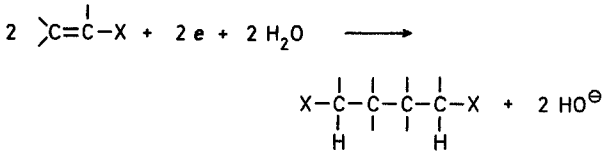
Using constant current electrolysis in this example gave a mixture of the phthalimidine and isoindoline[41].

Substituted benzyl esters are cleaved electrochemically to the substituted toluene at a mercury cathode in solutions containing tetramethylammonium iodide as the electrolyte. α-Benzoyloxy-4-methoxyphenylacetonitrile is converted to 4-methoxyphenylacetonitrile in 57% yield[42].



2.5. Reductive Coupling – Hydrodimerization

Bimolecular electrolytic reductions have been carried out with aryl-substituted olefins, α,β-unsaturated acids and their derivatives, α,β-unsaturated ketones, and pyridinium and quinolinium salts:



Such reductions have been carried out at mercury or a cathode of high hydrogen overvoltage in dimethylformamide[43], in aqueous solutions with or without dimethylformamide as a cosolvent containing high concentrations of tetralkylammonium tosylate as an electrolyte (similar to McKee's salts)[44], and in sulfuric acid[45]. The last method is least satisfactory.

The method using high concentration of tetraethylammonium tosylate and acrylonitrile is the basis for the commercial preparation of adipic acid dinitrile[46].

The use of alkali metal salts favors simple reduction to the saturated derivative. The reduction of cinnamic acid for example, using sodium sulfate as an electrolyte, gives 3-phenylpropanoic acid[47].

1,2-Bis-[9-fluorenyl]-1,2-diphenylethane[48]:

Anode: 18 gauge platinum wire sealed in glass.

Anolyte: 47% aqueous solution (20 g) of methyltributylammonium tosylate.

Cathode: Mercury.

Catholyte: 82.6% aqueous solution (59 g) of methyltributylammonium tosylate + dimethylformamide (58.9 g).

Starting Material: 9-Benzylidenefluorene (26.4 g).

The membrane was an alundum cup. An average current of 0.2 amp was passed at 45° for 1 hr at a cathode voltage of −1.5 to −1.6 volt (S.C.E.). The pH was moderated by the addition of ~3 ml of acetic acid in the course of the run. Product began precipitating after the first 30 min. At the end of the run, the mercury was separated and the product was removed by filtration and dried; yield: 11.5 g; m.p. 319–320°, from anisole. Additional product could be obtained by adding water to the filtrate.

Numerous cathodic cross dimerizations between ketones, and unsaturated compounds, have been reported. Acetone and acrylonitrile in 20% sulfuric acid gave a mixture of 4-hydroxy-4-methylpentanoic acid nitrile and γ,γ-dimethylbutyrolactone[49]. Similar mixed couplings with acrylonitrile are reported for benzophenone, acetophenone, ethyl acrylate, acetone, styrene, butadiene and stilbene[50], acetone and pyridine[51], ketones and pyridine bases[52], and acetone and allyl alcohol[53]. The last example gave 1,4-dihydroxy-4-methylpentane.

[38] cf. G. H. COLEMAN, H. L. JOHNSON, Org. Syntheses, Coll. Vol. III, 60 (1955).

[39] S. SWANN, Trans. Electrochem. Soc. **84**, 165 (1943).

[40] K. KINDLER, Arch. Pharm. **265**, 390 (1927).

[41] M. J. ALLEN, J. OCAMPO, J. Electrochem. Soc. **103**, 452 (1956).

[42] S. WAWZONEK, J. D. FREDRICKSON, J. Electrochem. Soc. **106**, 325 (1959).

[43] S. WAWZONEK, E. W. BLAHA, R. BERKEY, M. E. RUNNER, J. Electrochem. Soc. **102**, 235 (1955).

[44] M. M. BAIZER et al., Electrochim. Acta **12**, 1377 (1967). See this paper for references.

[45] C. L. WILSON, Trans. Electrochem. Soc. **92**, 369 (1947).

[46] M. M. BAIZER, J. Electrochem. Soc. **111**, 215 (1964).

[47] A. W. INGERSOLL, Org. Syntheses, Coll. Vol. I, 311 (1941).

[48] M. M. BAIZER, J. D. ANDERSON, J. Org. Chem. **30**, 1348 (1945).

[49] K. SUGINO, T. NONAKA, Electrochim. Acta **13**, 613 (1968).

[50] M. NICOLAS, R. PALLAND, C. R. Acad. Sci. [C] **265**, 1044 (1967); **267**, 1834 (1968).

2.6. Preparation of Acids

Generation of organic anions electrochemically in aprotic solvents in the presence of carbon dioxide has led to the formation of acids. *meso*-2,3-Diphenylsuccinic acid[43], 1,4-dihydronaphthalene-1,4-dicarboxylic acid, *trans*-9,10-dihydrophenanthrene-9,10-dicarboxylic acid, diphenylfumaric acid, diphenylmaleic anhydride[54], benzilic acid, 2,4-diphenyl-4-oxobutanoic acid, and 2-phenyl-4-oxopentanoic acid[55] have been prepared from stilbene, naphthalene, phenanthrene, diphenylacetylene, benzophenone, benzylideneacetophenone, and benzylideneacetone, respectively.

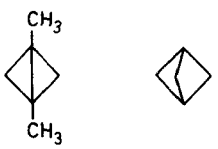
***meso*-2,3-Diphenylsuccinic Acid[53]:**
Anode: Platinum screen.
Anolyte: 0.0155 *M* Tetrabutylammonium iodide in dimethylformamide.
Cathode: Mercury.
Catholyte: Same as anolyte.
Starting Material: Stilbene (3.0 g).
For 1 hr prior to the electrolysis and during the electrolysis, carbon dioxide was passed through the catholyte containing the stilbene. The electrolysis was carried out with a current density of 0.0064 amp/cm^2 for 19 hr. Removal of the solvent under reduced pressure was followed by the addition of 10% sodium hydroxide (100 ml) and steam distillation. From the distillate, a small amount of bibenzyl (0.1 g) was obtained. The solution left in the distillation flask was filtered from the precipitated tetrabutylammonium iodide and bis-tetrabutylammonium tetraiodomercurate and acidified with excess hydrochloric acid. The *meso*-diphenylsuccinic acid obtained was recrystallized from methanol; yield: 4.1 g; m.p. 229°.

The reported reduction of carbon dioxide to malic acid at a mercury cathode[56] and glycolic acid at a lead cathode[57] could not be duplicated by other investigators.

