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RECENT DEVELOPMENTS IN ORGANIC SYNTHESIS BY ELECTROLYSIS

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I. INTRODUCTION AND APOLOGIA

Another review? Aren't there already sufficient recent ones both of the field in general[1] and of selected topics?[2] The justification for this one is comprised of several elements:

1. We see it as a variation on the old story of the tenor at LaScala who was wildly applauded after an aria, repeated it, was applauded again and again until someone in the audience shouted: "You'll sing it until you know it!" The practitioners of organic electrochemical synthesis will continue to sing their song until every experimental organic chemist as naturally considers (at least) using electrochemical methodology in a synthetic sequence as he/she accepts catalytic hydrogenation or ozonolysis or the use of exotic (expensive) reagents. There is some suspicion that additional presentations may be necessary before this objective is fully achieved.
2. This journal is a particularly appropriate medium since it is scored for organic chemists.
3. A reviewer with both industrial and academic experience may have viewpoints and interpretation not shared by those who have worked in only one of these environments. At the very least he is likely to be better acquainted with the rich patent literature perhaps overlooked by academics.
4. This is a very active area of research. New results appear daily.

Even the generous space allotment of a Tetrahedron Report does not permit the reviewer to start *ab initio* with an exposition of the principles and methods of organic electrochemical synthesis nor to define electrolysis, electrodes, divided and undivided cells, direct and indirect redox reactions, etc. The reader is referred to several recent papers which briefly but adequately provide this information *inter alia.*[1]

Fr. Fichter made great contributions to organic electrochemistry by his own researches and particularly by his classic 1942 book,[3] a veritable little Beilstein. Nevertheless two sentences in his Introduction[4] may have deterred more rapid progress in the field.

> „Mann kam del allegemeinen Grundsatz aufstellen dass alle elektrochemischen Oxydationen und Reduktionen auch auf rein chemischen Wege durchführbar sein müssen, und umgekehrt".

This statement, even if true in 1942 has been shown to be inaccurate by work in the succeeding decades.

There are now many electrochemical syntheses not (yet?) duplicated by chemical or catalytic means. The electrochemical generation of ion-radicals in an electric field in the vicinity of an electrode and the further chemical reactions of these reactive intermediates are of relatively recent development. Indeed the scope of organic electrochemical synthesis has now become so wide that "*und umgekehrt*" should be emphasised and made to pertain not only to obvious oxidation and reduction of functional groups: it includes generation and utilisation of anion radicals, carbanions, dicarbanions, cation radicals, cations, dications, radicals, acids/electrophiles, bases/nucleophiles.

Further:

> „Trotzdem muss an dem Grundsatz festgehalten werden, dass die electrochemischen Reaktionen nicht wesensverschieden sind von den rein chemischen Reaktionen".

Likewise unprophetic!

This review of recent developments does not aim to be comprehensive[1d] and must therefore reflect in its contents the reviewer's selection criteria. The expanding scope, alluded to above, of this field prompts a treatment which emphasises just this point: that organic electrochemical methodology have been used in ways that may surprise the secular[5] organic chemist not yet initiated into the rites of this practice. He/she will at least find one-step electrochemical syntheses to replace cleverly and laboriously executed multi-step syntheses! The organic chemist whether or not familiar with "Fichter" must be disabused of Fichter's dicta and must come to appreciate after reading only the few pages available here that organic electrochemistry comprises much more than polarography, the Kolbe Reaction, and redox conversion of functional groups. It is a methodology for doing organic syntheses!

II. SCOPE AND CLASSIFICATION OF ORGANIC ELECTROCHEMICAL REACTIONS

Primary events in electrolysis are the transfer of an electron from an electrode (cathode) to a species in solution or emulsion and from a substrate to an electrode (anode). By the very nature of the methodology both electrode reactions must occur simultaneously in a cell (paired reaction). Frequently only half the reactions have been considered of interest. The electron-transfer may occur before or after a chemical step (e.g. pre-protonation of ketones). Species capable of undergoing these electron-transfer reactions have been said to possess electrophores. Organic chemists' shorthand (and, as it turns out, simplistic) jargon for denoting "mechanisms" involves an array of $\underline{E}$lectrochemical and $\underline{C}$hemical steps in presumed proper sequence, e.g. EC, ECE, CEC, etc.

The types of intermediates that are generated by the primary events have been mentioned above. The synthetic chemistry that ensues can be understood as the chemistry of these intermediates with these provisos: they are formed at or near an electrode surface where they may/may not be adsorbed; they are under the influence of a strong electric field; they are in an environment where concentration gradients exist since the precursors are being depleted by the electrode reaction.

There are many schemes for classifying organic electrochemical reactions. It is important for the organic chemist who wishes to integrate this subject into the body of organic chemical theory and practice to examine each reaction from several points of view[7] a la *Rashomon*. This is a multi *n* disciplinary subject; *n* is large enough to be enlightening albeit sometimes distressing.

A. Cathodic *or* anodic reactions when only one of these is synthetically useful.

B. Paired reactions in which *both* in concert result in useful syntheses.

C. Transformation of functional groups, e.g. $-NO_2 \rightarrow -NH_2$, $-CH_2OH \rightarrow -CHO$. This may be "trivial" in Eberson's context[1e] but is of increasing importance to industrial organic chemists (who comprise much more than 50% of the corpus) when it allows an electroregeneratable "mediator" to be used in catalytic amounts in place of chemical redox reagents used stoichiometrically.[8]

D. In terms of the nucleophilic (basic) and electrophilic (acidic) character of the substrates.[1e] The important point here is that the electron-transfer step converts one type into the other! This was illustrated a number of years ago in reductive couplings of and between Michael acceptors: one view, often but not universally valid, of these reactions was that the *acceptor* upon reduction becomes a *donor* toward unreduced acceptors.[9] With the ready adoption of the term *umpolung*[10a,b] into the jargon of organic chemistry this principle is being increasingly stressed.[1b,e]

E. Coupling

F. Cleavage

G. Substitution

H. Elimination

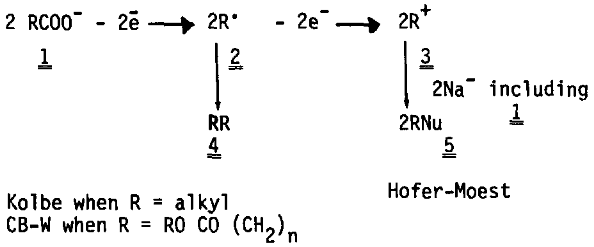
I. Addition
J. Electron-transfer to/from electrodes followed by homogeneous electron-transfers in solution.
K. Indirect electrolyses
L. Electrogenerated bases and acids
M. Photoelectrochemistry
N. Electrocatalysis
O. Cyclisations

As will become evident, these categories are often redundant.

III. SOME RECENT SYNTHETIC RESULTS

A. *The Kolbe reaction and its variants*

1. *Scope.* The Kolbe formation of alkyl dimers by anodic decarboxylation of alkyl carboxylates is the primordial defined organic electrochemical reaction. The Crum Brown-Walker (CB-W) and Hofer-Moest (H-M) reactions are now also "classical" but new findings, the "pseudo-Kolbe"[12], the "photo-Kolbe"[13] and oxidative decarboxylation by organic mediators[14] are of recent origin.



Scheme 1. Products from anodic oxidation of carboxylates.

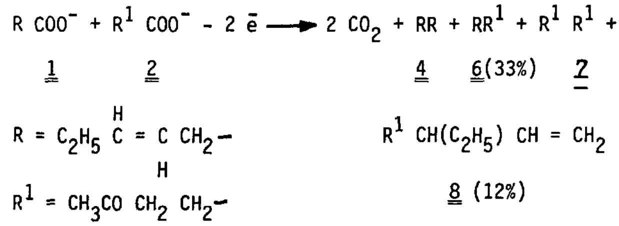
Control of the parameters such as electrode material, current density, presence/absence of additional supporting electrolytes, temperature and solvent in fairly well-defined ways permits the preparation of largely **2** or largely **4** as intermediates and therefore of the nature of the final products derived from them. Further, if two different carboxylates (**1**, *R* and *R*′) are co-electrolyzed, "mixed" or "cross" Kolbe products **4** (RR′) are obtained. Anodic bis-decarboxylation of *vic*-dicarboxylates is often a superior route to olefins. The Kolbe reaction with substituted cyclobutane-1,3-dicarboxylates yielded the bicyclobutane system. The radical intermediates **2** may, in addition to or in place of, dimerising to **4** be intercepted by suitable vinyl monomers to initiate polymerisation or by conjugated dienes to yield additive dimers or by ethylene under pressure to yield oligomeric saturated dicarboxylates or by oxygen to yield dialkyl peroxides.[21] Follow-up reactions of **3**, as is known in carbocation chemistry, may include in addition to conversion to **5**, rearrangements to more stable cations, elimination of protons to form olefins, ring expansion if, e.g. **3** is 2-cyclohexyl-2-hydroxyethanoic acid, reaction with *in situ* nitriles leading to iminium cations which can be hydrolysed to the Ritter products or, intramolecularly, to *N*-heterocycles. Since the *R* group of **1** may also bear functions which are inert to the usual Kolbe conditions (OH, Cl, F, CN, NH_2), dimeric products bearing substituted alkyl groups may be obtained.

Despite the enormous amount of work that has been done on Kolbe's reaction, its extension into directions "never dreamt of in his philosophy" has continued to present challenging research problems for the organic chemist who is interested in laboratory synthetic methodology or mechanism or industrial production.

Usually smooth Pt or some form of *C* is used as the anode material. The reactor (electrochemical cell) is almost always *undivided* and may be as simple as a beaker or multi-necked flask or may be rather complex. (The organic chemist does not hesitate to use a bottle in a shaker for catalytic hydrogenations under modest pressure or an autoclave behind a concrete barrier and external controls for safe hydrogenation under high pressure). The accompanying cathodic reaction is usually discharge of protons to hydrogen at any number of suitable cathodes.

2. *In syntheses of phermones.*[1b] Although the "mixed" or "cross-" Kolbe Reaction referred to above usually leads to *three* products it has been used successfully in foreshortened syntheses of intermediates

for at least the following pheromones: muscalure, looplure, dispalure, and brevicomin. The synthesis of *trans*-6-nonen-2-one (**6**) which is later converted by OsO_4/pyridine to brevicomin is illustrative.[15] It is



$$\underset{\underline{1}}{\mathrm{R\,COO^-}} + \underset{\underline{2}}{\mathrm{R^1\,COO^-}} - 2\,\bar{e} \longrightarrow 2\,\mathrm{CO_2} + \mathrm{RR} + \underset{\underline{4}}{\mathrm{RR^1}} + \underset{\underline{6}(33\%)}{\mathrm{R^1\,R^1}} + \underset{\underline{7}}{}$$

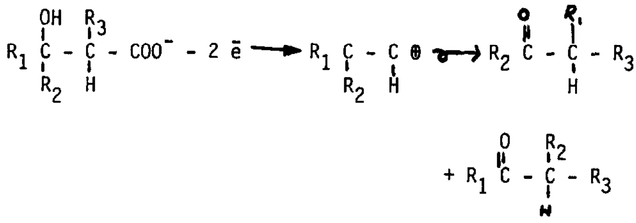
$$\mathrm{R} = \mathrm{C_2H_5\,\overset{H}{C} = \underset{H}{C}\,CH_2-} \qquad \mathrm{R^1\,CH(C_2H_5)\,CH = CH_2}$$

$$\mathrm{R^1} = \mathrm{CH_3CO\,CH_2\,CH_2-} \qquad \underline{8}\ (12\%)$$

Scheme 2. Pt electrodes, MeOH solution containing 0.1 mol KOMe, 0.5 mol **1**, 0.10 mol **2**, c.d. 166 mA/cm^2, 0.56F.

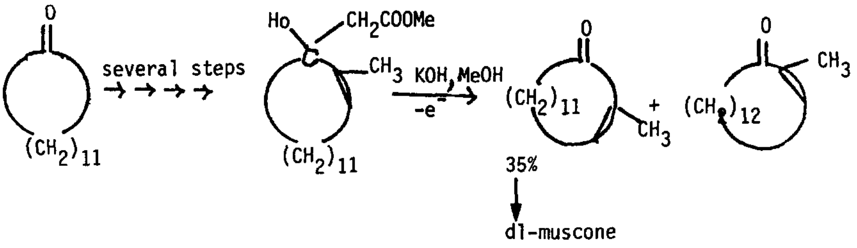
interesting that in this case only one self-coupling product (**7**) was reported and that the cross-coupled products (**6**, **8**) involved coupling of the radical derived from **2** at both the 1-and 3-positions of the allylic radical derived from **1**.

3. *In the synthesis of dl-muscone.*[16] Two-electron oxidation of β-hydroxy–carboxylates leads to intermediate β-hydroxy-carbocations which are similar to those formed in the familiar pinacol-



Scheme 3.

pinacolone rearrangement. A study of the migratory aptitude of R_1 and R_2 led to the order benzylic, cyclopropyl, olefinic > alkyl; these results were expoited in a synthesis of dl-muscone.



Scheme 4.

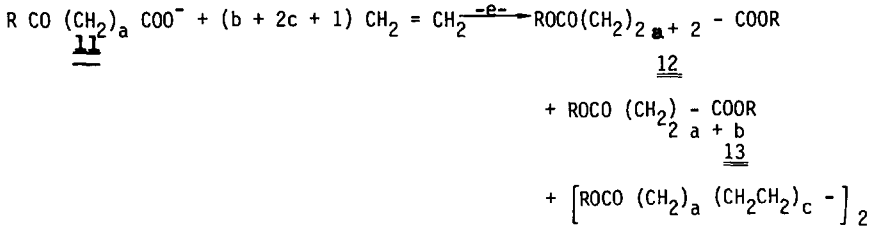
4. *Synthesis of dialkyl sebacates.* The CB–W process for the preparation of sebacate esters (and derived sebacic acid) has been intensively studied in many countries and is now practiced commercially in the USSR and in Japan:[17]

$$\underset{\mathbf{9}}{\mathrm{2ROCO(CH_2)_4COO^-}} - 2\bar{e} \rightarrow \underset{\mathbf{10}}{\mathrm{ROCO(CH_2)_4COOR}} + \mathrm{2CO_2, R = Me,\ usually.}$$

(Undivided cell. Bipolar electrodes with Pt plated anodes and Ti cathode. **9** (R = Me) partially neutralized with KOH or K_2CO_3 Curr dens. *ca* 10 A/dm^2. Selectivity to **10** *ca* 81%; curr. eff. *ca* 63%. Solvent: MeOH + *ca.* 0.5% H_2O). It is noteworthy that despite the fact that 30% of the starting material (adipic acid) is lost as CO_2, and that the yields of product are less than quantitative this process is more economical than the secular synthesis from ricinoleic acid; this derives largely from the circumstance that the latter raw material is obtained from a natural source of variable availability and price while the former, required in huge tonnage for the manufacture of Nylon 6.6, is the cheapest dicarboxylic acid on the market.

5. *Syntheses which involve trapping of "Kolbe-type" radicals.* Despite the fact that the optimum conditions for the Kolbe and allied reactions require a high anodic current density and therefore lead to the generation of a high local concentration of radicals, the usual course of the reaction, i.e. coupling of these radicals, may be altered if suitable radical traps, themselves not electrochemically active under the conditions of the electrolysis, are included in the medium. These radical traps may be simultaneously produced inorganic radicals (e.g. $.N_3$, $.NF_2$, $.NO_3$), "electron-rich" olefins like alkyl vinyl ethers, "electron-poor" olefins such as styrene, or 1,3-dienes like butadiene and isoprene. The synthetic results obtained with monoolefins are complex because among other reactions the "Kolbe radical" may add 1,2-to the double bond or may add to the 1-position and be followed by dimerisation of the adduct; these findings are adequately discussed in the literature.

Synthetically advantageous results have been obtained when the "CB-W radicals" from monoalkyl oxalates or monoalkyl adipates have been trapped by butadiene: 1,4-addition of the radicals gives diesters in which four carbon atoms from a relatively inexpensive source have been interposed between the ester-bearing functions; 1-addition followed by radical dimerisation interposes eight such carbon atoms. Yields as high as 88% of this mixture of products have been reported.



$$\underset{\underline{\underline{11}}}{\mathrm{R\,CO\,(CH_2)_a\,COO^-}} + (b + 2c + 1)\,\mathrm{CH_2 = CH_2} \xrightarrow{-e-} \underset{\underline{\underline{12}}}{\mathrm{ROCO(CH_2)_{2a+2} - COOR}}$$

$$+ \underset{\underline{\underline{13}}}{\mathrm{ROCO\,(CH_2)_{2a+b} - COOR}}$$

$$+ \left[\mathrm{ROCO\,(CH_2)_a\,(CH_2CH_2)_c -}\right]_2$$

Scheme 5.

The diesters obtained by the above route are still unsaturated and must be catalytically hydrogenated to yield the products of commercial interest. The need for this second step could be obviated if *ethylene* itself could serve as the radical trap. A paper summarizing several years' work with just this objective has been published recently.[18] Electrolysis of a methanol solution of **11** (R=Me, a=0) with ethylene under pressure yielded 70–90% (after partial saponification of dimethyl oxalate and recycling of the half ester) of the dimethyl esters of succinic, adipic, suberic, and sebacic acids. Decrease of ethylene pressure or increase of the current density led to a decrease in the content of the higher esters in the product mix. Electrolysis of **11** (R = Me, a = 4) under the above conditions yielded at Pt dimethyl sebacate, the usual CB-W product, as well as the dimethyl esters of 1,10-decade-decarboxylic and 1,12-dodecane-dicarboxylic acid; at a glassy C anode only the CB-W product was formed.

It is amusing that by accident or by design complementary anodic and cathodic processes have been/can be developed for the preparation of similar compounds. Different raw materials are of course required in the two cases. E.g. electroreduction of CO_2 under ethylene pressure in aprotic media yielded oxalate, the expected self-coupling product,[19] and succinate; the formation of higher dicarboxylate acids was not reported.[20] The anodic preparation of several dialkyl peroxides by *in situ* reaction of "Kolbe radicals" with oxygen[21] has its counterpart in the reaction of alkyl halides with electrogenerated superoxide.[22] For the researcher avid for challenging problems it would be an interesting exercise to attempt to combine in one undivided cell the reductive coupling of acrylonitrile to adiponitrile[23] with the Kolbe reaction of β-cyano-propionate[24] which would also lead to the same product.

6. *The "Pseudo-Kolbe" reaction.* In a careful study of the Kolbe reaction with unsubstituted and substituted phenylacetates which included effects of changes in current density, electrode potential and "foreign" anions (perchlorate) upon the distribution of products it was concluded that when the carboxylate contained an electron-donating group (p-methoxy-phenylacetate) electron-transfer from the substrate to the anode occurred initially from the aromatic nucleus rather than from the carboxylate groups[25]. Product distributions were related to structural, electrochemical, and adsorption parameters.

7. *The "Photo-Kolbe" reaction.* A. J. Bard *et al.*[26] have invented a photochemical means for oxidative decarboxylation of $RCOO^-$ which leads mainly to RH rather than to the "Kolbe dimer" RR. Aside from its scientific novelty, this procedure offers a potential means for converting unsubstituted carboxylic acids, particularly those derived from biomass, into fuels. Substituted biomass-derived carboxylic acids such as levulinic acid could by this methodology yield fuels or fuel additives and useful

organic chemicals. This possibility is under investigation at the Solar Energy Research Institute; the following discussion is taken from H. Chum's 1982 report.[27]

When acetate solutions are irradiated in the presence of particulate photoelectrochemical diodes of n-TiO_2/Pt, the major product of that reaction was methane; *ca* 10% of ethane, the Kolbe product, along with some hydrogen were also detected. Experiments with deuterated water yielded CH_3D as the major product, consistent with a reduction reaction involving the solvent water, and no hyrodgen abstraction from the acetic acid methyl groups. The platinized semiconductor particules act as short-circuited electrodes. Illumination with light of energy greater than the bandgap ($>3-3.2$eV) of the semiconductor causes the formation of electron-hole pairs. The recombination of the electron-hole pairs is partially prevented by the following fast chemical reactions. The holes oxidize acetate ions to $CH_3CO_2^{\cdot}$/radicals, which rapidly decompose to methyl radicals and carbon dioxide. The electrons reduce protons of the solvent to hydrogen. The by-product hydrogen and the isotopic substitution pattern indicate that the methane formed is a result of the reaction between methyl radicals and hydrogen (from the solvent).

This investigation was extended to other saturated carboxylic acids, namely, propionic, butyric, valeric, pivalic, adamantane-1-carboxylic acids. All these acids were photoelectrochemically decarboxylated to the corresponding hydrocarbons. The influence of solution composition, reaction temperature, light intensity, and semiconductor properties (crystallographic structure and doping) were investigated in detail for the acetic acid/acetate system. The optimum pH for the decarboxylation was found to be ~ 3.5, with one-half to one-third of the rate being found in the more acid (pH ~ 1) and neutral to more alkaline regions (pH ~ 6–8). The anatase powders were found to be more reactive than the rutile particles. The reactivity for anatase increased in the following order: undoped < doped < undoped, platinized < doped, platinized. The rate is decreased by decreasing the light intensity (from 1600 to 450 W) and temperature (from 55° to 45°). The decarboxylation rate was found to be a function of carboxylate concentration only at low concentrations of carboxylate ions. This finding suggested adsorption of the carboxylate anions or acids as an important step.

The mechanism proposed by Bard *et al.* for the reaction was the following (see also Scheme):

(1) excitation of electrons from valence band to the conduction band by light of energy greater than the semiconductor band gap

$$TiO_2 + h\nu \rightarrow e^-_{cb} + h^+_{vb}$$

(2) band bending at the interface; the electric field in the space charge region will promote the separation of electrons and holes.

This makes possible the trapping of the separated charges at the surface:

$$e^-_{cb} \rightarrow e^-_{tr}$$
$$h^+_{vb} \rightarrow h^+_{tr}.$$

(3) The trapped holes can oxidise carboxylate ions or water:

$$h^+_{tr} + RCO^-_{2ads} \rightarrow R. + CO_2$$
$$h^+_{tr} + H_2O_{ads} \rightarrow HO. + H^+.$$

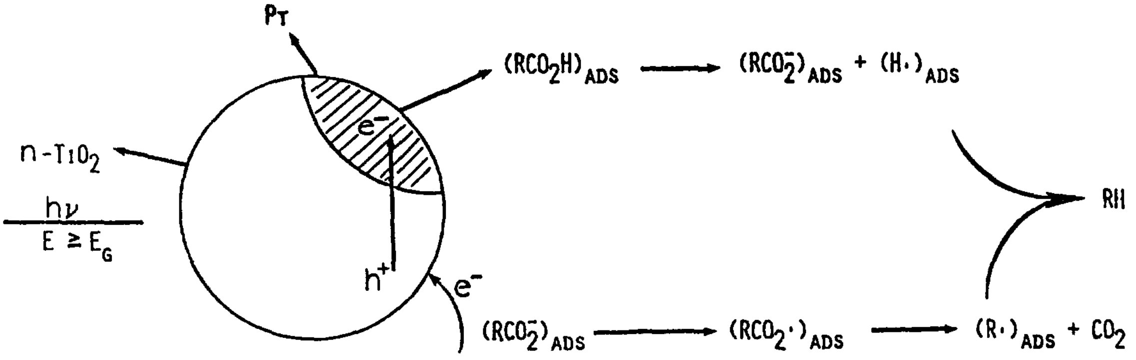
(4) The trapped electrons can perform reduction reactions, e.g.:

$$e^-_{tr} + RCO_2H \rightarrow H_{ads} + RCO_2^-$$
$$e^- + R. + RCO_2H \rightarrow RH + RCO_2^-.$$

(5) By-products result from radical recombination reactions:

$$2R. \rightarrow R_2$$
$$2H_{ads} \rightarrow H_2.$$

The participation of radical intermediates was directly observed by electron spin resonance.[26a] The methyl radicals were reacted with α-phenyl-n-tert-butylnitrone and the product gave the expected



Scheme 6.

spectrum. Direct radical detection was possible in the case of triphenylmethyl radical obtained from triphenylacetic acid.

Photodecarboxylation of adipic acid led to valeric acid and butane.[26c]

8. *By organic mediators.* Some of the features of ***heterogeneous*** oxidative decarboxylation at an anode are simulated by ***homogenous*** electron-transfer from the carboxylate to an oxidant which itself, at least in principle, could have been made at the anode. Obviously the special conditions which prevail in electrolysis, i.e. formation of high local concentration of intermediate radicals or carbocations, adsorption effects, and existence of a strong electric field do not obtain in homogeneous electron transfer; therefore a different distribution of products may be expected and is indeed found in applying one technique rather than the other.

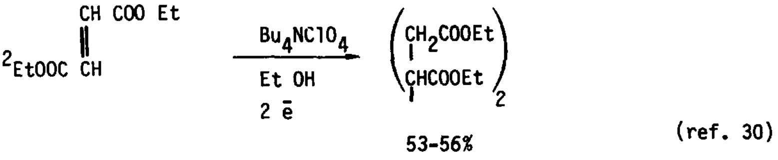
Aqueous persulfate or sulfuric acid, Co(III) in water or H_2O–CH_3CN and fluorine have been used in lieu of anodes.[28] When the mediator is oxidised in a cell more easily than is a carboxylate anion then, provided electron-transfer from the carboxylate to the oxidised mediator can occur at a synthetically useful rate, there is the possibility of reducing the amount of energy required for the overall process. This was the motivation for using for the first time an organic mediator tris-(p-bromophenyl) amine.[29] The latter is oxidised to its cation radical at a voltage ca 0.5V less positive than is required for the oxidation of carboxylates under the same conditions. Three representative *n*-alkylcarboxylates $RCOO^-$ ($R = C_7H_{15}, C_8H_{17}, C_{13}H_{27}$) were thus converted into esters RCOOR′ (H-M Reaction); the origin of the R′ is a question for further study.

B. *Coupling Reactions*

1. *Scope.* The joining of two molecules as a consequence of either cathodic or anodic events presents some of the finest examples of the types of reactions which can be done especially if not always uniquely well by electrochemistry. If the focus is upon the synthetic products rather than upon the mechanisms whereby they are obtained, the field has very broad scope indeed: The coupling may be the result of an anodic process or a cathodic process or both simultaneously (paired reactions); it may be intermolecular between two identical molecules (yielding hydrodimers) or two unidentical molecules (mixed or crossed-reductive coupling) leading usually to the formation of difunctional products from monofunctional precursors; it may be intramolecular (cyclisation); it may result from interactions of reactions of electrochemically formed intermediate molecules; it may involve the joining of two intact molecules followed by addition (cathodic) or removal (anodic) of protons or the combination of fragments formed after a substrate has undergone a preliminary cleavage reaction (e.g. the Kolbe). In view of this multiplicity of electrochemical routes to coupled products only a few representative examples can be cited.

2. *Syntheses.*

a. *Cathodic.*



Scheme 7. Intermolecular; hydrodimerization; no cleavage.

$$CH_3(CH_2)_2CHO + CH_2=CHCN \xrightarrow[\substack{K_3PO_4\\ \text{const. curr.}}]{\text{C cathode}} CH_3(CH_2)_2CH(OH)(CH_2)_2CN$$

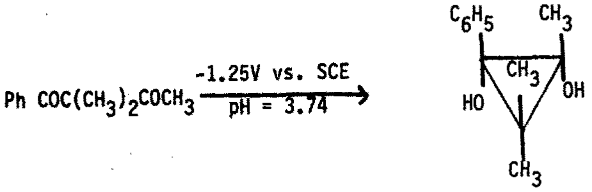
40.8% curr. eff. (ref. 31)

Scheme 8. Intermolecular; crossed; no cleavage.

$$PhCH_2Cl + RCOCl \xrightarrow[\substack{CH_3CN\\ -2.1 \text{ to } 2.4V \text{ vs. SCE}}]{\substack{\text{C cathode}\\ Et_4N^+ TSO^-}} PhCH_2COR$$

(ref. 32)

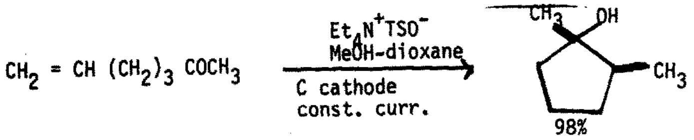
Scheme 9. Intermolecular; cleavage.



(ref. 33)

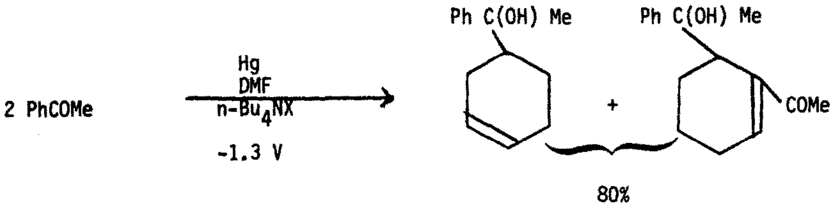
80% yield, 1:1 isomers

Scheme 10.

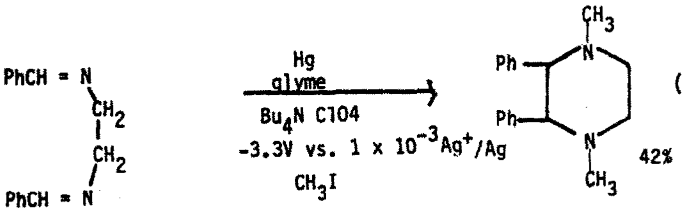


(ref. 34)

Scheme 11.

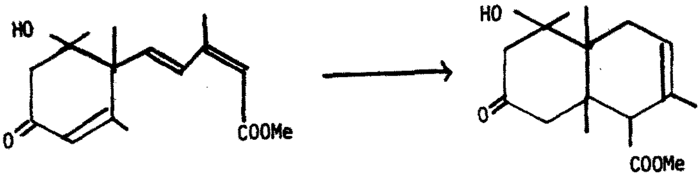


Scheme 12.



(ref. 35a)

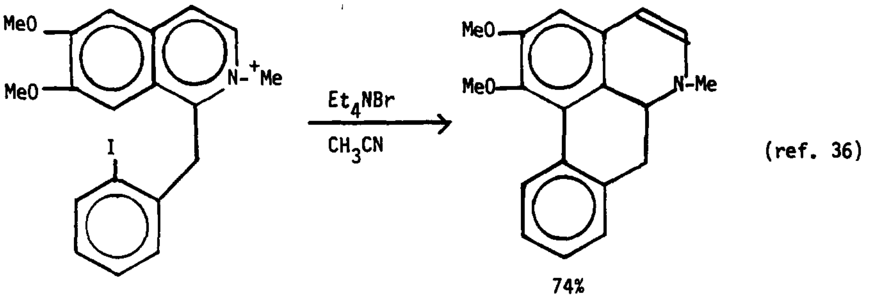
Scheme 12a.



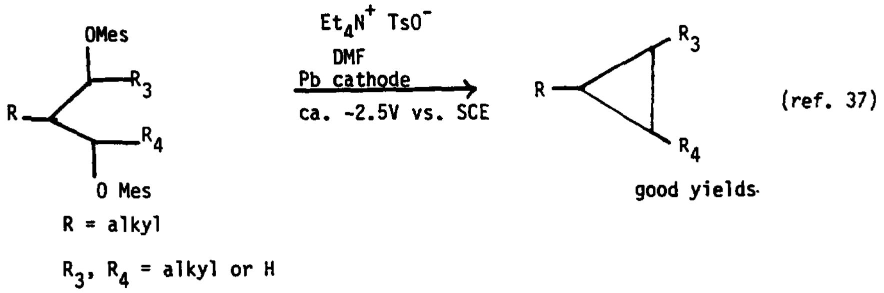
(ref. 35b)

Scheme 13.

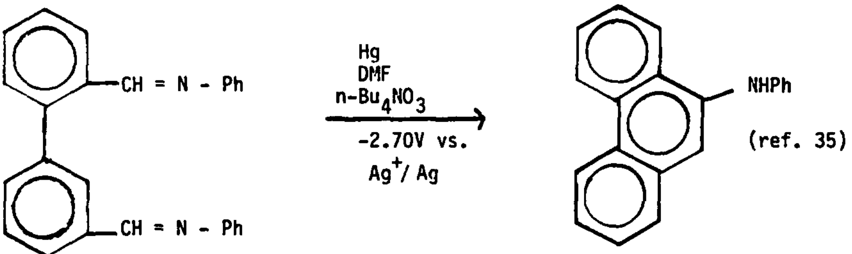
Schemes 11-13. Intramolecular; no cleavage.



Scheme 14.



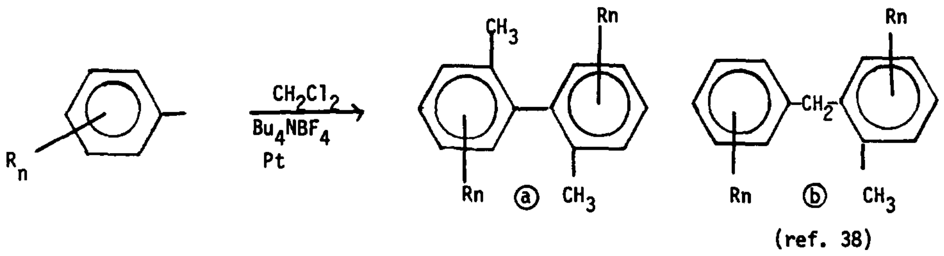
Scheme 15.



Scheme 16.

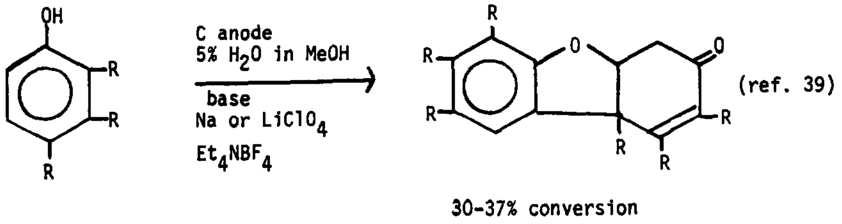
Schemes 14–16. Intramolecular; cleavage.

b. *Anodic.*

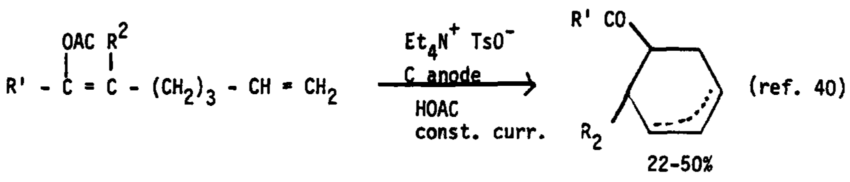


Substrate	Ratio a:b
R_n = 4-Me	1:99
R_n = 3,5-di-Me	100:0
R_n = 2,4,5-tri-Me	0:100

Scheme 17. Intermolecular; no cleavage.