2.7. Reduction of Halogenated Compounds

A variety of halogenated compounds has been reduced in aprotic solvents and has led to a number of unusual products.

The reduction of dihalohydrocarbons and related compounds has been used to prepare cyclopropane, cyclobutane, bicyclobutanes (e.g. **4**), and bicyclo-[1.1.1]pentane (**5**)[58]:



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1,3-Dimethylbicyclobutane (4)[58]:
Anode: Platinum wire.
Anolyte: 0.1 *M* Lithium bromide in dimethylformamide.
Cathode: Mercury.
Catholyte: 0.1 *M* Lithium bromide in dimethylformamide.
Reference Electrode: Saturated calomel electrode.
Starting Material: 1,3-Dibromo-1,3-dimethylcyclobutane (50 g).
A solution of the starting material (50 g) in the catholyte (230 ml) was electrolyzed at 55° for 16 hr using a voltage of 40 volt and a current of 0.5 amp. The volatile product obtained in a trap cooled with Dry Ice-acetone gave 1,3-dimethylbicyclobutane; *yield*: 9–15 g; *b.p.* 54.5°.

Electrolysis of 1,4-bis-[bromomethyl]-benzene under similar conditions gave poly-*p*-xylylene (92%) and [2.2]paracyclophane (5%)[59].

The reduction of carbon tetrachloride in the presence of tetramethylethylene in acetonitrile gave 1,1-dichloro-2,2,3,3-tetramethylcyclopropane (~10%). Carbon tetrachloride under these conditions is reduced to dichlorocarbene, which adds to the olefin and forms the cyclopropane[60].

$$CCl_4 + 2\,e \longrightarrow CCl_3^{\ominus} + Cl^{\ominus}$$

$$CCl_3^{\ominus} \rightleftharpoons CCl_2 + Cl^{\ominus}$$

The reduction of ethyl bromide at a lead cathode in aprotic solvents leads to the formation of tetraethyl lead[61,62,63].

Organometallic compounds involving cations from the electrolyte are reported to be formed from the reduction of arylated olefins and triphenylmethyl chloride using lithium bromide, sodium iodide, and calcium iodide as electrolytes in hexamethylphosphortriamide[64].

2.8. Reduction of Diazonium Salts

The electrolytic reduction of diazonium salts in acid medium gives phenylhydrazines in yields better than 60%[65]. This reduction is adversely affected by agitation and gives a better yield using a special cell in which the diazonium salt solution is introduced through a mercury electrode[66].

The electrolytic reduction of benzenediazonium tetrafluoroborate in acetonitrile containing aromatic hydrocarbons using potentials corresponding to the first polarographic reduction step gave nuclear phenylation (15–33% yield) and a mixture of isomeric biaryls[67].

$$ArN_2^{\oplus} + e \longrightarrow ArN_2^{\bullet} \longrightarrow Ar\bullet + N_2$$

[51] T. Nonaka, K. Sugino, J. Electrochem. Soc. **116**, 615 (1969).
[52] M. Ferles, M. Vanka, A. Silhankova, Collect. Czech. Chem. Commun. **34**, 2108 (1969).
[53] A. P. Tomilov, B. L. Klyuev, Zh. Obshch. Khim. **39**, 470 (1969); Engl. Edit., p. 446.
[54] S. Wawzonek, D. Wearring, J. Amer. Chem. Soc. **81**, 2007 (1959).
[55] S. Wawzonek, A. Gundersen, J. Electrochem. Soc. **107**, 537 (1960); **111**, 324 (1964).
[56] A. Bewick, G. P. Greener, Tetrahedron Lett. **1969**, 4623.
[57] A. Bewick, G. P. Greener, Tetrahedron Lett. **1970**, 391.

2.9. Generation of Anion-Radicals

Electrochemical reduction of organic compounds in aprotic solvents has proved useful for the preparation of anion radicals for electron spin-resonance studies[68]. The electrolysis is carried out in a cell placed directly within the resonance cavity of an E.S.R. spectrometer. The potential for generation of the anion radical is chosen on the basis of polaro-

$$A + e \longrightarrow A^{\ominus\bullet}$$

graphic data or ordinarily 0.1 volt more negative than the half-wave potential. Acetonitrile solutions containing 1 m*M* in parent molecule and 0.1 *N* in tetrapropylammonium perchlorate are used as the catholyte. The cathode is a mercury pool and the anode is an aqueous S.C.E. with an agar bridge[69]. This method offers two distinct advantages over oxidation or reduction by chemical reagents for the production of charged radicals:

- A continuous and easily adjustable range of oxidation or reduction potentials is available;
- tetraalkylammonium salts, which can be used as the electrolytes for electrolysis, interact with anion radicals to a much smaller extent than the smaller cations formed when alkali metal or similar metallic reductants are employed in non-polar solvents[70].

Such a technique was used to generate anion radicals from anthracene, anthraquinone, benzophenone[71], aromatic nitro compounds, aromatic aldehydes, nitriles[72], and other compounds.

2.10. Reduction of Aromatic Hydrocarbons and Olefins

Benzene and olefins are reduced electrochemically under specialized conditions[73]. Reduction of benzene in ethanol/hexamethylphosphoramide (66.6 mol% ethanol) at an aluminum cathode gave a mixture of 22.8% cyclohexadiene, 10% cyclohexene, and 67.2% cyclohexane. The electrolysis was interrupted after 15% of the available benzene had been reduced. Evidence presented favors the involvement of solvated electrons in the reduction.

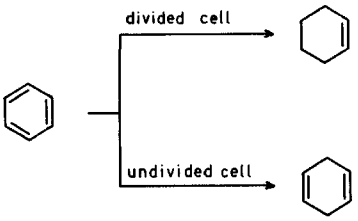
$$e(C_2H_5OH) + C_6H_6 \longrightarrow C_6H_6^{\ominus\bullet} + C_2H_5OH$$

$$C_6H_6^{\ominus\bullet} + C_2H_5OH \longrightarrow C_6H_{7\bullet} \text{ etc.} + C_2H_5O^{\ominus}$$

2,3-Dimethyl-2-butene was reduced under similar circumstances with a current efficiency of 30%.

In solvents with smaller proton availability such as ethylenediamine[74] or in methylamine containing lithium chloride[75], the reduction of isolated double bonds is slower and the reduction resembles the Birch reduction.

Cyclohexene was produced from the reduction of benzene in methylamine containing lithium chloride in a divided cell and dihydrobenzene was formed in an undivided cell.



The former arrangement prevents the lithium methylamide, generated at the cathode, from interacting with methylamine hydrochloride formed at the anode. The lithium methylamide can cause rapid isomerization of the unconjugated dihydro compound to the conjugated product which can undergo further reduction.