Scheme 18. Intramolecular; no cleavage.



Scheme 19. Intramolecular; cleavage.

c. *Paired.* The attractiveness and problems involved in devising, for undivided cells, syntheses in which the simultaneous anodic and cathodic reactions produce useful product(s) have been discussed.[41] Whilst other pairs comprising cathodic *and* anodic coupling have been studied, the results are not yet cleared for publication; the reductive dimerisation of acrylate esters to adipate diesters and oxidative dimerisation of malonate to bimalonate have, however, been investigated both in static[42] and in flow cells.[43] The excellent yields and acceptable current efficiency obtained illustrate that even in such a case, which is replete with possibilities for side-reactions, a proper *modus operandi* can be developed.

A more general discussion of paired reactions is given in V.

$$2CH_2{=}CHCOOEt + 2\ CH_2(COOEt)_2 \ \pm\ 2e^- \rightarrow \underset{95\%}{EtOCO(CH_2)_4COOEt} + \underset{95\%}{[-CH(COOEt)_2]_2}$$

Scheme 20. Pb cathode, C anode, Bu_4NI/CH_3CN · Curr. eff. 60%.

d. *Mechanisms.* Many of the papers cited above which deal with such a great variety of electrolytic coupling reactions contain in addition to synthetic results at least hypotheses concerning the routes leading to major and minor products. The reductive coupling of activated olefins, particularly 1,2-diactivated olefins (diethyl fumarate is a favourite substrate) has inspired many mechanistic investigations; a variety of techniques has been employed singly and in combination for the elucidations. At issue has been the question of the contribution to the overall results of radical-anion dimerisation (EC) and radical-anion-substrate coupling followed by a second one-electron-transfer (ECE) and the effects upon this competition of solvent, presence/absence of water, and nature of the cation of the supporting electrolyte. The reader is referred to the papers by A. J. Bard,[44] J.-M. Savéant,[45] V. D. Parker[46] and their respective co-workers and by others[47] on this still controversial subject.

C. *Reductive carboxylation*

1. *Scope.* Organic species which bear a negative charge (anions from carbon, nitrogen, sulfur acids; anion radicals; dianions), unless they are sterically hindered from doing so, react with CO_2 to yield carboxylates. The needed intermediates can be made from the corresponding precursors (a) by direct cathodic reduction when they are electroactive or (b) by deprotonation using an electrogenerated base (EGB) (v.i.). In addition, CO_2 is itself reducible to its anion-radical (*ca* -2.3 V vs S.C.E., DMF/R_4N^+, Hg) which may add to olefinic substrates which are not electroactive and not carbon acids of accessible pKa range (*cf* reaction with ethylene discussed above). Electrochemical formation of carboxylates thus covers almost the entire gamut of possibilities; it is a method of choice when the secular alternatives require the use of expensive reagents (Grignard, LDA, NaH, etc.) or large excesses of mediators such as

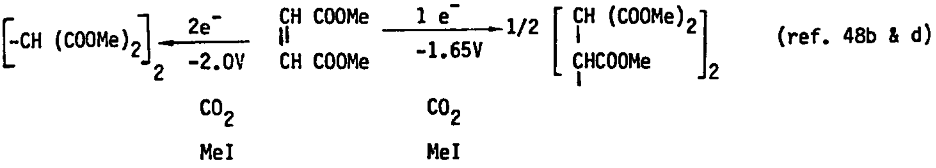
the alkali metal-phenoxide-CO_2 complexes or prior partial reduction of a substrate by electron-transfer from an alkali metal.

2. *Syntheses.*

$$CH_2 = CHCN + CO_2 + H_2O \xrightarrow[\substack{CH_3CH_2CN- \\ Bu_4NBF_4}]{\substack{e^- \\ Hg}} HOCO\,CH_2\,CH_2CN$$

50% curr. eff. (ref. 24)

Scheme 21.



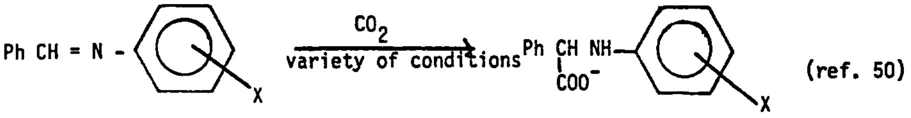
Scheme 22.

$$PhCH = CH\,E \xrightarrow[\substack{Hg \\ DMF - Et_4NClO_4 \\ R'I}]{CO_2} Ph\,\underset{COOR'}{CH}\,CH_2E$$

E = CN, CO Me, COOR .

moderate yields (ref. 49)

Scheme 23.



Scheme 24.

N-Heterocycles
quinolines, isoquinolines, quinoxalines, phenanthrolines, pyridazines quinazolines, pyridines

$$\xrightarrow[\substack{Bu_4NI \\ CO_2}]{DMF}$$

carboxylated products (ref. 51)
moderate yields

Scheme 25.

Schemes 21-25. Reduction of substrate + coupling with CO_2; no cleavages.

$$2\,RX + CO_2 \xrightarrow[Z_4N^+Br^-]{\substack{Hg \\ DMF}} [RCO\bar{O}\ Z_4N^+] \longrightarrow R\,COOR$$

(ref. 50)

allyl crotonate;

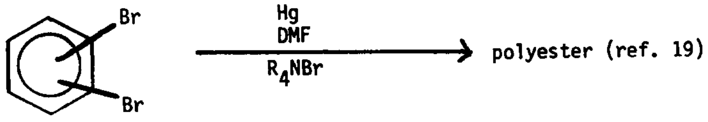
benzyl phenylacetate

R = allyl, benzyl

X = Cl, Br

Z = alkyl

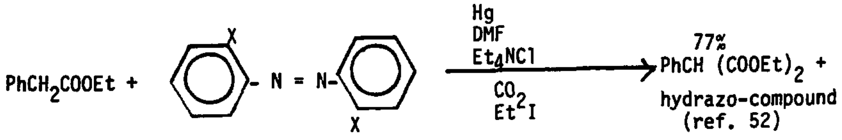
Scheme 26.



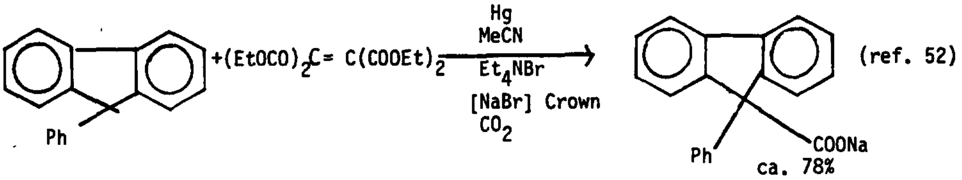
Scheme 27.

Schemes 26-27. Reductive cleavage & carboxylation.

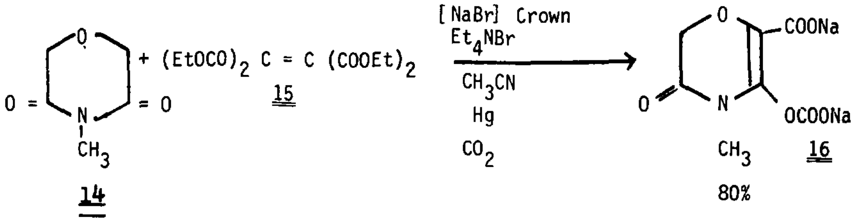
Compounds (probases) which are electrochemically reduced intact to anion-radicals or anions before CO_2 is reduced can deprotonate electro-inactive carbons acids of appropriate pKa; the intermediate carbanions formed may be trapped by *in situ* CO_2. In some cases it is necessary to choose a probase which has bulky blocking groups flanking the multiple bond to be reduced in order to generate a useful EGB.



Scheme 28.



Scheme 29.



Scheme 30.

Schemes 28–30. Carboxylation of anions prepared by EGB's.

3. ***Products from carbon dioxide itself.*** There is increasing desire to use biomass-derived (renewable) materials and coal as sources which are alternatives to petroleum for producing the feedstocks for the organic chemical industry. Most of the world-wide work in this area involves catalysis but electrochemistry will continue to contribute importantly and sometimes uniquely to this endeavour.[54,55] In this connection Scheme 31 shows the products that have been made from CO_2 and its electrochemically derived products.

D. *Syntheses Involving Carbon Monoxide*

Carbon monoxide has been employed as a building block in both cathodic and anodic syntheses of organic and organometallic compounds. For best results the reactor/cell is designed to allow electrolysis under pressure. An excellent design is illustrated in the literature.[56,57]

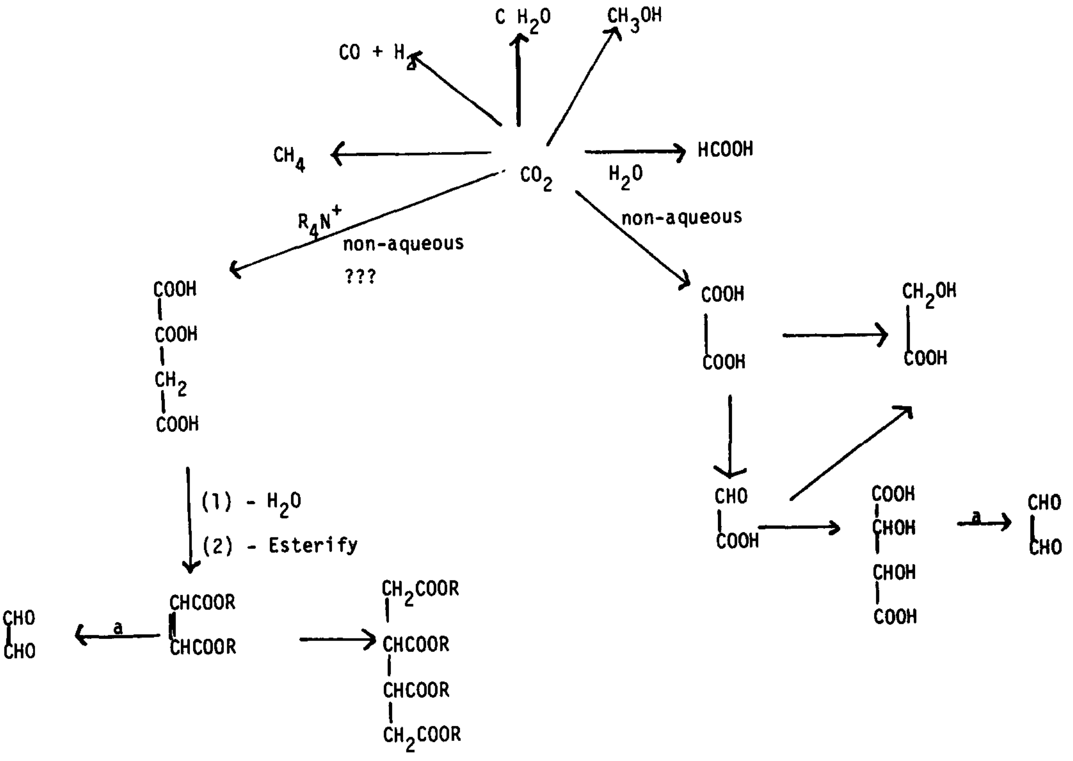
From CO alone "squaric" ("quadratic") acid[56] has been formed cathodically in moderate yields under the conditions given in Scheme 32. Reduction of methanol in the presence of CO yields methyl formate; if a dialkylamine is also present it reacts *in situ* with the intermediate ester to furnish N,N-dialkyl-amides (Schemes 33–34).[58]

On the other hand if the base which catalyses the addition of CO to RO^- is a complexed alkoxide or an electrogenerated carbanion alkyl glyoxylate hemiacetals are formed.[59]

Transition metal carbonyls, very useful as catalysts constituents, are (most?) conveniently made by reduction in the presence of CO of the metal liganded to halides, *acac* or cyclopentadiene.[61] Thus chromium hexacarbonyl can be prepared[56] in up to 85% yield under the conditions shown in Scheme 36; several other metal carbonyls have been made from the appropriate *acac* derivative (Scheme 37).[61]

Anodic reactions with CO have also been used to prepare (complexed) metal carbonyls (Scheme 38);[62] this complements the cathodic method cited above.[60]

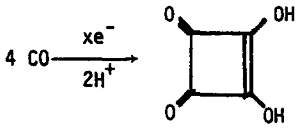
While cathodic reduction of MeOH in the presence of CO yields methyl formate (Scheme 33),



[a]Oxidation

Scheme 31. Products from electroreduction of CO_2.

Cathodic synthesis of "squaric" (quadratic) acid



(ref. 57)

CONDITIONS

Al anode, steel cathode

DMF/Bu_4NBr

Pressure: 120 atm

Temp. 80°

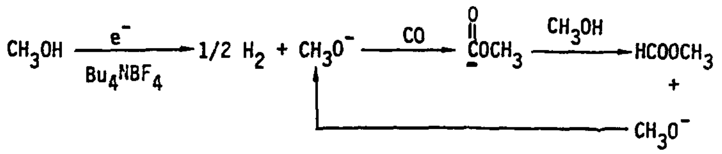
100 mA @ ca. 3V

Al salt formed which is then acidified

Scheme 32.

CATHODIC SYNTHESES WITH CO

Of formates

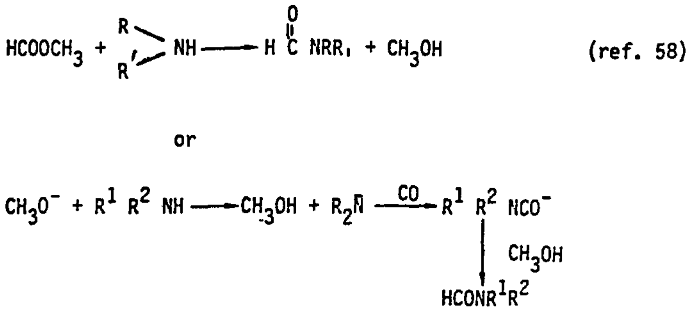


$$CH_3OH \xrightarrow[Bu_4NBF_4]{e^-} 1/2\ H_2 + CH_3O^- \xrightarrow{CO} \overset{O}{\overset{\|}{\underset{-}{C}}}OCH_3 \xrightarrow{CH_3OH} HCOOCH_3 + CH_3O^-$$

Scheme 33.

Of N,N-dialkylamides

In presence of mono- or dialkyamines:



$$HCOOCH_3 + \begin{matrix} R \\ R' \end{matrix}\!\!>NH \longrightarrow H\overset{O}{\overset{\|}{C}}NRR' + CH_3OH \qquad \text{(ref. 58)}$$

or

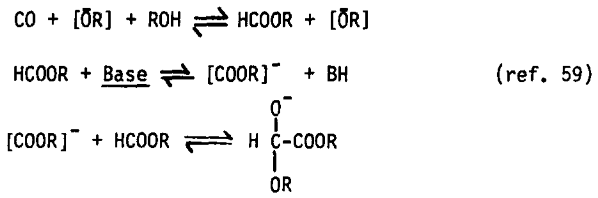
$$CH_3O^- + R^1R^2NH \longrightarrow CH_3OH + R_2\bar{N} \xrightarrow{CO} R^1R^2NCO^- \xrightarrow{CH_3OH} HCONR^1R^2$$

Scheme 34.

CATHODIC SYNTHESES WITH CO

Of glyoxylic acid derivatives

Start with CO + ROH or HCOOR



$$CO + [\bar{O}R] + ROH \rightleftharpoons HCOOR + [\bar{O}R]$$

$$HCOOR + \underline{Base} \rightleftharpoons [COOR]^- + BH \qquad \text{(ref. 59)}$$

$$[COOR]^- + HCOOR \rightleftharpoons H\underset{OR}{\overset{O^-}{C}}\text{-}COOR$$

Base may be $M^+\ \bar{O}R$ complexed with crown ethers, polyamines, pentaglyme or electrogenerated carbanion

Scheme 35.

CATHODIC SYNTHESES WITH CO

Of Cr $(CO)_6$

$$CrX_3 \xrightarrow[\substack{CO \\ Bu_4NBr}]{pyridine} \underset{85\%}{Cr(CO)_6} \qquad \text{(ref. 56)}$$

X = acac or Cl

Conditions

Pressure: 50-180 atm.

Temp: ca. 85^0

cd: ca 50 mA

Cathode: stainless steel

Anode: Al

Solvents: Pyr, THF, MeCN, dimethoxy-ethane, propylene carbonate

Scheme 36. Ref 56 has drawing of the high pressure cell.

CATHODIC SYNTHESES WITH CO

Of transition metal carbonyls

$$M\ (acac)_x \xrightarrow[CO]{e^-} M(CO)_x$$

M = V, Cr, Mn, Fe, CO, Ni (ref. 61)

Conditions

Cathode: graphite or stainless steel

Anode: Al

SSE: Pyridine ± DMF/Bu_4NBr

Temp: $25\text{-}85^0$

Pressure: 1-190 atm

C.d. 1-10 mA/cm^2

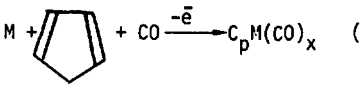
Voltage: 3-150V

Typical by-products: $C_5H_5N\ Cr\ (CO)_5$

$(C_5H_5N)_2\ Cr(CO)_4$

Scheme 37.