The reduction in methylamine containing lithium chloride has also been used to reduce acetylenes to *trans* olefins[76], and ketones to alcohols or N-methylamines[77].

Dihydrobenzenes[78]**:**

An electrolysis cell 170 mm in length by 100 mm in diameter was fitted with two Dry Ice condensers, or an ordinary three-necked flask was fitted with a condenser, and two platinum electrodes (2 × 5 cm) were inserted. The cell was charged with lithium chloride (34.0 g, 0.8 mol), anhydrous methylamine (900 ml), and the aromatic compound to be reduced (0.1 mol). A total of 50000 coulomb was passed through the solution in 7 hr (2.0 amp, 85 volt). At the end of this time, solvent was allowed to evaporate and the residue was hydrolyzed by the slow addition of water. Extraction with ether gave the product which was distilled.

This reduction of cumene gave an 81% yield of the dihydro derivative and 6% of the substituted cyclohexene.

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[58] M. R. Rifi, Tetrahedron Lett. **1969**, 1043.
[59] F. H. Covitz, J. Amer. Chem. Soc. **89**, 5403 (1967).
[60] S. Wawzonek, R. C. Duty, J. Electrochem. Soc. **108**, 1435 (1961).
[61] E. F. Silversmith, W. J. Sloan, U.S. Patent 3197392 ≡ Brit. Patent 949925 (1961), DuPont; C.A. **61**, 3935 (1964).
[62] H. E. Ulery, J. Electrochem. Soc. **116**, 1201 (1969).
[63] G. Reno, J. Electroanal. Chem. Interfacial Electrochem. **212**, 75 (1969).
[64] L. D. McKeever, R. Waack, J. Organometal. Chem. **17**, 142 (1969).
[65] M. Y. Fioshin, G. P. Girina, V. P. Mamaev, Zh. Obshch. Khim. **26**, 2311 (1956).
[66] P. Rüetschi, G. Trümpler, Helv. Chim. Acta **36**, 1649 (1953).
[67] F. F. Gadallah, R. M. Elofson, J. Org. Chem. **34**, 3335 (1969).
[68] D. H. Geske, A. H. Maki, J. Amer. Chem. Soc. **82**, 2671 (1960).
[69] A. H. Maki, D. H. Geske, J. Amer. Chem. Soc. **83**, 1852 (1961).
[70] P. H. Rieger, I. Bernal, W. H. Reinmuth, G. K. Fraenkel, J. Amer. Chem. Soc. **85**, 683 (1963).
[71] D. E. G. Austen, P. H. Given, D. J. E. Ingram, M. E. Peover, Nature **182**, 1784 (1958).
[72] A. H. Maki, J. Chem. Phys. **35**, 761 (1961).
[73] H. W. Sternberg, R. E. Markby, I. Wender, D. M. Mohilner, J. Amer. Chem. Soc. **91**, 4191 (1969).

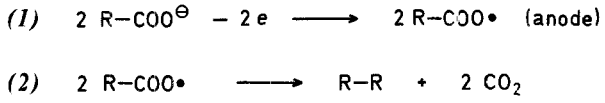
Polynuclear aromatic hydrocarbons such as naphthalene and phenanthrene behave differently from benzene and its homologs and are reduced electrochemically by direct electron transfer. Electrochemical reduction of naphthalene at a mercury cathode in acetonitrile containing 25% water and tetraethylammonium tosylate as an electrolyte in a divided cell, for example, gave an 83% yield of 1,4-dihydronaphthalene[79]. The same reduction using solvated electrons[73] gave a mixture of dihydronaphthalene, tetralin, hexalin, octalin, and decalin.

3. Oxidations

Oxidations of organic compounds may take place by direct electron transfer to the anode or by the action of hydroxyl radicals, atomic oxygen, or hydrogen peroxide generated at the anode. The latter type of oxidation is usually very complex and will not be discussed.

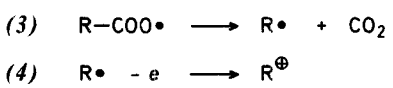
3.1. Electrolysis of Salts of Carboxylic Acids

The electrolysis of salts of carboxylic acids at a platinum anode, or the Kolbe reaction, is a very useful method for producing hydrocarbons. The reaction proceeds as follows:

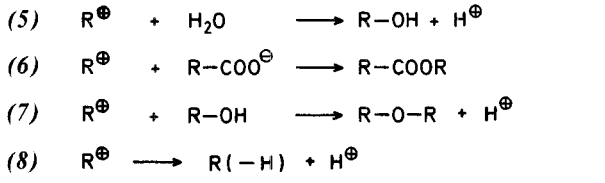


The first mechanism ever proposed and shown above has remained as the most general and satisfactory explanation of this reaction[80].

More recent work has suggested that the intermediate radical R•, depending on its structure, can be further oxidized to a carbonium ion (equation *4*):



This ion can rearrange to another carbonium ion, react with nucleophiles present in the solution, or undergo an elimination reaction, and give the by-products often isolated in this reaction.



The products obtained in this reaction will depend therefore on the structure of the acid and the experimental conditions employed.

The lower members of the aliphatic acids with the exception of acetic, α-substituted aliphatic acids, α,β-unsaturated acids, β,γ-unsaturated acids, aromatic, and phenylacetic acids give very little of the coupled product, R—R. Such structures influence the stability of the intermediate radical and favor carbonium ion formation. Acids in the alicyclic and bicyclic series and acids with electron donating groups, —OR and —NH—COR, in the α-position show a similar behavior. Acids with electron-withdrawing substituents such as —CN, —COOR, $—CONH_2$ in the α-position which favor the radical step give higher yields of coupled products.

Experimentally, the following factors are important in controlling the products in the Kolbe Synthesis.

Solvent. Methanol and aqueous methanol have been found to be superior to aqueous media. Dimethylformamide, acetonitrile, and anhydrous acetic acid have been used in special cases and will be discussed later.

Composition of Electrolyte. Potassium or sodium salts of organic acids are usually electrolyzed in a cell without a diaphragm. In aqueous solutions, high concentrations of the salt are required for coupling. In non-aqueous solutions, the concentration of the salt has little influence. In general, electrolytes should be kept acidic with the acid of the salt used. Side reactions are promoted in aqueous alkaline electrolytes and tend to give products involving the carbonium ion.

Anode Material. In aqueous electrolytes, good yields of coupled products are obtained only at anodes of smooth platinum. In non-aqueous solutions, other anodes such as platinum black, gold, or carbon may be used. The last mentioned material favors carbonium ion formation.

Added Compounds. Carbonium ion reactions are favored by the addition of other anions such as hydrogen carbonate, sulfate, perchlorate, dihydrogen phosphate, and fluoride.

Current Density. In aqueous solution, better yields are obtained at high current densities. In non-aqueous solution, the current density is comparatively unimportant.

Temperature. High temperatures do not favor good yields in aqueous solution. In non-aqueous solution, the temperature is relatively unimportant.

[74] H. W. STERNBERG, R. MARKBY, I. WENDER, J. Electrochem. Soc. **110**, 425 (1963).

[75] R. A. BENKESER, E. M. KAISER, R. E. LAMBERT, J. Amer. Chem. Soc. **86**, 5272 (1964).

[76] R. A. BENKESER, C. A. TINCHER, J. Org. Chem. **33**, 2727 (1968).

[77] R. A. BENKESER, S. J. MELS, J. Org. Chem. **35**, 261 (1970).

[78] R. A. BENKESER, E. M. KAISER, J. Amer. Chem. Soc. **85**, 2858 (1963).

[79] A. MISONO, T. OSA, T. YAMAGISHI, Bull. Chem. Soc. Japan **40**, 427 (1967).

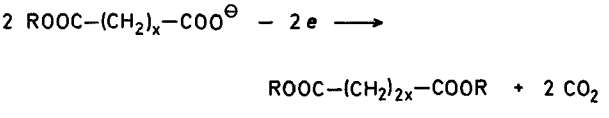
Duration of Reaction. The anode current efficiencies are not high and more than the theoretical amount of current is usually necessary.

Potential. The yields are insensitive to the potential used[81].

Electrolysis of Salts of Carboxylic Acids; General Procedure: The acid (0.2 mol) is electrolyzed in methanol (100 ml) containing enough sodium methoxide to neutralize 2% of the acid, in a cell similar to that used in reductions with the exception that no separation of the electrodes by a porous cup or diaphragm is necessary. The electrodes are smooth platinum plates (4 × 2.5 cm) and are placed a few centimeters apart. The temperature is maintained at 40–50° by external cooling and a current of 1.5–2.0 amp is maintained until the electrolyte becomes alkaline. This point is reached when about 20–40% more current than that calculated is used. Removal of the solvent is followed by extraction with ether and purification of the product.
If aqueous methanol is used, petroleum ether (60–80°) is added to form a layer which will dissolve the products formed. These products will otherwise coat the electrodes.

This method can employ mixtures of acids and is useful if the three possible products can be separated.

Diesters may be prepared by electrolysis of the salts of mono esters of dibasic acids:



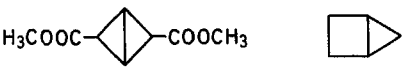
$$2\ ROOC-(CH_2)_x-COO^{\ominus} - 2e \longrightarrow ROOC-(CH_2)_{2x}-COOR + 2\ CO_2$$

This coupling reaction which is often known as the Crum-Brown-Walker synthesis is carried out in exactly the same manner as the Kolbe reaction[82].

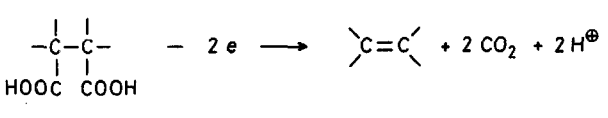
Esters may be prepared by electrolysis of a mixture of a monobasic acid and a monoester of a dibasic acid[83].

Functional groups such as carbonyl, ether, acyloxy, and acylamino if far enough removed from the carboxyl group will not interfere in the reaction. The yields of coupled products will vary with the group involved and are low (<24%) for N-acylamino acids and high for ω-acyloxy alkanoic acids[84] (see Table 1).

Intramolecular Kolbe reactions have been carried out with *trans,trans,trans*-1,3-dicarboxy-2,4-dimethoxycarbonylcyclobutane[85] and cyclopentane-*cis*-1,3-dicarboxylic acid[86] and gave 2,4-dimethoxycarbonylbicyclobutane and bicyclo[2.1.0]pentane in yields of 15 and 2%, respectively.



Electrolysis of salts of vicinal dicarboxylic acids produces olefins:



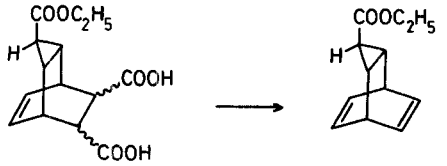
$$-\overset{|}{C}-\overset{|}{C}- \;(HOOC\ COOH) - 2e \longrightarrow >C=C< + 2\ CO_2 + 2H^{\oplus}$$

Table 1. Kolbe Electrolysis of ω-Acyloxyalkanoic Acids[84]

Acid	Product	Yield %	Current efficiency
$H_3C-CO-O-(CH_2)_5-COOH$	$H_3C-CO-O-(CH_2)_{10}-O-CO-CH_3$	83.1	66.4
$HCO-O-(CH_2)_5-COOH$	$HCO-O-(CH_2)_{10}-O-CHO$	82.2	49.2
$H_3C-CO-O-(CH_2)_4-COOH$	$H_3C-CO-O-(CH_2)_8-O-CO-CH_3$	80.5	66.3
$HCO-O-(CH_2)_4-COOH$	$HCO-O-(CH_2)_8-O-CHO$	83.4	60.8
$H_3C-CO-O-(CH_2)_3-COOH$	$H_3C-CO-O-(CH_2)_6-O-CO-CH_3$	72.7	59.6
$H_3C-\underset{\displaystyle O-CO-CH_3}{\underset{\vert}{CH}}-CH_2-COOH$	$H_3C-\underset{\displaystyle O-CO-CH_3}{\underset{\vert}{CH}}-CH_2-CH_2-\underset{\displaystyle O-CO-CH_3}{\underset{\vert}{CH}}-CH_3$	81.0	54.9
$H_3C-CO-O-CH_2-CH_2-COOH$	$H_3C-CO-O-(CH_2)_4-O-CO-CH_3$	72.8	60.6
$H_3C-\underset{\displaystyle O-CO-CH_3}{\underset{\vert}{CH}}-COOH$	$H_3C-\underset{\displaystyle H_3C-CO-O}{\underset{\vert}{CH}}-\underset{\displaystyle O-CO-CH_3}{\underset{\vert}{CH}}-CH_3$	1.5	0.8
$H_3COOC-\underset{\displaystyle O-CO-CH_3}{\underset{\vert}{CH}}-CH_2-COOH$	$H_3COOC-\underset{\displaystyle O-CO-CH_3}{\underset{\vert}{CH}}-CH_2-CH_2-\underset{\displaystyle O-CO-CH_3}{\underset{\vert}{CH}}-COOCH_3$	59.2	48.7