ANODIC SYNTHESES WITH CO



(ref. 62)

Anode M	x =
Fe	2-dimer
Co	2
Ti	2
V	4
Ni	no

Scheme 38.

(indirect) anodic oxidation in similar systems results in the formation of dimethyl carbonate (Scheme 39).[58,63]

Trapping of anodically generated carbocations with CO to form acylium intermediates to alcohols esters, etc. was explored some years ago with moderate success. Interesting new results have been reported using super-acids (plus their salts) as electrolytes for this type of carbonylation (Scheme 40).[64] While synthetically useful results have been obtained using cycloparaffins the expected multiplicity of products is obtained from acyclic hydrocarbons (Scheme 41). This is the electrochemical equivalent of the Koch Reaction; exploitation on an industrial scale awaits the development of means for recovering and recycling economically the solvent-electrolyte system.

ANODIC SYNTHESES WITH CO

Of dialkyl carbonates

$$\mathrm{MBr + CO + ROH} \xrightarrow{-2e^-} \left[\mathrm{COBr_2}\right] \longrightarrow \mathrm{CO(OR)_2}$$

(refs.58,63)

$M = NH_4$ or Li

Scheme 39. Reaction takes different course if electrolyte is Bu_4NBF_4: → alkyl formates or, in presence of 2° amines → N,N-dialkylamides.

ANODIC SYNTHESES WITH CO

KOCH REACTION

$$\mathrm{RH} - 2\bar{e} - \mathrm{H^+} \xrightarrow[\mathrm{CO}]{\mathrm{Pt}} [\mathrm{R^+}] \longrightarrow \mathrm{RCO^+} \xrightarrow{\mathrm{H_2O}} \mathrm{RCOOH}$$

Conditions

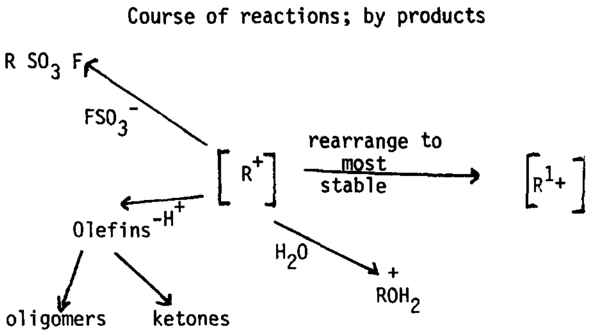
Electrodes: Pt

Electrolytes: FSO_3H . FSO_3K or $FSO_3H.H_2O$

Pressure: Atm. to 1000 psig

RH = cyclohexane, cyclopentane, n-pentane, n-hexane

Scheme 40.



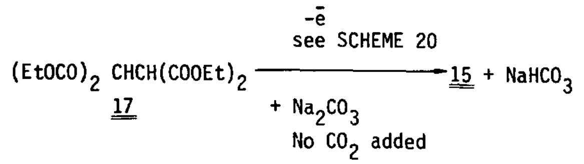
Scheme 41.

E. *Synthetic Utilisation of Electrogenerated Bases* (EGB)

1. *Introduction.* The recommendation (Section II above) that organic electrochemical reactions be viewed each in two or more contexts leads to improvement of the understanding but awkwardness in expository writing since one wishes to achieve clarity and avoid redundancy. Thus some of the principles which guide the design of EGB's have been alluded to above; their use in carboxylations (Section C) has been illustrated.

The long-range objective of the work with EGB's is to develop methodology which will permit deprotonation of acids of "high" pKa and the reaction of the derived necessarily relatively unstable anions *in situ* with selected electrophiles by organic bases which are electrogenerated and preferably easily regenerable. By "high" pKa is meant a value large enough so that in secular syntheses expensive, difficult-to-handle, one-shot reagents would have to be used. From modest beginnings[65,66] this area of investigation now engages the attention of scientists in several countries. The road to the ultimate goal is being paved with many interesting syntheses.

The above statement of the ultimate goal of this line of research carries with it intrinsically a definition of the technical problems which must first be solved: (a) The probases (PB) must be more readily electroreduced than the electrophile (which is also generally electroactive); (b) In spite of its "easy" reducibility the probase must yield an EGB of adequately "high" pKa; (c) The EGB must be a poor nucleophile in order not to consume *in situ* electrophile; (d) the EGBH resulting from the deprotonation of the acid in question should be oxidised by air or anodic reactions to $PB + H^+$; (e) the H^+ must be trapped by any means which allow the regenerated PB to be re-used. Lest these strictures appear to impose impossible experimental conditions let us now add to Scheme 30 which shows only the events occurring in the cathode chamber of a divided cell the simultaneous reactions in the anodic chamber of this cell.



$$\underset{\underline{\underline{17}}}{(EtOCO)_2CHCH(COOEt)_2} \xrightarrow[\substack{+\ Na_2CO_3 \\ \text{No } CO_2 \text{ added}}]{\substack{-\bar{e} \\ \text{see SCHEME 20}}} \underline{\underline{15}} + NaHCO_3$$

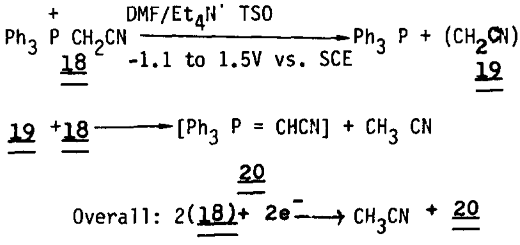
Scheme 42.

The PB **15** was regenerated. It was necessary to filter the *anolyte* to remove $NaHCO_3$ and fortify it with **14** in order to use it as the catholyte for the next run; the filtered *catholyte* was charged with Na_2CO_3 and used next as *anolyte*. Three successive runs by this procedure gave **16** in yields of 87, 85, 88% with only the original charge of **15** and **17**.

2. *Syntheses.* a. *Probases in general.* Electroreducible organic compounds after one- or two-electron cathodic reduction yield species (anion-radicals, anions, radicals→anions) which are nucleophiles and bases. As in secular organic chemistry one or the other property is favoured by proper choice of the structure. Many species which are good bases/poor nucleophiles and vice versa are known.

The EGB's may be made from PB's which remain intact in this process (ketones, activated olefins, azo-compounds,[66,67a] imines, etc.) or from PB's which are cleaved in the course of the reduction [e.g.

$\mathrm{RX \rightarrow R^- + X^-}$]; $\mathrm{Ph_3\overset{+}{P}CH_2CN \rightarrow Ph_3P + (CH_2CN)^-}$, etc. If the PB happens to be a compound which is also a carbon acid the PB itself may then transfer a proton to the EGB that has been generated from it ("auto-protonation").[67b] The phenomena of Scheme 43 have been studied with other onium and with



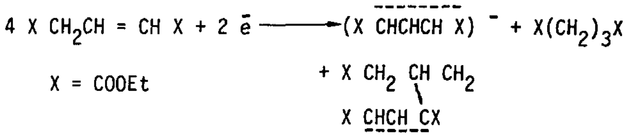
$$\mathrm{Ph_3\overset{+}{P}CH_2CN}\ \underline{\mathbf{18}} \xrightarrow[-1.1\text{ to }1.5\text{V vs. SCE}]{\mathrm{DMF/Et_4N^+\ TSO}} \mathrm{Ph_3P} + (\mathrm{CH_2CN})^-\ \underline{\mathbf{19}}$$

$$\underline{\mathbf{19}} + \underline{\mathbf{18}} \longrightarrow [\mathrm{Ph_3P=CHCN}]\ \underline{\mathbf{20}} + \mathrm{CH_3CN}$$

$$\text{Overall: } 2(\underline{\mathbf{18}}) + 2e^- \longrightarrow \mathrm{CH_3CN} + \underline{\mathbf{20}}$$

(ref. 65)

Scheme 43.

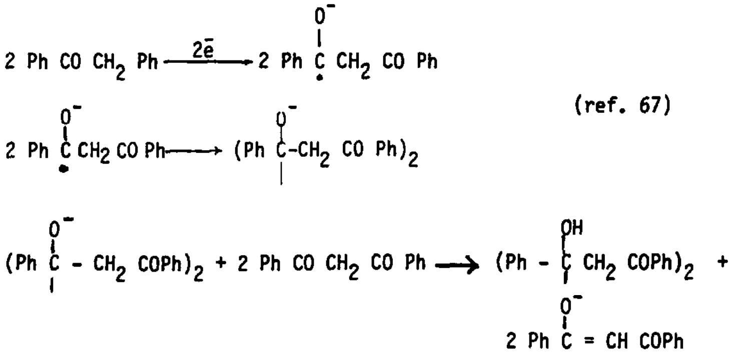


$$4\ \mathrm{XCH_2CH=CHX} + 2\bar{e} \longrightarrow (\overline{\mathrm{XCHCHCHX}})^- + \mathrm{X(CH_2)_3X} + \begin{array}{l}\mathrm{XCH_2\,CH\,CH_2}\\ \mathrm{X\,\underline{CHCH\,CX}}\end{array}$$

X = COOEt

(ref. 67a)

Scheme 44. Overall results of reduction of diethyl glutaconate.



$$2\ \mathrm{PhCOCH_2Ph} \xrightarrow{2\bar{e}} 2\ \mathrm{Ph\overset{O^-}{\dot{C}}CH_2COPh}$$

$$2\ \mathrm{Ph\overset{O^-}{\dot{C}}CH_2COPh} \longrightarrow (\mathrm{Ph\overset{O^-}{C}\text{-}CH_2COPh})_2$$

$$(\mathrm{Ph\overset{O^-}{C}-CH_2COPh})_2 + 2\ \mathrm{PhCOCH_2COPh} \longrightarrow (\mathrm{Ph-\overset{OH}{C}CH_2COPh})_2 + 2\ \mathrm{Ph\overset{O^-}{C}=CHCOPh}$$

(ref. 67)

Scheme 45.

phenylsulfonyl compounds[68] and have been used to devise an- "electro-Wittig" reaction.[69] The mechanism has been studied in detail.[70]

PB's which have been used successfully thus far in devising organic syntheses are: carbon tetrachloride, azobenzenes, ethenetetracarboxylates, oxygen, acetonitrile,[71,72] dicyano (fluoren-9-ylidene)methane.[69] Other candidates are being studied.[73] Oxygen will be discussed separately below.[74]

b. *Utilisation.* Reductive carboxylations and the "electro-Wittig" reaction mediated by EGB's have been mentioned above. The paired reaction of Scheme 20 involves as a crucial step proton transfer from malonic ester to the EGB formed by reductive coupling of acrylate. *Michael reactions* have been initiated by reducing either a very small quantity of the acceptor to an EGB (Table 1) or a small quantity of the PB azobenzene (Scheme 46).

Donor	Acceptor	PB	Products	
$\mathrm{CH_2(COOEt)_2}$	$\mathrm{CH_2{=}CHCOOEt}$	PhN=NPh	1:1 adduct (75%)	(ref. 75)
$\mathrm{RCH_2NO_2}$	$\mathrm{R^1CH=CH\overset{O}{\overset{\Vert}{C}}-}$	"	$\mathrm{\underset{NO_2}{RCH}\overset{R^1}{C}H\,CH_2\overset{O}{\overset{\Vert}{C}}-}$ High yields. Used as intermediates	(refs. 74,75)

Scheme 46. Inititation of Michael reactions by EGB's.

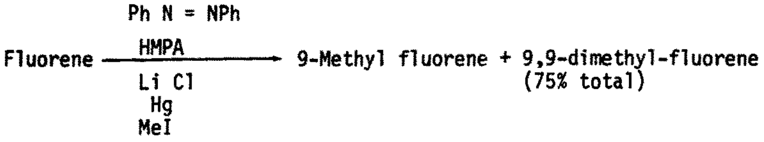
Table 1. Initiation of Michael reactions by EGB's prepared from the Michael Acceptor.[75] (see Scheme 46).

Donor	Acceptor	Faradays/ mole acceptor	Product
$CH_2(COOEt)_2$	$CH_2{=}CHCN$	0.024	1:1 adduct (18.5%)
$CH_2(COOEt)_2$	$(EtOCO)_2C{=}C(COOEt)_2$	0.10	1:1 adduct (93%)
$CH_2(COOEt)_2$	$CH_2{=}CHCOOEt$	0.055	1:1 adduct (77%)
Cyclohexen-2-one	cyclohexen-2-one	ca. 0.13	dimer (65%)

These are cases "electrochemistry without electricity" -well, almost without electricity.[75] The language of polymer chemistry is being used deliberately. Initiation is by the EGB formed by minor reduction of the PB; propagation is, as usual in Michael Reactions, by the adduct anion; termination comes by reaction of the carbanions by internally or externally supplied proton sources of lower pKa than the donor. Hydrodimerisations and mixed reductive couplings may be regarded as aborted oligomerisations/polymerisations.[76]

Other examples of EGB-mediated reactions are:

1. Alkylation of fluorene[77]

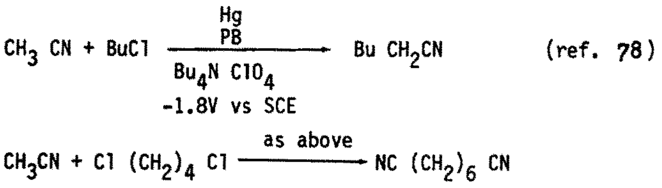


$$\text{Fluorene} \xrightarrow[\text{Li Cl, Hg, MeI}]{\text{Ph N = NPh, HMPA}} \text{9-Methyl fluorene} + \text{9,9-dimethyl-fluorene (75\% total)}$$

Scheme 47. Alkylation of fluorene (Ref. 77).

In the absence of the fluorene under the above conditions a 70% yield of N,-N-dimethylhydrazobenzene was obtained.

2. Cyanomethylations of 1-chloroalkanes and α, ω-dichloroalkanes.[78]

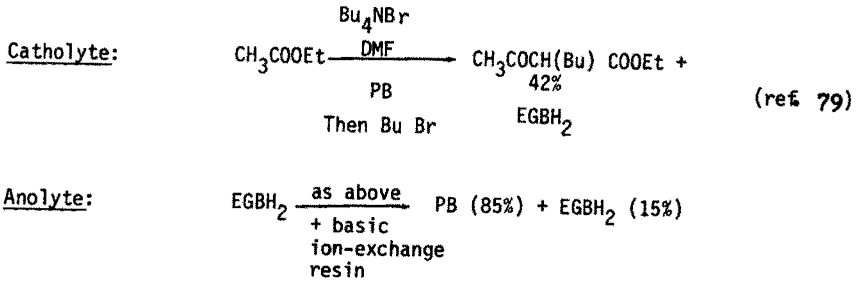


$$CH_3\,CN + BuCl \xrightarrow[Bu_4N\ ClO_4,\ -1.8V\ \text{vs SCE}]{Hg,\ PB} Bu\ CH_2CN \qquad \text{(ref. 78)}$$

$$CH_3CN + Cl\,(CH_2)_4\,Cl \xrightarrow{\text{as above}} NC\,(CH_2)_6\,CN$$

Scheme 48. EGB-promoted cyanomethylations PB as in Scheme 49.

3. Acetoacetic ester condensation:[79]



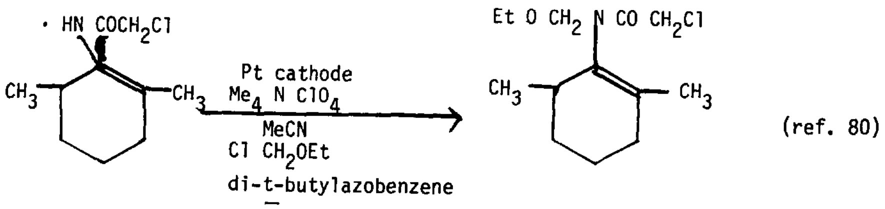
Catholyte: $$CH_3COOEt \xrightarrow[\text{PB, Then Bu Br}]{Bu_4NBr,\ DMF} CH_3COCH(Bu)\,COOEt\ (42\%) + EGBH_2 \qquad \text{(ref. 79)}$$

Anolyte: $$EGBH_2 \xrightarrow[\text{+ basic ion-exchange resin}]{\text{as above}} PB\ (85\%) + EGBH_2\ (15\%)$$

Scheme 49. "Electro-Acetoacetic Ester Synthesis" Paired reaction in a divided cell. The PB used was 2, 4, 6, 2′, 4′, 6′-hexaisoproplyazobenzene.

This is a particularly amusing case since whilst the condensation is initiated by an EGB it can be propagated by the base (OR^-) liberated in the reaction.

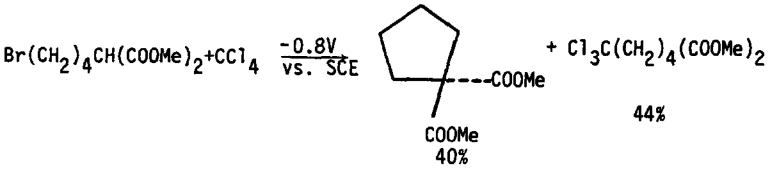
4. Alkylation of an amide.[80]



Scheme 50. Alkylation of a N-acid. There is no good chemical alternative.

In this case there was no satisfactory non-electrochemical means for preparing this product.

5. Either carbon tetrachloride or azobenzene was used as a PB in the α-deprotonation-ω-cyclization of dimethyl ω-bromoalkylmalonates.[81]



21

Scheme 51. Reductive cyclization using $ClCl_4$ as PB. Use of Ph N = NPh as PB in the above reaction gave 21 in 80% yield.