[80] L. EBERSON, *Acidity and Hydrogen Bonding of Carboxyl Groups*, in S. PATAI, *The Chemistry of Carboxylic Acids and Esters*, John Wiley & Sons, New York · London · Sidney · Toronto, 1969, p. 211.
[81] W. H. HARWOOD, R. M. HURD, E. S. SNAVELY, Ind. Eng. Chem., Prod. Res. Develop. **3**, 105 (1964).
[82] S. SWANN, R. OEHLER, P. S. PINKNEY, Org. Syntheses, Coll. Vol. III, 401 (1955).
[83] W. S. GREAVES et al., J. Chem. Soc. **1950**, 3326.
[84] J. HAUFE, F. BECK, Chem.-Ing.-Tech. **42**, 170 (1970).
[85] A. F. VELTTURO, G. W. GRIFFIN, J. Amer. Chem. Soc. **87**, 3021 (1965).
[86] T. CAMPBELL, A. VELTTURO, G. W. GRIFFIN, Chem. & Ind. **1969**, 1235.
[87] E. J. COREY, J. CASANOVA, J. Amer. Chem. Soc. **85**, 165 (1963).
[88] P. RADLICK et al., Tetrahedron Lett. **1968**, 5117.
[89] H. H. WESTBERG, H. J. DAUBEN, Tetrahedron Lett. **1968**, 5123.

The electrolysis, which is carried out in 90% pyridine/water containing triethylamine[87], has proved very useful in preparing olefins in bicyclic systems[88,89], e. g.



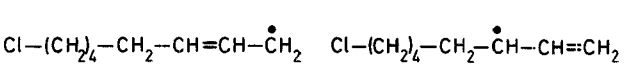
6 **7**

(exo, trans, or endo)

The related chemical method using lead tetraacetate gave low and variable yields with these compounds.

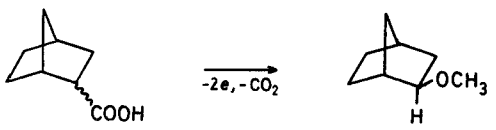
3-Ethoxycarbonyltricyclo[3.2.2.0^{2,4}]nona-6,8-diene (7)[89]: 6,7-Dicarboxy-3-ethoxycarbonyltricyclo[3.2.2.0^{2,4}]non-8-ene (**6**; 1.25 g) was dissolved in water (10 ml) to which had been added triethylamine (1.25 ml) and the resulting solution was treated with pyridine (95 ml). Electrolysis was carried out in a cell cooled in an ice bath so that the internal temperature remained at ~20°. The initial current of 0.8 amp after 8 hr dropped to less than 0.2 amp. Addition of water (250 ml) followed by extraction with pentane gave the diene; yield: 0.33 g.

Electrolysis of acids in the presence of butadiene has led to complex mixtures of products resulting from the addition of the radical to the diene. Oxalic acid gave 3,7-decadienedioic acid[90], and 5-chloropentanoic acid gave five products involving the dimerization of the following three radicals[91]:



Examples that give products resulting from a carbonium ion are numerous. Certain ones are of interest synthetically and form the methyl ether or olefin in methanol.

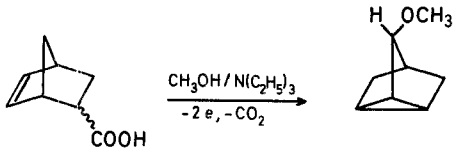
Anodic oxidation of *exo*- or *endo*-norbornane-2-carboxylic acid (**8**) gave *exo*-2-methoxynorbornane (**9**) in 35–40% yield[92] with no *endo* isomer detectable:



8 **9**

(exo or endo) (exo)

Under similar conditions, anodic oxidation of *exo*- or *endo*-5-norbornene-2-carboxylic acid (**10**) gave 7-methoxynortricyclene (**11**; 56%):



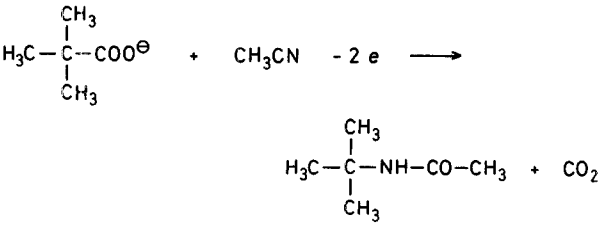
10 **11**

(exo or endo)

1-Hydroxycyclohexylacetic acid in acetonitrile upon electrolysis gave cycloheptanone (45–53%):

Electrolysis of diphenylacetic acid in methanol containing triethylamine as a base gave benzhydryl methyl ether in 80% yield. The same electrolysis in dimethylformamide gave tetraphenylethane (24%)[93].

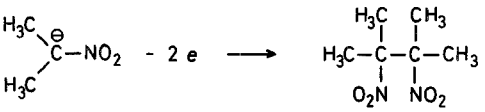
Generation of carbonium ions from acids in moist acetonitrile will yield amides[94].



The electrochemical method offers no advantage over the chemical Ritter reaction.

3.2. Electrolysis of Carbanions

Carbanions of organic compounds generated by treating nitroparaffins, ethyl cyanoacetate, and other compounds with active methylene groups with alkali are oxidized electrochemically to radicals which dimerize.

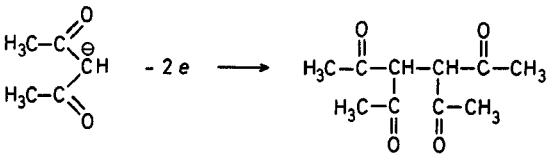


This reaction has been carried out at platinum and lead oxide anodes. Although the optimum conditions have not been determined, a high concentration of anion would seem desirable.

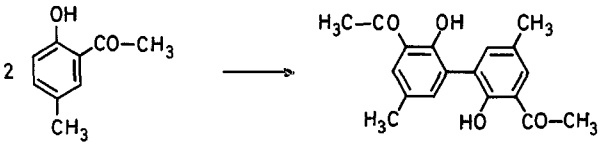
[90] A. G. KORNIENKO, L. A. MIRKIND, M. Y. FIOSHIN, Elektrokhimiya **5**, 1003 (1969).
[91] M. A. KHRIZOLITOVA, L. A. MIRKIND, M. Y. FIOSHIN, Zh. Org. Khim. **4**, 1705 (1968).
[92] E. J. COREY et al., J. Amer. Chem. Soc. **82**, 2645 (1960).
[93] M. FINKELSTEIN, R. C. PETERSEN, J. Org. Chem. **25**, 136 (1960).
[94] L. EBERSON, K. NYBERG, Acta Chem. Scand. **18**, 1567 (1964).
[95] C. T. BAHNER, Ind. Eng. Chem. **44**, 317 (1952).
[96] K. M. JOHNSTON, J. D. STRIDE, Chem. Commun. **1966**, 325.
[97] K. M. JOHNSTON, Tetrahedron Lett. **1967**, 837.
[98] H. SCHÄFER, Chem.-Ing.-Tech. **41**, 179 (1969).
[99] D. G. BRAITHWAITE, German Patent 1231700 (1963), Nalco Chemical Co.; C.A. **66**, 76155 (1967).
[100] H. LEHMKUHL, R. SCHÄFER, K. ZIEGLER, Chem.-Ing.-Tech. **36**, 612 (1964).
[101] K. ZIEGLER, H. LEHMKUHL, German Patent 1161562 (1959); C.A. **60**, 11623 (1964).

3,4-Dinitro-3,4-dimethylhexane and 2,2-Dinitrobutane[95]:
Anode: Polished platinum foil.
Anolyte: Sodium hydroxide (55 g) in water (100 ml).
Cathode: Copper-wire spiral.
Catholyte: 25% aqueous sodium hydroxide in a 27 mm diameter alundum cup.
Starting Material: 2-Nitrobutane (126 g).
The electrolysis was carried out at 23–27°, 6–10.5 volt, and 1.5–4.0 amp for a sufficient time to be equivalent to 16 hr at 8 volt and 4 amp and gave 85 g of an oil. Distillation under reduced pressure gave a 70% yield of 3,4-dinitro-3,4-dimethylhexane, m.p. 78.5–79°, and a 20% yield of 2,2-dinitrobutane, b.p. 194–198°/740 mm.

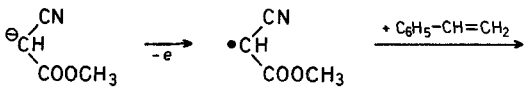
Electrolysis of β-diketones in 0.1 *M* sodium hydroxide containing methanol between smooth platinum electrodes gives dimers in yields of 11–50% depending on the structure. A current density of 1 amp/cm^2 was used and electrolysis was carried out 10–20% longer than the theoretical time[96].



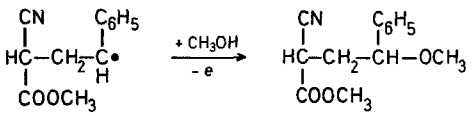
Under similar conditions, *o*-hydroxyacetophenones are converted to biphenyls in yields varying from 7–52%[97]:



The radical (e.g. **13**) if generated in this manner from the carbanion (**12**) in the presence of styrene, vinyl ethyl ether, cyclohexene, or butadiene will add to the double bond and give a new radical (e.g. **14**) which can lose hydrogen, dimerize, or be oxidized further to a carbonium ion which undergoes solvolysis[98] (e.g. **15**).



12 **13**



14 **15**

[102] H. Schäfer, H. Küntzel, Tetrahedron Lett. **1970**, 3333.
[103] H. Schäfer, Chem.-Ing.-Tech. **42**, 164 (1970).
[104] S. Wawzonek, T. W. McIntyre, J. Electrochem. Soc. **114**, 1026 (1967).
[105] V. D. Parker, R. N. Adams, Tetrahedron Lett. **1969**, 1721.
[106] L. Eberson, K. Nyberg, J. Amer. Chem. Soc. **88**, 1656 (1966).

3.3. Electrolysis of Organometallic Compounds

The electrolysis of Grignard reagents or sodium tetraalkylaluminum in non-aqueous solvents produces radicals which at a platinum anode will give disproportionation products. At reactive anodes such as lead, lead tetraalkyls are formed.

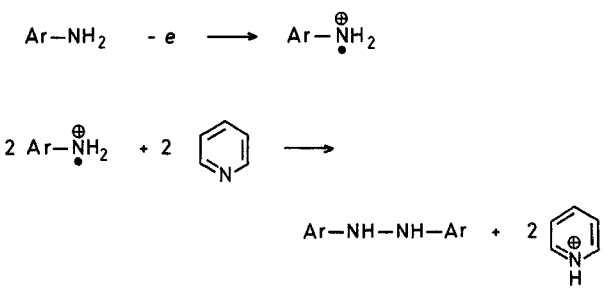
This reaction using Grignard reagents is the basis for the commercial production of tetraethyl- and tetramethyllead[99].

The method employing sodium tetraalkylaluminum[100] as the electrolyte has been also used to prepare other types of metal alkyls by substituting other metals for the lead anode[101].

If the electrolysis of Grignard reagents is carried out at platinum, graphite, or copper anodes in the presence of styrene, butadiene, or vinyl ether, the intermediate alkyl radical can be trapped and unusual products can be formed. The complexity of these products will depend on the anode employed[102]. Electrolysis of butylmagnesium bromide at a copper anode in ether containing lithium perchlorate and styrene gave 2,7-diphenyldodecane with a current efficiency of 30%[103].

3.4. Oxidation of Aromatic Amines

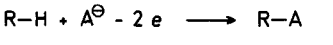
Primary aromatic amines are oxidized electrochemically in acetonitrile to cation radicals. In the presence of a base such as pyridine, the cation radical is converted to the hydrazo compound which is further oxidized to the azo derivative:



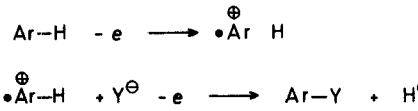
The yields of the azo compound will depend upon the substituents present. 2,4,2',4'-Tetrachloroazobenzene, for example, was formed in 30% yield from 2,4-dichloroaniline[104].

3.5. Anodic Substitution Reactions

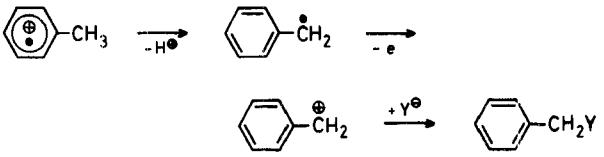
Acetoxylation, formoxylation, benzoxylation, cyanation, thiocyanation, selenocyanation, methoxylation, acetamidation, azidation, fluorination, chlorination, bromination, and iodination have been carried out by electrolyzing an organic substance in the presence of the appropriate anion in a suitable solvent:



Recent work on the anodic acetoxylation and cyanation of organic compounds indicates that, at least in these examples, the reaction involves a loss of an electron from the organic molecule followed by a reaction with the anions in solution:



Alkyl side chains if present on the aromatic ring are found to undergo side-chain substitution. The initial cation radical produced loses a proton and forms a benzyl radical which is oxidized further to a benzyl cation[105]:



3.5.1. Acetoxylation

This reaction has been carried out with aromatic compounds and olefins in glacial acetic acid containing 0.5 *M* sodium acetate using a platinum anode and cathode and can be useful synthetically[106].