While both trichloromethyl carbanion and azobenzene anion radical/dianion were effective as bases, the former was a better nucleophile and therefore formed more of the linear product arising from S_N2 reaction at the ω-carbon.

c. *Oxygen as probase.* (*i*) *Introduction.* The electrochemical reduction of dioxygen in dipolar aprotic media containing R_4NX as supporting electrolytes to R_4N^+ ($O_2^{\dot-}$ or O_2^-) was reported[82] in 1966. This remains the method of choice for preparing these reagents and using them *in situ*, more satisfactory than using KO_2 or (an improvement) KO_2-Crown Ether or Me_4NO_2 prepared by metathesis.

Early on it was recognised that towards suitable organic substrates superoxide could function as a radical, a nucleophile, or a base. Examples of the behaviour of $O_2^{\dot-}$ as a radical and as a nucleophile have been accumulating and are cited; the full possibilities of using $O_2^{\dot-}$ as an EGB for *synthetic* purposes are now being explored.[83] In connection with the latter category Sawyer[84] has pointed out forcefully that although $O_2^{\dot-}$ is a weak base (the conjugate acid HO_2 has a pKa of 4.88) its disproportionation[85] in the presence of proton donors leads to bases of high pKa (>23):

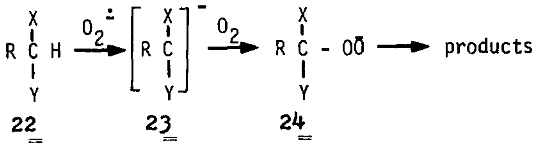
$$O_2 + \bar{e} \rightarrow O_2^-$$

$$2O_2^{\dot-} + BH \rightarrow O_2 + HO_2^- + B^-.$$

Even CH_3CN and n-BuOH have been deprotonated[86] by $O_2^{\dot-}$!

(*ii*) *Use in synthesis.* When oxygen is bubbled through a catholyte contained in an ordinary H-cell and the cathodic voltage is set at the value necessary for reducing only it, part of the O_2 is reduced to its anion radical (superoxide) and part escapes reduction and is available for reaction with the intermediates that have been formed by interaction of superoxide and the organic substrate. A variety of oxygenated products can result *under reducing conditions.*

If we confine our attention to transformation of carbon-acids then the *overall* results of the EGB reaction are:[87]



Scheme 52.

X and/or Y are electron-withdrawing groups of sufficient "acidfying" effect to render **22** susceptible to deprotonation by superoxide. The sequence from **22** to **24** is mechanistically multi-step since preliminary one-electron transfer from carbanions to oxygen has been amply demonstrated.[88] The types of products that are formed from **24** depend upon the nature of R, X and Y. The results obtained so far fall into these categories:

(a) Presumably by oxygen transfer from **24** to **23** alcohols derived from intact **22** are formed. An undefined catalytic sequence was involved since less than 1F/mole of **22** was required (Schemes 53–54).

$$\text{R CH(COOEt)}_2 \xrightarrow[\substack{\text{Hg} \\ \text{DMF} \\ \text{Et}_4\text{NBr} \\ -1.0\ \text{V vs. SCE}}]{O_2} \text{R C(OH)COOEt)}_2 \quad \substack{\text{R = Me, 95\%} \\ \text{R = Et, 62\%}} \qquad \text{(ref. 83a)}$$

$$\text{Me}_2\text{CHCOOMe} \longrightarrow \text{Me}_2\text{C(OH) COOH} \qquad \text{(ref.83b)}$$

$$\text{Ph}_2\text{CHCOOMe} \longrightarrow \underset{45\%}{\text{Ph}_2\ \text{C(OH) COOMe}} + \text{Ph}_2\text{CO} \qquad \text{(ref. 83a)}$$

$$\text{Ph CH(COOEt)}_2 \longrightarrow \underset{74\%}{\text{Ph COCOOEt}} + \underset{7\%}{\text{Ph C(OH) (COOEt)}_2} \qquad \text{(ref. 83a)}$$

Scheme 53. Electro-oxygenations with substrate cleaved *in parte.*

$$\text{Ph}\cdot\text{(CH}_3\text{) CHCONEt}_2 \longrightarrow \text{Ph (CH}_3\text{) C(OH)CONEt}_2 \qquad \text{(ref.83b)}$$

Scheme 54.

Schemes 53–54. Electro-oxygenations when substrate remains intact.

(b) X (or Y) is expelled *in toto* (Schemes 55–56) from **25** resulting in oxygenated products from fragments of **25**. It is to be noted that the nitro-compounds below are of the type prepared according to

$$\text{R (R}^1\text{) CHCN} \xrightarrow[O_2]{O_2^{\overset{\cdot}{-}}} \text{R(R}^1\text{)C = O + (CN}^-\text{)}$$

95% yield, $R = R^1 = Ph$

75% conversion, $R = Ph, R^1 = Me$

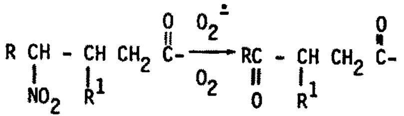
$$\text{(CN}^-\text{)} + O_2^{\overset{\cdot}{-}} \longrightarrow \text{(CNO)}^- \xrightarrow{\text{MeI}} \text{trimethyl isocyanurate}$$

Scheme 55. Electro-oxygenations with substrate cleaved *in toto.*

$$\text{CH}_3\ \text{CH}_2\ \text{CN} \xrightarrow[O_2]{O_2^{\overset{\cdot}{-}}} \text{CH}_3\text{COOH} \qquad \text{(ref.83b)}$$

15% conversion

$$\text{CH}_3\text{CH}_2\text{CN} \xrightarrow[\substack{O_2 \\ \text{Ac}_2\text{O}}]{O_2^{\overset{\cdot}{-}}} \underset{5\%\ \text{conv.}}{\text{CH}_3\text{COOH}} + \underset{18\%\ \text{conv.}}{\text{CH}_3\text{CH (OAc)}_2}$$



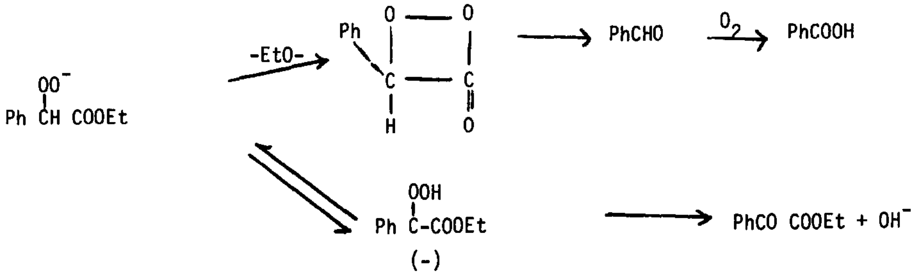
$$\text{R}\underset{\substack{| \\ \text{NO}_2}}{\text{CH}} - \underset{\substack{| \\ \text{R}^1}}{\text{CH}}\ \text{CH}_2\ \overset{\text{O}}{\overset{\|}{\text{C}}}- \xrightarrow[O_2]{O_2^{\overset{\cdot}{-}}} \underset{\substack{\| \\ \text{O}}}{\text{RC}} - \underset{\substack{| \\ \text{R}^1}}{\text{CH}}\ \text{CH}_2\ \overset{\text{O}}{\overset{\|}{\text{C}}}-$$

25 (ref. 74)

Scheme 56.

Scheme 46 by an EGB-initiated Michael Reaction. It was necessary only to introduce and reduce oxygen in the same cell to achieve a one-pot electrochemical equivalent of the Nef Reaction in excellent yield without the need for strong bases and acids. Examples of this transformation using acyclic and cyclic precursors are given in the papers cited.

(c) (CO X(or Y) is expelled *in parte* (Scheme 57)



Scheme 57.

(d) **44** may epoxidise certain olefins[89] present *in situ* to yield both epoxides and an oxygenated derivative stemming from **24**.

IV. DEVELOPING AREAS OF ORGANIC ELECTROCHEMICAL SCIENCE

A. *Elucidation of mechanisms*

1. *General comments.* In this area advances comprising new instrumentation[90] and techniques, particularly electrochemistry-*cum*-spectroscopy are so complex and so numerous that each component would require a review article of its own. We are obtaining more information which is based on experimental evidence rather than conjecture about the adsorption and orientation of organic molecules at clean electrode surfaces[91] and about the identity and to some extent the first stages of the "evolution" (as our French colleagues say) of primary electrochemical intermediates toward final products. The results will have important impact not only on the understanding of how multiple products are formed from a given intermediate, how coupling occurs, etc. but upon the factors influencing stereo and regio-specific syntheses, chiral induction, catalysis, and others. It is also hoped that the results will enable the organic electrochemist to plan in advance the means for achieving a desired goal. The reader is referred to recent publications by groups led by A. Bewick, D. H. Evans, A. Fry, A. T. Hubbard, T. Kuwana, V. D. Parker and J.-M.Savéant. One development, electrode-initiated homogeneous electron-transfer, is chosen for more detailed discussion below because it is readily integrated into the bulk of secular organic chemistry.

2. *Homogeneous electron transfer.* a. *Indirect electrochemical reactions.* Oxidation or reduction of organic substrates in solution by hyper-or hypo-valent ions (respectively) which have been brought and then restored to that state by an appropriate heterogeneous electrode reaction is the major feature of "indirect" electrochemical reactions. Certain organic "mediators" have also been used for this purpose. Two other categories of homogeneous electron-transfers (designated by Savéant as solution electron-transfers SET)[92] are involved in other contexts.

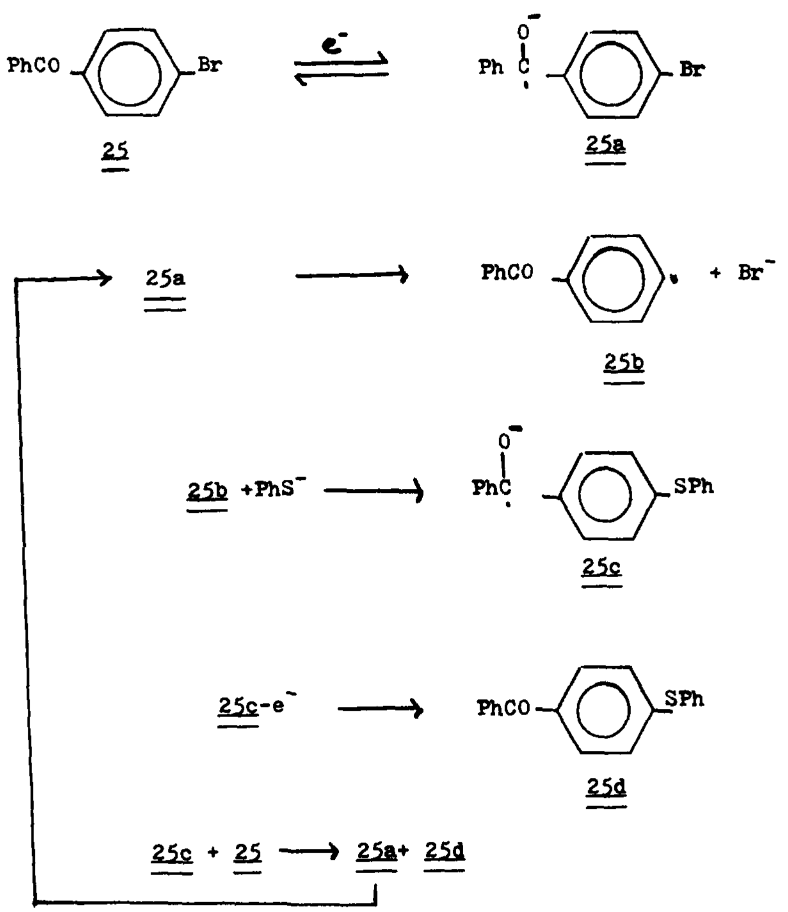
b. *Dismutation of intermediates.* The dismutation of superoxide to dioxygen and the equivalent of $O_2^{=}$ and of azobenzene anion radical to azobenzene and its dianion has already been mentioned. It is often the case that when reduction of a substrate A can occur in two successive one-electron transfers the second reduction occurs via dismutation of the intermediate anion radical (SET) rather than

$$\underset{E_1}{A + \bar{e} \rightarrow} A^{\cdot-} \underset{E_2}{+ e^- \rightarrow} A^{=}$$

by reduction of $A^{\cdot-}$ at $E_2(E_2 > E_1)$. Savéant has shown how this SET must enter into a mechanistic analysis of the overall process. From the point of view of synthesis, particularly of using reduced A as an EGB it allows the generation of the stronger base $A^{=}$ rather than the weaker $A^{\cdot-}$ even while operating at the lesser cathodic potential E_1.

c. *Electro-initiated radical-chain processes.* Following pioneering work by N. Kornblum,[93] G. A. Russell[88] and others[94] there has been increasing recognition of the role of SET reactions as intermediate stages in processes that superficially appear to be simple nucleophilic displacements. More and more illustrative examples of this mechanistic nuance are appearing.[95,96]

When the electron donor is an anion, the latter has been made by the reaction of the appropriate precursor acid with a catalytic amount of base or electrochemically;[95] when the electron-donor is an anion-radical, the latter had been made by supplying an electron to the precursor by using an alkali metal or by photochemical initiation. This class of reactions has become known as $S_{RN}1$.[97] The initiating electron may however be supplied by a cathode. The electrochemical $S_{RN}1$ has been elegantly developed and analysed by Savéant.[86] Scheme 58 illustrates one of his electro-initiated sequences.



Scheme 58. Electro-$S_{RN}1$ reaction.[98]

The anodically initiated counterpart of the $S_{RN}1$ reaction, named the $S_{ON}2$ mechanism, has been analysed in broad terms and shown to be operative in the conversion of 4-fluoroanisole to 4-acetoxyanisole.[99]

B. *Chemically modified electrodes* (*CME's*)

This name has been given to electrodes whose surfaces have been altered by one of two major means: (1) molecules are attached by covalent bonds to superficial functional groups such as -OH, -COOH, C = O in preoxidised graphite or -OH in metal oxides, (2) polymeric films which act as "fixed" electron-transfer agents are deposited by a variety of techniques on electrodes surfaces.

The first reports in about 1974 concerning the preparation and use of CME's broke upon the electrochemical community with explosive force. The logarithmic increase in the number of investigations has now perhaps become merely arithmetical. It is still early days for utilising this technique in organic electrochemical synthesis. Early reports of chiral induction in an alcohol by reducing the precursor ketone at a modified carbon cathode to which had been attached a chiral moiety proved to be disappointing. Along with the search for reactions which differ in course or in required energy expenditure when done at CME's rather than at conventional electrodes must come the quest for means for enhancing the durability of the surface alterants beyond the period required to run a few experiments and obtain the fundamental data. The hunt is on!

Outside the domain of organic synthesis many interesting results have been obtained crucial to the development of electrocatalysis. The reader is referred to a selected bibliography of recent papers.[100] Most relevant perhaps to the organic chemist is the ongoing work on "electroenzymology"; CME's are being used as "fixed" electron-transfer agents toward enzymes and co-enzymes which, to remain catalyts, after they have functioned as oxidants would otherwise have to be reduced by another biochemical system. A favourite model substrate has been cytochrome c, and frequently used CME's are ones which have been covered with a film of 4,4'-bipyridyl or 1,2-bis-(4-pyridyl) ethane. An example of potential model synthetic importance is the enzymic/electrochemical oxidation of methane to methanol.[101]

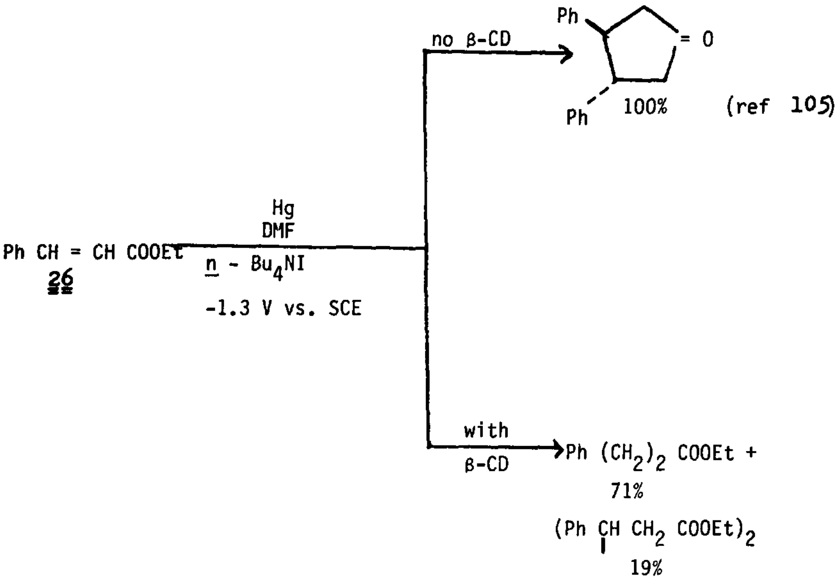
C. *Complexed substrates*

The intermediates formed by the reaction of an electroactive organic molecule at an electrode can usually lead to more than one product. Several means are available for directing the course of the "evolution" of the intermediate at least largely toward one product desired above others:

1. Control of the electrochemical parameters as well as the constituents of the solvent-electrolyte system. Illustrative examples (among many) are found in procedures for (a) reductively coupling activated olefins rather than converting them to saturated monomers (b) inducing chirality in alcohols formed by reduction of ketones in the presence of chiral electrolytes or solvents.
2. Exploiting the intrinsic adsorption of certain species at given electrodes.
3. *Controlling* the adsorption and orientation of organic molecules at clean electrode surfaces. Unfortunately as of now these findings still remain to be developed into controlled syntheses.[91]
4. Using orientation and adsorption effects at CME's.
5. Restricting the environment of the organic molecule by incarcerating it snugly within the meager quarters offered by a penurious gaoler/"host"[102] before it has access to the electrode.