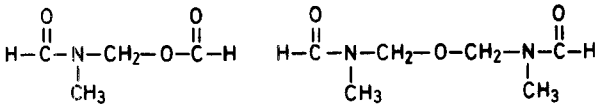
cis- and *trans*-**7,8-Dihydroxybicyclo[4.2.0]octane (16)**[107]:

***trans* – 16** ***cis* – 16**

A solution of pure cyclooctatetraene (16.0 g) in glacial acetic acid (160 ml) containing anhydrous sodium acetate (12.0 g) was electrolyzed at a carbon anode using an anode potential of +1.5 volt and a current of 0.2–0.3 amp for 30 hr. Upon catalytic hydrogenation over platinum at room temperature and 4.2 atm, the isolated crude product in ether (100 ml) absorbed 0.26 mol of hydrogen. The resulting product was refluxed in methanol (30 ml) for 7 hr with potassium hydroxide (20 g) in water (30 ml). Removal of the methanol was followed by treatment with salt water and extraction with ether. Evaporation of the ether gave a residue which upon crystallization from benzene gave the *trans*-diol; yield: 29%. The filtrate upon removal of the benzene and addition of hexane and cooling gave the *cis*-diol; yield: 20%.

3.5.2. Formoxylation

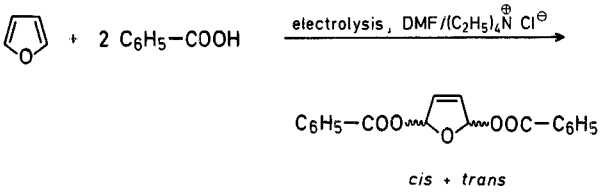
Formoxylation has been found to occur in the electrolysis of a solution of potassium formate and formic acid in dimethylformamide. Two compounds, N-methyl-N-formyloxymethylformamide (**17**; 44.2%) and 2,6-diformyl-2,6-diaza-4-oxaheptane (**18**; 8.4%) were isolated[108].



17 **18**

3.5.3. Benzoxylation

The introduction of the benzoyloxy group can be accomplished by the electrolysis of an organic compound in the presence of benzoate ion in acetonitrile[109,110]. This reaction has been carried out with naphthalene, the isomeric stilbenes[111], and

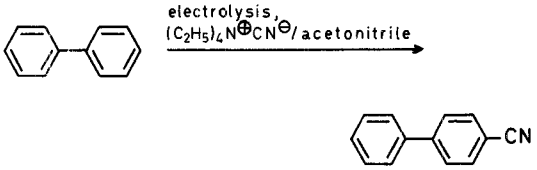


cis + *trans*

furan[112] and probably proceeds by a mechanism similar to that for acetoxylation[113].

3.5.4. Cyanation

This reaction involves the electrolysis of an organic compound in methanol in the presence of sodium cyanide[114], and causes aromatic substitution of



hydrogen, replacement of an aromatic methoxy group by the cyano group, and introduction of a

cyano group into the α-position of tertiary amines:

[107] M. Finkelstein, R. C. Petersen, S. D. Ross, Tetrahedron **23**, 3875 (1967).
[108] S. D. Ross, M. Finkelstein, R. C. Petersen, J. Amer. Chem. Soc. **86**, 2745 (1964).
[109] J. F. K. Wilshire, Austral. J. Chem. **16**, 432 (1963).
[110] K. Koyama, K. Yoshida, S. Tsutsumi, Bull. Chem. Soc. Japan **39**, 516 (1966).
[111] K. Koyama, T. Ebara, T. Tani, S. Tsutsumi, Can. J. Chem. **47**, 2484 (1969).
[112] S. Arita, Y. Takahashi, K. Takeshita, Kogyo Kagaku Zasshi **72**, 1896 (1969).
[113] K. Koyama, T. Ebara, S. Tsutsumi, Bull. Chem. Soc. Japan **41**, 2668 (1968).
[114] V. D. Parker, B. E. Burgert, Tetrahedron Lett. **1965**, 4065.

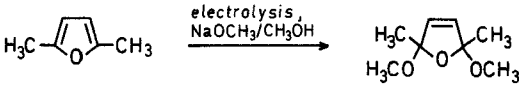
3.5.5. Thiocyanation and Selenocyanation

These reactions are carried out electrolytically using concentrated aqueous solutions of ammonium or alkali salts[116,117].

3.5.6. Methoxylation

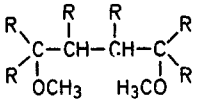
Methoxylation is carried out in a 1% methanolic potassium hydroxide solution using a platinum anode and a nickel cathode[118] or in methanol containing sodium methoxide[119], and occurs preferentially at the α-carbon of a side chain of an aromatic compound. The mechanism of the reaction is still in doubt; both free radical ($H_3CO\bullet$) and ionic pathways are possible.

This reaction has been widely used in the furan series and gives dihydrofuran derivatives:



If isomeric products are possible, the composition obtained electrochemically is similar to that obtained chemically[120]. Side-chain substitution in the above example occurs to the extent of a few percent.

Olefins, $R_2C{=}CH{-}R$, when electrolyzed in methanol containing sodium iodide between graphite electrodes give dimers[121]:



3.5.7. Acetamidation

Acetamidation involves electrolysis of an aromatic compound with a side chain in acetonitrile containing anhydrous sodium perchlorate as an electrolyte at a platinum anode. Electrolysis of 1,2,4,5-tetramethylbenzene under these conditions gave N-(2,4,5-trimethylbenzyl)-acetamide[122].

Electrolysis of cycloheptatriene under similar conditions gave tropylium perchlorate; the yield was quantitative when the water content was less than 5–10%[123].

3.5.8. Azidation

This reaction involves the oxidative addition of azide ion to olefins. Electrolysis of solutions of olefins and sodium azide in acetic acid gives 1,2-diazidoalkanes or cycloalkanes which can be hydrogenated to diamines[124].

3.5.9. Fluorination

Fluorination reactions have been carried out in liquid hydrogen fluoride at a nickel anode[125], or in acetonitrile containing silver fluoride[126]. The former method is applicable to virtually all kinds of organic compounds and in general leads to polyfluorinated compounds. The anode potential is held below that needed for the liberation of fluorine.

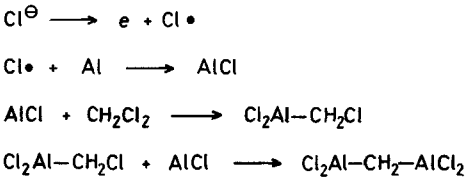
3.5.10. Chlorination, Bromination, Iodination

These halogenations proceed electrochemically either by a direct reaction with the halogen or indirectly through the intermediate formation of hypohalite. The latter may act as an oxidizing agent in some examples.

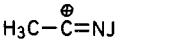
Direct substitution of chlorine and bromine into aromatic compounds has been reported in a halogen acid electrolyte.

Interesting reactions have been reported for chlorination and iodination in aprotic solvents. Electrolysis of dichloromethane solutions using an aluminum anode and a passive cathode in an undivided cell yields methylene bis-[aluminum dichloride], $Cl_2Al{-}CH_2{-}AlCl_2$. Suitable electrolytes are $AlCl_3$, $HOAlCl_2$, and salts sufficiently soluble in dichloromethane to give a conducting solution.

It has been postulated that the following reactions occur at the anode[127]:



Iodination of aromatic hydrocarbons can be accomplished best in acetonitrile by performing iodine oxidation first and adding the aromatic hydrocarbon to this mixture. High yields (80–100%) of monoiodoaromatics are produced from benzene, toluene, xylene, and anisole. It is suggested that N-iodoacetonitrilium ion and N-iodoacetamide are the iodinating agents[128].



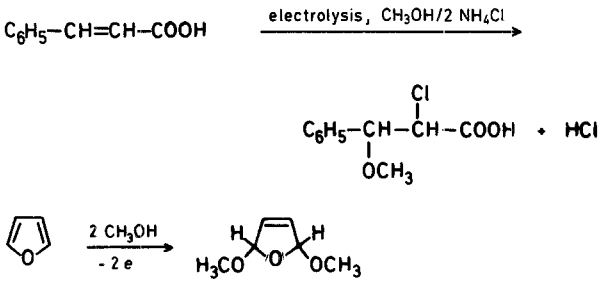
[115] S. Andreades, E. W. Zahnow, J. Amer. Chem. Soc. **91**, 4181 (1969).
[116] F. Fichter, P. Schönmann, Helv. Chim. Acta **19**, 1411 (1936).
[117] N. N. Melnikov, E. M. Cherkasova, Zh. Obshch. Khim. **16**, 1025 (1946).
[118] B. Belleau, N. L. Weinberg, J. Amer. Chem. Soc. **85**, 2525 (1963).
[119] T. Inoue, S. Tsutsumi, Bull. Chem. Soc. Japan **38**, 661 (1965).
[120] S. D. Ross, M. Finkelstein, J. J. Vebel, J. Org. Chem. **34**, 1018 (1969).
[121] H. Schäfer, E. Steckhan, Angew. Chem. **81**, 532 (1969); Angew. Chem., Internat. Edit. **8**, 518 (1969).
[122] L. Eberson, K. Nyberg, Tetrahedron Lett. **1966**, 2389.
[123] J. Mizuguchi et al., Denki Kagaku **34**, 124 (1966).
[124] H. Schäfer, Angew. Chem. **82**, 134 (1970); Angew. Chem., Internat. Edit. **9**, 158 (1970).
[125] J. Burdon, J. C. Tatlow, Advan. Fluorine Chem. **1**, 129 (1960).

The preparation of hypohalites for substitution, addition, and oxidation reactions is carried out at usually smooth platinum electrodes in a solution containing an alkali or alkaline earth salt of the halide. The halogen is liberated at the anode and hydrogen at the cathode. The hydroxide formed at the cathode diffuses to the anode and forms the hypohalite.

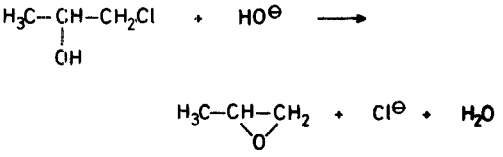
This reaction has been used to prepare chloroform from ethanol[129] and iodoform from ethanol and acetone[130].

A great many aldehyde sugars have been oxidized to the corresponding acids by electrolysis in a solution of calcium bromide between carbon electrodes[131].

In methanol, electrolysis of halides in the presence of olefins and furans leads to methoxy halogenated compounds and 2,5-dialkoxy-2,5-dihydrofuran derivatives, respectively[132,133]:



The electrochemical generation of halogens in the presence of olefins has recently received considerable attention in the production of epoxides. The olefin is converted to the halohydrin at the anode and the resulting solution is allowed to diffuse into the cathode compartment where it is converted by the alkali into the epoxide[134,135]:



3.6. Generation of Cation-Radicals

Electrochemical oxidation of organic compounds has proved useful for the preparation of cation-radicals for electron-spin resonance studies. The technique used is similar to that described under anion-radicals. Dichloromethane is a more suitable solvent than acetonitrile for such studies since the cation-radicals are more stable[136] in this medium.

3.7. Oxidation by Electrochemically Generated Oxidizing Agents

Oxidations by electrochemically generated hydroxyl radicals, atomic oxygen, or hydrogen peroxide occur in aqueous media and are complex. Examples may be found in a review on electrolytic oxidation of organic compounds[137].

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[126] H. SCHMIDT, H. MEINERT, Angew. Chem. **72**, 109 (1960).
[127] E. H. MOTTUS, M. R. ORT, J. Electrochem. Soc. **117**, 885 (1970).
[128] L. L. MILLER, E. P. KUJAWA, C. B. CAMPBELL, J. Amer. Chem. Soc. **92**, 2821 (1970).
[129] J. FEYER, Z. Elektrochem. **25**, 115 (1919).
[130] G. A. ROUSH, Trans. Electrochem. Soc. **8**, 283 (1905).
[131] H. S. ISBELL, H. L. FRUSH, F. J. BATES, Ind. Eng. Chem. **24**, 375 (1932).
[132] R. LENINGER, L. A. PASIUT, Trans. Electrochem. Soc. **88**, 73 (1945).
[133] N. CLAUSEN-KAAS, F. LIMBORG, K. GLENS, Acta Chem. Scand. **6**, 73 (1945).
[134] J. A. M. LEDUC, U.S. Patent 3379627 (1966), Pullman Inc.; C. A. **69**, 73488 (1968).
[135] A. P. TOMILOV, M. Y. FIOSHIN, Khim. Prom. **45**, 413 (1969).
[136] J. PHELPS, K. S. V. SANTHANAM, A. J. BARD, J. Amer. Chem. Soc. **89**, 1752 (1967).
[137] N. L. WEINBERG, H. R. WEINBERG, Chem. Rev. **68**, 449 (1968).