α- Cyclodextrin has recently hosted first anisole in an investigation concerning regio-selectivity in anodic chlorination[103] and second only the *o*-isomer of a mixture of *o*- and *p*-nitrophenols in a study probing the selective reduction of positional isomers.[104] · In the first case a small but significant preference for *p*-chlorination in the complexed material was found. In the second case the preferential confinement of the *p*-isomer—and the concomitant shift of its reduction potential to a more negative value-allowed the *o*-isomer to be reduced ten times as rapidly as the *p*-isomer. Less favourable selectivity was shown if the α-cyclodextrin was part of a CME.

More dramatic effects were shown when β-cyclodextrin (β-CD) was used as host in reductions[105] of ethyl cinnamate **26** benzaldehyde **27** and benzophenone **28** at Hg in DMF/Bu_4NBF_4. The radical anion of **26** was largely protonated by its not indifferent host so that the major product was thehydrogenated monomer rather than the hydrodimer (Scheme 59). Benzaldehyde (**27**) does hydrodimerise (to hydrobenzoin) but whereas the (±): meso ratio of the products is always ≫1 in the absence of β-CD it is 1:3 in its presence.



Scheme 59.

Benzophenone (**28**) hydrodimerises in a manner not previously observed for it: coupling occurs not by ketyl-ketyl combination but between the *o*- and *p*-positions of the ketyl[106] intermediate and a second molecule of **28**.[106] Benzophenone (Ph_2CO) yielded only Ph_2CHOH even in the presence of β-CD.

D. *Glow discharge (plasma) electrolysis*

In spite of enthusiastic stimuli by A. Hickling[107] this area remained quiescent for a number of years which witnessed only occasional publications and patents relating to organic syntheses. (The reviewer has personal knowledge of only one company's considerable undisclosed work). A major factor impeding more rapid progress has been the scatter of energy involved in the gas-phase ionisation so that many products were formed from a given pair of reactants; as a corollary, the energy requirements were too high for the synthesis of a given target molecule. Thus what would have been an "elegant" one-step synthesis of cyclohexanone oxime (for caprolactam, Nylon6) from cyclohexanone and nitric oxide was not further developed.[108]

New life has been infused into this area by the more recent work of groups under H. Suhr[109c] and L. L. Miller.[109a,b] Especially noteworthy have been results obtained by "plasmolysis" of cyanogen in the presence of (a) benzene and derivatives, (b) certain olefinic compounds. Direct nuclear and side-chain cyanations of (a) are of course desirable short-cut synthetic results: benzonitrile was obtained in 78–92% yield from benzene at 50% conversion; the energy requirement was only 0.67 kWh/mol. When substituted benzenes were used as substrates, mixtures of products resulting from *o*, -*m*-*p*, and *ipso*-substitution were obtained.

Many novel synthetic results have been obtained in category (b), the plasmolysis of cyanogen in the presence of olefins. Acrylonitrile along with several minor products was formed from ethylene, propylene, acrolein, methyl vinyl ketone, and 1,1,1-trifluoropropylene; under favourable conditions excellent net yields were obtained but with a rather high power requirement (17 kWh/mol). *Cis*-2-Butene yielded *cis*- and *trans*-crotononitrile; 1-butene formed largely acrylonitrile and allyl cyanide.

E. *Photo-assisted organic electrochemistry*

This rather awkward caption is being used to distinguish it from photoelectrochemistry with semiconductor electrodes as, e.g. in the "photo-Kolbe" reaction discussed above.

The photochemical component of this hybrid techniques has in different systems served several purposes as illustrated in the following examples:

1. Photoexicted anthraquinone derivatives attached to glassy carbon anodes (a CME) was used in catalysed oxidations of 2-propanol.[110].
2. The oxidation of 1,1-diphenylethylene by a photo-excited "mediator" was contrasted to the oxidation by ground-state mediator.[111]
3. Photo-induced electron-transfer oxygenation reactions are being intensively explored.[112]
4. Photo-excited quinones (*cf* 1 above) abstract hydrogen atoms from certain toluene derivatives. The resultant benzyl radicals dimerise in high yield; the formed hydroquinones are re-oxidised at an anode thus making possible syntheses in which the mediator is used in catalytic quantities (Scheme 60).[113]

F. *Electropolymerisation (ECP)*[114]

The systematic exploration of this area began only in about 1960. Methods and systems have developed for: (a) initiation of anionic and cationic polymerization of vinyl monomers, (b) formation and termination of "living" ionic polymeric intermediates, (c) controlled termination of polymer growth, (d)

$$AQS \xrightarrow{h\nu} AQS^*$$

$$AQS^* + 2RH \longrightarrow 2R. + AQSH_2$$

$$AQSH_2 - 2\bar{e} \longrightarrow 2H^+ + AQS \qquad \text{(ref.113)}$$

$$2R. \longrightarrow RR$$

Scheme 60. Photochemistry + electrochemistry in oxidative dimerizations. AQS = Anthraquinone-2-sulfonic acid, RH = toluene, p-xylene, ethylbenzene, 2-propanol, SSE = $CH_3CN + H_2O + LiClO_4$, Curr. eff. = 60–100%.

formation of block copolymers, (d) polymerisation of pre-complexed monomers, (e) condensation polymerisation which requires ongoing electrolysis rather than simple initiation of a process (*cf* a above); (f) *Ziegler-Natta polymerization of olefins.*[115] In spite of these many advances no industrial process to the best of our knowledge, employs ECP. Polymer chemists have generally eschewed ECP, in spite of the special features it sometimes offers, because (a) they are comfortable with the now mature and sophisticated non-electrochemical methodology, (b) ECP requires an electrochemical "cell"—dread word—and a solvent/electrolyte, (c) they can used crypto-electrochemical reagents (e.g. sodium metal, butyl lithium) in the preparation of which commercial suppliers have used the electrochemistry, (d) polymers of industrially useful high molecular weight when made within a cell deposit on and insulate the electrodes.

A number of publications have described making only the initiator in a cell and adding it thereafter to a monomer contained in a conventional reactor. A recent patent[116] discloses a novel application of this principle. Intercalation compounds[117] of electroreduced graphite$^{\cdot -}$–R_4N^+ are removed from the cell and used to initiate externally anionic polymerization of suitable manomers; the "spent" initiator is returned to the cell, re-reduced and used again and again. Surely the reactivity of growing anionic polymer chains associated with R_4N^+ counterions must be different from that involving alkali metal counterions!

V. DEVELOPMENTS OF TECHNOLOGICAL IMPORTANCE

A. *Introduction*

The translation of a laboratory organic electrochemical synthesis to pilot-plant and larger scale has become more systematised and facile in the last two decades, since electrochemical engineers are now active participants in the research and development stages of a project.[118] It is not appropriate to discuss the engineering aspects here (cell and systems design) but it is obvious that to make a process economical the durability of cell components, appropriate electrodes and supporting electrolytes must be maximised, complexity of operation and energy requirements must be minimised. Chemical yields and current efficiencies may often be less critical to the overall process economics than are the factors above and the space-time yield.

The following discussion will be restricted to (a) promising changes in the *modus operandi* which have potential value in affecting the factors above and (b) changes in raw materials and feedstocks which will affect the entire organic chemical industry by the end of this century.

B. *Changes in the modus operandi*

1. *Undivided rather than divided cells.* For anything but a laboratory preparation it would untuitively appear desirable to use undivided cells: one solvent/electrolyte system, one pumping/circulating system and one products isolation scheme instead of two. Traditionally this has already almost always been the case in anodic oxidations. Reductions, however, carry the greater risk that the starting material, intermediates, or products may react adversely at the counterelectrode or with species generated at the counter-electrode. They have therefore most frequently—almost dogmatically—been carried out in divided cells.

Examples are beginning to accumulate in the literature, however, which demonstrate that the adverse effects which were to be minimised by the use of membranes can often be overcome by proper choice of the material of the counter-electrode and by control of the hydrodynamics within the cell. The following Schemes illustrate what should be considered startling successes in using undivided cells.

a. Adiponitrile from acrylonitrile. The original laboratory work[119] showed that (a) quantitative yields

Cathode

$$4\ CH_2=CHCN + 4H_2O + 4\bar{e} \longrightarrow 2NC(CH_2)_4CN + 4OH^-$$

Anode

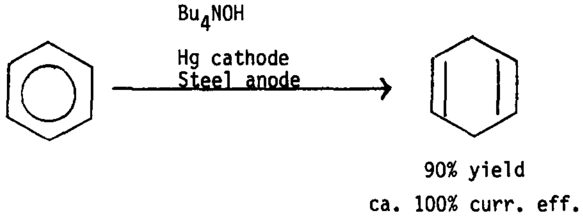
$$4\ OH^- - 4\bar{e} \longrightarrow 2H_2O + O_2$$

Scheme 61.

and current efficiencies could be obtained using a divided cell, (b) a variety of quaternary ammonium salts, including phosphates, were satisfactory, (c) good but less than quantitative yields were obtained in an undivided cell.

Because the data were more complete with respect to divided cells at the time the starting date for first commercial production was fixed, the initial years of production indeed used divided cells. Concurrently research and development projects were pursued which permitted the eventual use of undivided cells. As anticipated, there were some yield losses but their economic effect was more than offset by the types of positive gains mentioned in A.

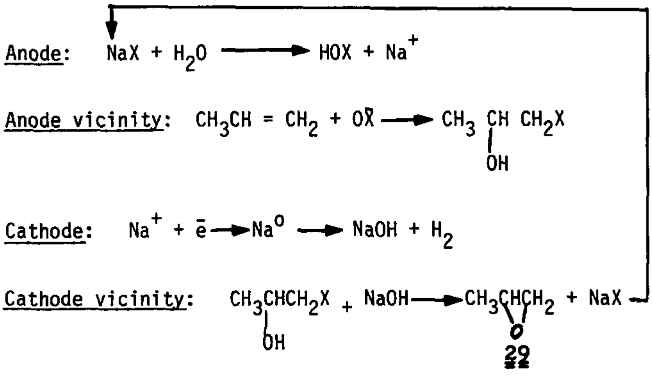
b. 1,4-*Cyclohexadiene from benzene.* Although a variety of means for carrying out "electro-Birch" reactions in *divided* cells have been reported, it was found surprisingly that the above reaction which gave a dihydroaromatic compound (supposedly easily oxidised/re-aromatised) could be carried out very well in undivided cells.[120] Obviously conditions were chosen which favoured anodic discharge of hydroxide ions rather than oxidation of the product.



Scheme 62.

2. ***Paired syntheses.*** As mentioned before, all electrochemical reactions, by the very nature of the methodology, come in pairs. While the concept of using both simultaneous reactions, preferably in an undivided cell (v.s.), is an old one, it has been "honoured more in the breach than in the observance". The bulk of the literature on organic electrochemical synthesis deals with useful reactions which are *either* cathodic *or* anodic. However an increasing number of paired reactions is being reported.[122] When the anodic and cathodic reactions act in concert to produce one product, this mode of synthesis must be compared for industrial considerations with alternative methods for preparing the same compound; when the paired reactions lead to two products, the economics of the process must be compared to those in which the products are made in two separate cells. An intuitive judgment would suggest that capital outlays for a single cell and system must be substantially lower than for two cells and systems. These putative savings, however, could be offset by enhanced formation of troublesome by-products and by greater difficulty in products' separation in a single cell.

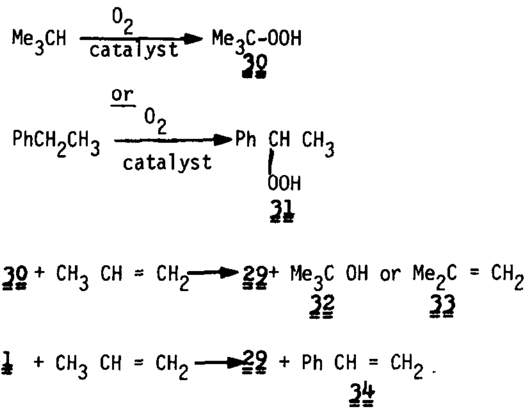
The following examples from the recent literature illustrate promising paired syntheses. This is in principle a chlorine-caustic cell in which propylene is included in the electrolyte. Under ideal conditions propylene oxide with only hydrogen as a by-product is formed. The electrolyte is recycled and therefore the by-product disposal problem ($CaCl_2$) inherent in the chemical process is avoided. This process has



(ref. 121)

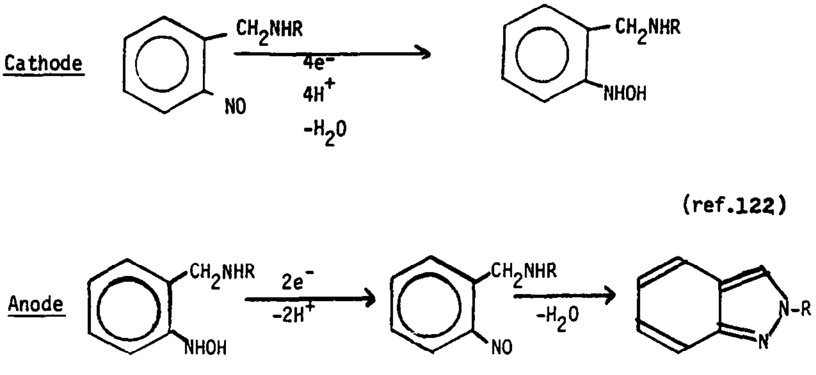
Scheme 63.

seen many years of development in several countries but has not yet been commercialised.[121] Ironically it is Halcon/Oxcrane's *paired* catalytic system which presents a major block to the adoption of the electrochemical process.



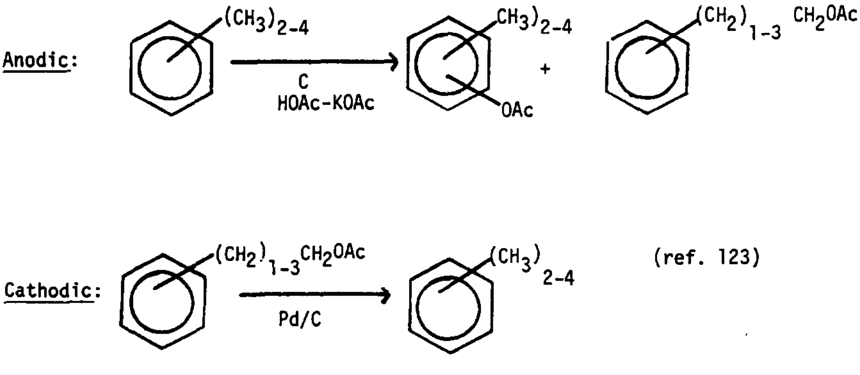
Scheme 64.

All co-products have present utility in industry. However, as in all paired processes including chlorine-caustic, there must be a balanced demand for all products (which are produced in stoichiometric ratios). If a severe imbalance develops between **29** and **32**, **33**, **34**, then the prospects for the single product electrochemical process may improve.



Scheme 64a.

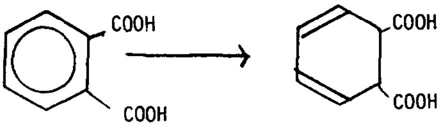
Schemes 20 and 30 + 42 have already been described. The former leads to two useful products in excellent yield; the latter permits a PB (and EGB) to be used in only catalytic quantities.



Scheme 65.

Anodic acetoxylation yields a mixture of nuclear and side-chain substituted product. Cathodic hydrogenolysis at Pd of only one of the isomers to starting material occurs and therefore provides high selectivity for the other.[123] The reduction of phthalic acid, long practiced by BASF as a solo reaction has been paired with oxidation of acetylenic alcohols.[124]

Cathode:



(ref. 124)

Anode: $HOCH_2\ C{\equiv}C\ CH_2\ OH \longrightarrow HOCO\ C{\equiv}C\ COOH$

or

$HC{\equiv}C\ CH_2OH \longrightarrow HC\ C{\equiv}COOH$

Special Ti/PbO_2 anode with Ti carbide interlayer

Scheme 66.

Cathodic

glucose ⟶ sorbitol + mannitol

Anodic

glucose ⟶ [glucono-δ-lactone] ⟶ gluconic acid

Scheme 67.

Each of these processes separately has been practiced on a commercial scale.[125] An attempt to combine them in a single undivided cell is in progress.[126] This is one of many projects being pursued world-wide with the objective of converting electrochemically biomass-derived materials into fuels/fuel components and/or useful organic chemicals (v.i.). It is well known that aliphatic alcoholic groups are difficult to reduce to the hydrocarbon stage unless they are adjacent to electron-withdrawing groups.[127] Since **35** is the biomass-derived material in question it is necessary to oxidise it selectively to **36** without over-oxidation to the diketone) and to reduce **36** selectively to **37** as a means of converting **35** to a very useful industrial chemical. This paired synthesis has succeeded in producing **37** with very minor amounts of by-products. The overall current efficiency must still be optimised.[128]

Anodic: $\underset{\mathbf{35}}{CH_3\ CH\ (OH)\ CH(OH)\ CH_3} \longrightarrow \underset{\mathbf{36}}{CH_3\ CO\ CH(OH)CH_3}$

(ref.128)

Cathodic: $\underset{\mathbf{36}}{CH_3CO\ CH(OH)\ CH_3} \longrightarrow \underset{\mathbf{37}}{CH_3\ CO\ CH_2\ CH_3}$

Scheme 68.

C. *Non-petroleum-derived raw materials*

1. ***Introduction.*** In anticipation of the gradual depletion (and concomitant increasing cost) of petroleum as the primary raw material for producing the feedstocks for the organic chemical industry,

exploratory work is now in progress world-wide to develop processes using alternative sources. In chronological order, they will be coal and then biomass. The use of coal will be, for those old enough to remember, a reversion to the state of affairs in our youth; the conversion of biomass into fuels/fuel components and/or useful organic chemicals is largely a new undertaking. In both cases the development of new technologies which will serve presently installed processes and products with the smallest requirement for revolutionary changes is a formidable task. Electrochemical methodology along with catalysis and photochemistry, some times in concert, will have its place in this endeavour.

2. *Electrochemistry of coal.* Coal "molecules" are of very complex structure indeed[12] but examination of some of the proposals indicates that several of the units are electroactive in the sense of providing sites for adsorption at suitable electrodes or possess electrophores which render them susceptible to direct or indirect electrochemical redox reactions: (a) phenolic, thiophenolic and primary amino groups, (b) pyridine, thiophene, carbazole, furan and dibenzothiophene heterocycles, (c) carbocyclic (benzene and hydroaromatic) rings, benzylic hydrogens, and cyclopentadienyl rings, (d) -S- and -S-S-bridges, (e) carbonyl functions (ketones, carboxylic acids). The electrochemistry of all these functionalities in simpler substances is known. It is precisely the fine control made possible by potentiostatic means which makes possible *selective* manipulation of the vulnerable parts of the coal "molecule" and the conversion of the substance to useful larger molecular weight fragments; this contrasts to the enormous efforts now being expended on degrading coal to "syngas" and re-synthesising organic chemicals from carbon monoxide and hydrogen. The challenge is there!

Reduction of coal and model substances by the electrogenerated solvated electron was vigorously investigated, mainly at the U.S. Bureau of Mines in Pittsburgh, PA in the 1960s. In retrospect, this work may have been too anticipatory[130] but it is now receiving new attention and further development. Both reduction and reductive alkylation of coals result in dramatic increases in the solubility of coal derivatives in pyridine and even in benzene. Due to solubility and heterogeneity problems an alternative to the above "electro-Birch" reaction was sought:[129] the use of anion-radicals of polycyclic hydrocarbons—made electrochemically or by addition of an alkali metal—as electron-transfer "mediators". The latter procedure not only reduces some of the aromatic rings but reductively cleaves aryl ether groups. Further, since amine solvents used in the Birch Reaction and the polycyclic compounds used as "mediators" may introduce fragments which obscure the primary products of coal reduction, glymes have been investigated as inert solvents;[131-2] now reduction of aromatic rings occurs as well as cleavage of methylene or ethylene bridges to methyl.

Anodic oxidation of coal slurries in aqueous sulfuric acid has been studied as a means of pairing oxidation to CO_2 and reduction of protons to hydrogen; in fact this method has been proposed as a possible economical alternative method for the production of hydrogen.[133] While a portion of the anodic oxidation is direct, some must be indirect *via* electrogenerated (Fe(III)).[134] There is the likelihood that oxidation is not complete and leads to an accumulation of organic products.

Anthracite itself has been used as an anode in electrolyses in aqueous media.[135] The products were presumably formed *via* hydroxy radicals and were uncharacterised carboxylic acids. It is interesting that sometimes the coal was held within a graphite cup: we have seen above how *reduced* graphite has been used as an electron-transfer agent.

There are now many programs not using electrochemistry whose aim is to convert coal to a more useful fuel or to industrial organic chemicals.[136] Many of these processes are convertible to perhaps more advantageous electrochemical equivalents; others are "crypto-electrochemical", i.e. they use reagents which themselves have been made electrochemically so that they may be considered indirect electrochemical processes.[137]

The facile *in situ* alkylation of quaternary onium salts of a variety of carboxylates and phenates has recently been applied to the alkylation of acidic hydroxyl groups (phenolic and carboxylic) in coal.[139] Under ambient conditions THF was used as the medium and concentrated aqueous Bu_4NOH as the preferred base. A variety of RBr's were satisfactory alkylating agents although the rate of reaction decreased with increasing size of R. It is interesting that complete alkylation of all OH and COOH groups occurred; by contrast "coal anion" prepared with alkali metal counterions was only partially C-alkylated with respect to the number of carbanions sites available.[130] This may well be due to the fact that R_4N^+ as counterion gives more solvent-separated ("naked") carbanions that does M^+($M =$ alkali metal). Since the rate of O-alkylation is faster than that of C-alkylation it is likely that a two-stage sequence involving first O-alkylation and then reduction to carbanions and alkylating anew would lead to even more soluble products.

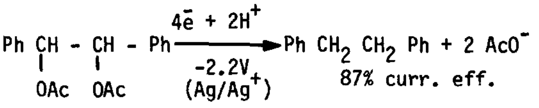
The use of various "chemical" (usually crypto-electrochemical) reagents (air, performic acid, sodium dichromate, sodium hypochlorite, potassium permanganate) for oxidising coal not to CO_2 nor to "humic acids" but rather to a variety of discrete carboxylic acids has been reviewed.[137]

3. *Electrochemistry of biomass and derived materials.* The list of organic entities which are now known to be obtainable from renewable aquatic and terrestial sources is formidable;[140] further it includes aliphatic (from cellulose, hemicelluloses, etc.) and aromatic (from lignins) compounds. A variety of means including electrochemical, has been proposed for altering the primal macro-molecular structures as mildly as in consistent with converting them to useful industrial products. A second-best option is to degrade the native raw materials by hydrolysis, enzymatic reaction, pyrolysis, etc. in order to obtain smaller molecular units which can be elaborated by synthesis to desired end-products.

Here too there is a world-wide electrochemical effort in progress centred in the United States in the Solar Energy Research Institute which has pursued "in house" as well as externally funded research (not exclusively in the USA). Lignin, particularly "steam-exploded" lignin is being converted to products which may substitute for phenol-formaldehyde resins. Levulinic acid abundantly available from glucose (*ex* cellulose) has been electrochemically oxidised, reduced, and subjected to the "photo-Kolbe" reaction.[141]

Paired syntheses using glucose and 2,3-butanediol have been discussed above. In addition, there have been efforts to convert the diol to butene or butane. As mentioned above, reductive removal of an alcoholic group in a diol directly is very difficult: one of the groups must first be oxidised to ketone or, alternatively, the alcohol groups may be first derivatised to acyclic or cyclic intermediates to facilitate reductive cleavage.

A variety of derivatising reagents is suitable when the alcohol (or diol) bears aromatic rings in the α-position (Schemes 69–71); the choice is so far much more limited when the α-substituents are aliphatic. Alcohol mesylates are electroreducible to hydrocarbons (Scheme 72) as are of course 1,2-dibromides.[146] Propylene carbonate has been reduced to propylene under rather extreme conditions. Only one pertinent case has been reported in which reduction of a phenythio-derivative was successful (Scheme 73).

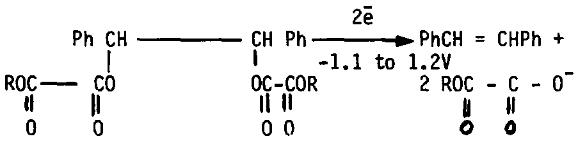


$$Ph\underset{OAc}{CH}-\underset{OAc}{CH}-Ph \xrightarrow[-2.2V\ (Ag/Ag^+)]{4\bar{e} + 2H^+} Ph\,CH_2\,CH_2\,Ph + 2\,AcO^-$$

87% curr. eff.

(ref 142)

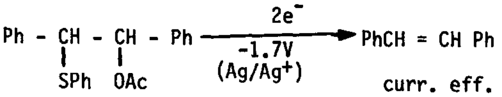
Scheme 69.



$$\underset{\underset{O}{\|}}{ROC}-\underset{\underset{\underset{O}{\|}}{CO}}{PhCH}-\underset{\underset{\underset{O\ O}{\|\ \|}}{OC-COR}}{CHPh} \xrightarrow[-1.1\text{ to }1.2V]{2\bar{e}} PhCH=CHPh + 2\,\underset{\underset{O}{\|}}{ROC}-\underset{\underset{O}{\|}}{C}-O^-$$

(ref. 143)

Scheme 70.



$$Ph-\underset{SPh}{CH}-\underset{OAc}{CH}-Ph \xrightarrow[-1.7V\ (Ag/Ag^+)]{2e^-} PhCH=CH\,Ph$$

curr. eff. 99%

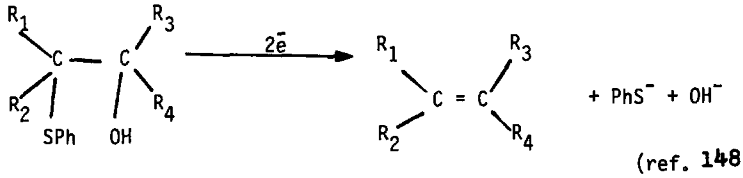
(ref. 144)

Scheme 71.

$$R\,SO_2\,Me \xrightarrow[H^+]{2\bar{e}} RH + MeSO_3^-$$

(ref. 145)

Scheme 72.



(ref. 148)

Scheme 73.

A search[149] for other electroreducible derivatives of 2,3-butanediol examined (among others) the cyclic borate, carbonate, sulfite, sulfate and formal and the acyclic diformate, dibenzoate and diacetate. The cyclic sulfate showed remarkable behaviour: it was reduced at mercury in a one-electron transfer, to butene and (presumably) persulfate. Further elucidation of the "evolution" of the latter fragments is in progress.

Scientific papers describing all the above work are in various stages of consummation and will be published in due course.

It is hoped that this mere sampling of the recent literature serves to stimulate rather than overwhelm the organic chemist not previously acquainted with this field. Organic chemists have diverse interests. Not all can be addressed in one review but perhaps[150]

„Wer vieles bringt wird manchem etwas bringen
Und jeder geht zufrieden aus dem Haus".

REFERENCES AND NOTES

[1a]P. Seiler and P. M. Robertson, *Chimia* **36**, 305 (1982); [b]H. J. Schäfer, *Angew. Chem. Int. Ed. Eng.* **20**, 911 (1981); [c]J. H. P. Utley, *Annu. Rep. Prog. Chem. Sect. B* (1981, Published 1980) **77**, 79; [d]J. Grimshaw, In *Electrochemistry, A Specialist Periodical Report*. Edited by H. R. Thirsk, 7, 1 (1980); [e]L. Eberson, In *Mod. Synth. Methods, Conf. Pap. Int. Semin* Vol. 7, p. 1 (Edited by R. Scheffold), 2nd Edn, p. 1 (1980); [f]M. Taniguchi, *Kaguku Keizai* **28**, 35 (1981) *Chem. Abstr*. **95**, 14931x (1981); [g]A. P. Tomilov, *Elektrosint. Monomerov* (Edited by L. G. Feoktistov), Vol. 7 (1980); *Chem. Abstr.* **93**, 122341c (1980); [h]W. J. M. von Tlborg (Ed.) *Electro-organische Syntheses* 1978, collection of articles from *Chem. Weekblad.*

[2a]D. Pletcher, *Chem. Ind.* 358 (1982); [b]A. J. Fry, In *Chemistry of Amino Nitroso, Nitro Compounds* (Edited by S. Patai), Vol. 1, p. 319 (1982); [c]D. Hammerich and V. D. Parker, *Sulfur Rep.* **1**, 317 (1981); [d]J. Ludvik and J. Volke, *Chem. Listy* **76**, 113 (1982); [e]C. L. Bird and A. T. Kukn, *Chem. Soc. Rev.* **10**, 49 (1981); [f]R. E. W. Jansson, *Phil. Trans. R. Soc. London, Ser A* **302**, 285 (1981); [g]*Encylopaedia of Electrochemistry of the Elements* (Edited by A. J. Bard and H. Lund), Vols. XI–XIV. Marcel Dekker, New York (1978–80); M. M. Baizer, *J. Appl. Electrochem.* **10**, 285 (1980).

[3]Fr. Fichter, *Organische Elektrochemie.* Theodor Steinkopff, Dresden and Leipzig (1942).

[4]Also quoted by L. Eberson, In *Organic Electrochemistry* (Edited by M. M. Baizer). p. 866. Marcel Dekker, New York (1973).

[5]This term was introduced[6] to distinguish nonelectrochemical from electrochemical methodologies.

[6]R. C. Hallcher, D. A. White and M. M. Baizer, *J. Electrochem. Soc.* **126**, 404 (1979).

[7]J. K. Kochi, *Organometallic Mechanisms and Catalysis*, p. XIII; M. M. Baizer in Ref. 4, p. iv. Academic Press, New York (1978).

[8]E. g., N. Ibl, K. Kramer, L. Ponto and P. Robertson, *A.I.Ch.E. Symp. Series* 185 **75**, 45 (1979).

[9]M. M. Baizer and J. D. Anderson, *J. Org. Chem.* **30**, 3138 (1965) and refs therein.

[10a]Und zwar mit einem kleinen "u"; [b]D. Seebach, *Angew. Chem. Int. Ed. Eng.* **18**, 239 (1970) and prior refs.

[11]L. Eberson and K. Nyberg in Ref. 2g, Vol. XII, 261; L. Eberson and J. H. P. Utley, In *Organic Electrochemistry*, Edited by M. M. Baizer and H. Lund. 2nd Edn. Marcel Dekker, New York in press.

[12]J. P. Coleman, R. Lines, J. H. P. Utley and B. C. L. Weedon, *J. Chem. Soc. Perkin II* 1064 (1974).

[13]B. Kraeutler and A. J. Bard, *J. Am. Chem. Soc.* **100**, 2239, 4903, 5985 (1978).

[14]W. Schmidt and E. Steckhan, *J. Electroanal. Chem.* **89**, 215 (1978).

[15]K. Knolle and H. J. Schäfer, *Angew Chem. Int. Ed. Eng.* **14**, 758 (1975).

[16]T. Shono, J. Hayashi, H. Omoto and T. Matsumura, *Tetrahedron Letters* 2667 (1977).

[17]M. Seko, A. Yomiyama and T. Isoya, *Chem. Econ. Engng Rev.* **11**, 48 (1979).

[18]Yu B. Vassiliev, V. S. Bagotsky, E. P. Kovsman, V. A. Grinberg, L. S. Kanevsky and V. R. Polischyuk, *Electrochim Acta* **27**, 919 (1982).

[19]D. A. Tyssee, J. H. Wagenknecht, M. M. Baizer and J. L. Chruma, *Tetrahedron Letters* 4809 (1972).

[20]S. Gambino and G. Silvestri, *Ibid.* 3025 (1973).

[21]J. E. Barry, M. Finkelstein, E. A. Mayeda and S. D. Ross, *J. Am. Chem. Soc.* **98** 8098 (1976).

[42]R. Dietz, M. E. Peover, and P. Rothbaum, *Chem. Ing. -Tech.* **42**, 185 (1970).

[23]M. M. Baizer, *Tetrahedron Letters* 973 (1963); *J. Electrochem. Soc.* **111**, 215 (1964).

[24]Itself made by reductive coupling of acrylonitrile and carbon dioxide: D. A. Tysee and M. M. Baizer, *J. Org. Chem.* **39**, 2819 (1974).

[25]J. P. Coleman, R. Lines, J. H. P. Utley and B. C. L. Weedon, *J. Chem. Soc. Perkin II* 1064 (1974).

[26a]B. Kraeutler, C. D. Jaeger and A. J. Bard, *J. Am. Chem. Soc.* **100**, 4903 (1978); [b]B. Kraeutler and A. J. Bard, *Ibid.*, 2239; [c]*Idem, Ibid.*, 5985, [d]I. Izuki, F. F. Dan and A. J. Bard, J. Phys. Chem. in press.

[27]H. Chum (Ed.), Solar Energy Research Institute, *Rep. SERI/PR*-622-1321, April 1982. Available from National Technical Information Service, U.S. Dept. of Commerce, 5285 Port Royal Rd., Springfield, VA 22161.

[28]Ref. 4, p. 499.

[29]W. Schmidt and E. Steckhan, *J. Electroanal. Chem.* **89**, 215 (1978).

[30]D. A. White, *Org. Syn.* **60**, 58 (1981).

[31] N. L. Askerov, S. I. Mekhtiev, V. M. Mamedova and A. P. Tomilov, *J. Gen. Chem. (USSR)* **48**, 787 (1978).

[32] T. Shono, I. Nishiguchi and H. Ohmizu, *Chem. Lett.* 1021 (1977).

[33] J. Armand and L. Bulares, *Can. J. Chem.* **54**, 1197 (1976).

[34] T. Shono, I. Nishiguchi, A. Ohmizu and M. Mitani, *J. Am. Chem. Soc.* **100**, 545 (1978).

[35a] R. W. Koch and R. E. Dessy, *J. Org. Chem.* **47**, 4452 (1982); [b] B. Terem and J. H. P. Utley, *Electrochim. Acta* **24**, 1081 (1979).

[36a] J. Grimshaw and R. J. Haslett, *J. Chem. Soc. Perkin I* 657 (1980); [b] R. Gottlieb and J. L. Neumeyer, *J. Am. Chem. Soc.* **98**, 7108 (1976).

[37] T. Shono, Y. Matsumura, K. Tsubata and Y. Sugihira, *J. Org. Chem.* **47**, 3090 (1982).

[38] K. Nyberg, *Acta Chem. Scand.* **24**, 1609 (1970) 25, 2499 (1971).

[39] L. L. Miller, R. F. Stewart, J. P. Guilespie, V. Ramachandran, J. H. So and F. R. Stermitz, *J. Org. Chem.* **41**, 1580 (1978).

[40] T. Shono, I. Nishiguchi, S. Kashimura and M. Okawa, *Bull. Chem. Soc. Jpn.* **51**, 2181 (1978).

[41] M. M. Baizer, Abstr. 395, *Meeting of the Electrochemical Society*, Montreal, Canada, May 1982. To appear in a Symposium Volume.

[42a] H. G. Thomas and E. Lux, *Tetrahedron Letters* 965 (1972); [b] M. M. Baizer and R. C. Hallcher, *J. Electrochem. Soc.* **123**, 809 (1976).

[43] D. K. Johnson and R. E. W. Jansson, *J. Chem. Technol. Biotechnol.* **30**, 200 (1980); *Chem. Abstr.* **93**, 113509 m (1980).

[44] M. J. Hazelrigg, Jr. and A. J. Bard, *J. Electrochem. Soc.* **122**, 211 (1975) and refs cited therein.

[45] L. Nadjo, J.-M. Savéant and D. Tressler, *J. Electroanal. Chem.* **64**, 143 (1975).

[46] V. D. Parker, *Acta Chem. Scand. Ser. B* **35**, 295 (1981). Part IV of a series.

[47a] M. D. Ryan and D. H. Evans, *J. Electrochem. Soc.* **121**, 881 (1974); [b] A. P. Korotkov and L. N. Nekr, *Elektrokhimiya* **18**, 39 (1982); *Chem. Abstr.* **96**, 161888t (1982); [c] R. Guidelli, G. Piccardi and M. R. Moncelli, *J. Electroanal. Chem.*, **129**, 373 (1981); [d] N. Egashira *et al.*, *Denki Kagaku* **47**, 673 (1979), *Chem. Abstr.* **92**, 118493*r* (1980).

[48a] D. A. Tyssee and M. M. Baizer, *J. Org. Chem.* **39**, 2823 (1974); [b] *Idem.*, *Ibid.* 2823; [c] Ube Industries, Jpn. Kokai Tokyo Koho, JP 81,136,988, 26 Oct. 1981; *Chem. Abstr.* **96**, 13111u (1981). [d] W. J. Tilborg, *Eur. Pat. appl.* 28,430 of 1 Nov. 1979, *Chem. Abstr.* **95**, 69965x (1981).

[49] E. Lamy, L. Nadjo and J.-M. Savéant, *Norw. J. Chim* **3**, 21 (1979).

[50a] N. L. Weinberg, A. K. Hoffmann and T. B. Reddy, *Tetrahedron Letters* 2274 (1971); [b] Tokoyama Soda Co., Ltd., Jpn. Kokai Tokkyo Koho, 81,90,045 of 21 July 1981, *Chem. Abstr.* **95**, 204438v (1981); [c] Y. Kato, Jpn. Kokai Tokkyo Koho, 80,06432 of 28 June 1978, *Chem. Abstr.*, **93**, 46197t (1980); [d] D. K. Root and W. H. Smith, *J. Electrochem. Soc.* **129**, 1231 (1982); [e] V. Hess and M. Ziebig, *Pharmazie* **37**, 107 (1982).

[51] P. Fuchs, U. Hess, H. H. Holst and H. Lund, *Acta. Chem. Scand. B* **35**, 185 (1981).

[52] M. M. Baizer and J. L. Chruma, *J. Org. Chem.* **37**, 1951 (1972).

[53] R. C. Hallcher and M. M. Baizer, *Liebigs Ann. Chem* **737** (1977).

[54] R. C. Hallcher, D. A. White and M. M. Baizer, *J. Electrochem. Soc.* **126**, 404 (1979): *U.S. Pat.* 4,072,583 of Feb. 1978.

[55] H. L. Chum and M. M. Baizer, *Electrochemsitry of Biomass and Derived Materials*, American Chemical Society Monograph Series, in preparation.

[56] M. Guainazzi, G. Silvestri, S. Gambino and G. Filardo, *J. Chem. Soc. Dalton* 927 (1972).

[57] R. Ercoli, G. Silvestri, S. Gambino, M. Guainazzi and G. Filardo, *Ger. Offen.* 2,235,882 of 2 Jan. 1973, *Chem, Abstr.*, **78**, 97190h (1973); a recent review of oxocarbons is given by A. H. Schmidt, *Chemie in Unsrer Zeit* **16**, 47 (1982).

[58] D. Cipis, *J. Electrochem. Soc.* **127**, 1045 (1980).

[59] M. M. Baizer and R. D. Goodin, *U.S. Pat.* 4,351,951 of 28 Sept. 1982.

[60] N. El Murr and A. Chaloyard, *J. Organomet. Chem.* **231** (1982).

[61] R. Ercoli, M. Guainazzi, and G. Silvestri, *Chem. Commun.* 927 (1967), G. Silvestri *et al.*, *J. Chem. Soc. Dalton* 2558 (1972).

[62] J. Grobe, B. H. Schneider and H. Zimmermann, *Z. Anorg. Allg. Chem.* **481**, 107 (1981); *Chem. Abstr.* **96**, 104327k (1982).

[63] Inclusion of Pd/C in electrolysis cell: R. A. Bell, *U.S. Pat.* 4,306,947 of 4 June 1980, 4,310,393 of 29 May 1980.

[64] J. P. Coleman, *J. Electrochem.* Soc. **128**, 2561 (1981) and refs cited therein.

[65a] J. H. Wagenknecht and M. M. Baizer, *J. Org. Chem.* **31**, 3885 (1966); [b] *Idem. J. Electrochem. Soc.* **113**, 1095 (1967).

[66] P. E. Iversen and H. Lund, *Tetrahedron Letter* 3523 (1969). First use of azobenzene as a PB.

[67a] M. M. Baizer, J. L. Chruma and D. White, *Tetrahedron Letters* 5209 (1973); [b] R. C. Buchta and D. H. Evans, *J. Electrochem. Soc.* **117**, 1494 (1970).

[68] A. J. Bellamy, *J. Chem. Soc. Perkin II* 1093 (1981).

[69] V. L. Pardini, L. Roullier and J. H. P. Utley, *Ibid.*, 1520 (1981).

[70] J.-M. Savéant, *Bull. Soc. Chim. Fr.* 3549 (1972).

[71a] A. J. Bellamy, J. B. Kerr, C. J. McGregor and I. S. MacKirdy, *J. Chem. Soc.*, *Perkin Trans.* **2**, 161 (1982) and previous refs.

[72] K. Kistenbrügger, P. Miscke, J. Voss and G. Wiegand, *Liebigs Ann Chem.* 461 (1980):

[73] M. M. Baizer *et al.*, work in progress.

[74] W. T. Monte, M. M. Baizer and R. D. Little, *J. Org. Chem.* **48**, 803 (1983).

[75] This type of Michael reaction has also been catalyzed by *tert*-phosphines: D. A. White and M. M. Baizer, *Tetrahedron Letters* 3597 (1973).

[76] M. M. Baizer and J. D. Anderson, *J. Org. Chem.* **30**, 1351 (1965).

[77] T. Troll and M. M. Baizer, *Electrochim Acta* **20**, 33 (1975).

[78] R. C. Hallcher, R. D. Goodin and M. M. Baizer, *U.S. Pat.* 4,293,392 of 6Oct. 1981.

[79a] R. C. Hallcher, R. D. Goodin and M. M. Baizer, *U.S. PAT.* 4,293,393 of 6 Oct., 1981; [b] N. M. Arakelian, G. O. Torosyan, S. L. Paraviyon and A. T. Babayan, *Arm. Khim. Zh.* **34**, 888 (1981).

[80] R. D. Goodin, R. C. Hallcher and M. M. Baizer, *U.S. Pat.* 4,248,678 of 3 Feb. 1981.

[81] S. T. Nugent, M. M. Baizer and R. D. Little, *Tetrahedron Letters* 1339 (1982).

[82a] M. E. Peover and B. S. White, *Electrochim. Acta* **11**, 1066 (1966); [b] D. T. Sawyer and J. L. Roberts, *J. Electroanal. Chem.* **12**, 90 (1966).

[83a] P. M. Allen, U. Hess, C. S. Foote and M. M. Baizer, *Synth. Commun.* **12**, 123 (1982); [b] M. Sugawara, M. M. Baizer, W. T. Monte and R. D. Little, *Acta Chem. Scand. B* in press.

[84a] D. T. Sawyer and J. S. Valentine, *Acc. Chem. Res.* **14**, 400 (1981) and refs cited; [b] J. Wilshire and D. T. Sawyer, *Ibid.* **12**, 105 (1979) and refs cited.

[85] This is analogous to the disproportionation of azobenzene anion radical in the presence of H$^+$ or Li$^+$.

[86a] D.-H. Chin, G. Chericato, Jr., E. J. Nanni, Jr. and D. T. Sawyer, *J. Am. Chem. Soc.* **104**, 1296 (1982); [b] D. T. Sawyer *et al.*, *Tetrahedron* **35**, 1471 (1979).

[87] Superoxide acts as a nucleophile in saponifying monocarboxylic esters: J. S. Fillipo, Jr., L. J. Romano, C.-I. Chern and J. S. Valentine, *J. Org. Chem.* **41**, 586 (1976).

[88] G. A. Russell, E. G. Jantzen, A. G. Bemis, E. J. Geels, A. J. Moys, S. Mak and E. T. Strom. *Adv. Chem.* **51**, 112 (1965).

[89a] M. Sugawara and M. M. Baizer, manuscript in preparation. α-Hydroperoxides from alkyl diphenyl-acetates and diphenylacetonitrile, made by conventional means, have been used to epoxidise unactivated olefins; J. Rebek, Jr., R. McReady and R. Wolak, *J. Chem. Soc. Chem. Commun.* 705 (1980); J. Rebek, Jr., *Heterocycles* **15**, 517 (1981).

[90] J. Osteryoung, *Science* **218**, 261 (1982).

[91] M. P. Soriaga and A. T. Hubbard, *J. Am. Chem. Soc.* 104, 2735, 2742 (1982).

[92] Recently used also to designate *s*ingle *e*lectron-*t*ransfer: E.g., E. C. Ashby, A. B. Goel, R. N. DePriest and H. S. Pradad, *J. Am. Chem. Soc.* **103**, 973 (1981).

[93] E.g., R. C. Kerber, G. W. Urry and N. Kornblum, *J. Am. Chem. Soc.* **87**, 4520 (1965).

[94] E.g., K. A. Bilevich and O. Yu. Okhlobystin, *Russ. Chem. Rev.* 954 (1968).

[95a] H. Lund and L. H. Christensen, *Acta Chem. Scand. B.* **33** 1975 (1979); [b] J. Simonet, M. Carriou and H. Lund, *Liebigs Ann. Chem.* 1665 (1981).

[96a] P. G. Gassman and R. Yamaguchi, *Tetrahedron* **38**, 1113 (1982); [b] E. C. Ashby, A. B. Goel and W. S. Park, *Tetrahedron Letters* **22**, 4209 (1981); [c] L. Eberson, *Adv. Phys. Org. Chem.*, **18**, 79 (1982); [d] G. R. Newkome *J. Org. Chem.*, **47**, 599 (1982.

[97] J. F. Bunnett, *Acc. Chem. Res.* **11**, 413 (1978).

[98] J.-M. Savéant, *Ibid.* **13**, 323 (1980).

[99] L. Eberson, L. Jönsson and L.-G. Wistrand, *Tetrahderon* **38**, 1087 (1982).

[100] *American Chemical Society Symposium Series* **192** (1982). J. S. Miller (Ed.).

[101] H. A. O. Hill, *Br U.K. Appl.* 2,033,428 of 21 May 1980.

[102] With apologies to D. J. Cram.

[103] T. Matsue, M. Fujihira and T. Osa, *J. Electrochem Soc.* **128**, 1473 (1981).

[104] *Idem., Ibid.* **129**, 1681 (1982).

[105a] C. Z. Smith and J. H. P. Utley, *J. Chem. Soc. Chem. Commun* 492 (1981); [b] L. H. Klemm and D. R. Olson, *J. Org. Chem.* **38**, 3390 (1973); [c] J. P. Petrovich, M. M. Baizer and M. R. Ort, *J. Electrochem. Soc.* **116**, 749 (1969).

[106] J. Grimshaw and E. F. J. Rea, *J. Chem. Soc.* C 2628 (1967).

[107a] A. Hickling *et al., J. Electroanal. Chem.* **8**, 65 (1974); [b] *Idem., Mod. Aspects Electrochem.*, 329 (1971).

[108a] J. H. Wagenknecht, *Ind. Engng Chem. Prod. Res. Develop.* **10**, 184 (1971); [b] S. Tsutsumi *et al.*, Japan 73 22, 691 of 7 July 1973, *Chem. Abstr.* **80**, 3176z (1974).

[109a] L. H. So and L. L. Miller, *J. Am. Chem. Soc.* **103**, 4204 (1981); [b] N. B. H. Henis and L. Miller, *Ibid.* **104**, 2526 (1982); [c] H. Suhr, *Angew. Chem. Int. Ed. Engng.* **11**, 78 (1972).

[110a] M. Fujihira, S. Tasaki, T. Osa and T. Kuwana, *J. Electroanal. Interfacial Electrochem.* **137**, 163 (1982).

[111a] J. C. Moutet and G. Reverdy, *Sci. Rech.* 20 (1982); [b] J. C. Moutet *et al., Tetrahedron Letters* 2389 (1979).

[112a] H. S. Carlsson and H. Lund, *Acta Chem. Scand B.* **34**, 409 (1980); [b] L. E. Manring, J. Eriksen and C. S. Foote, *J. Am. Chem. Soc.* **102**, 4275 (1980).

[113] J. M. Bobbitt and J. P. Willis, *J. Org. Chem.* **42**, 2347 (1977).

[114a] G. Parravano in Ref. 4, 948-974; [b] B. L. Funt and J. Tanner In *Technique of Electro-Organic Synthesis* (Edited by N. L. Weinberg), Part II, 559–665. Wiley-Interscience, New York (1975).

[115] M. R. Ort, E. H. Mottus, M. M. Baizer and D. E. Carter, *U.S. Pat.*, 3,546,083 of 8 Dec. 1970.

[116] M. M. Baizer and T. E. Rogers, *U.S. Pat.*, 4,246,888 of 20 Jan. 1981.

[117a] J. Simonet and H. Lund, *J. Electroanal. Chem.* **75**, 719 (1977); [b] J. O. Besenhard, *Carbon* **14**, 111 (1976).

[118a] D. Danly, Ref. 4, pp. 907–946; [b] various authors in Ref. 114[b] (N. L. Weinberg and B. V. Telak, Eds.) Part III, 1982.

[119a] M. M. Baizer, *J. Electrochem. Soc.* **111**, 215 (1964); [b] *Idem. Chem. Ind.* 436 (1979); [c] *Idem. CHEMTECH* **10**, 161 (1980).

[120] J. P. Coleman and J. H. Wagenknecht, *J. Electrochem. Soc.* **128**, 322 (1981).

[121] K. H. Simmrock, In *Electro-organic Synthesis Technology* (Edited by M. Krumfelt, E. Y. Weissman and R. C. Alkire), American Instute of Chemical Engineers Symposium Series 185, Vol. 75, p. 89 (1979).

[122] R. Hazard *et al., Bull. Soc. Chim. Fr.* (3–4, *Pt.* 2) 679 (1975).

[123] L. Eberson and E. Oberrauch, *Acta Chem. Scand. B.* **35**, 193 (1981).

[124] D. Degner in Ref. 114*b*, pp. 251–282.

[125] The reduction was abandoned some years ago in favour of a catalytic process; the oxidation is still being used.

[126] Work in progress at the University of California, Los Angeles.

[127] H. Lund in Ref. 4, p. 767.

[128] M. M. Baizer, T. Nonaka, K. Park, Y. Saito and K. Nobe, Final Report to Solar Energy Research Institute, Aug. 1982.

[129a] J. W. Larson (Ed.), *Organic Chemistry of Coal* American Chemical Society Symposium Series 71., Washington, D.C., 1978; [b] M. L. Gorbaty and K. Ouchi (Eds.), *Coal Structure*, ACS Advances in Chemistry Series 192, Washington, D.C., 1981.

[130] A review has been given by H. W. Sternberg, *Reduction, Catalytic Dehydrogenation and Reductive Alkylation of Coal*, Report of 1 March 1977.

[131a] L. Schanne and M. W. Haenel, *Tetrahedron Letters*, 4245 (1979); [b] K. Niemann and H.-P. Hombach, *Fuel* **58**, 853 (1979).

[132] C. J. Collins, H.-P. Hombach, B. Maxwell, M. C. Woody and B. M. Benjamin, *J. Am. Chem. Soc.* **102**, 851 (1980).

[133] R. W. Coughlin and M. Faroque, *J. Appl. Electrochem.* **10**, 729 (1980).

[134a] R. P. Baldwin, K. F. Jones, J. T. Joseph and J. L. Wong, *Fuel* **60**, 739 (1981); [b] G. Okada, V. Gurnsway and J. O'M. Bockris, *J. Electrochem. Soc.*, **128**, 2097 (1981); [c] P. M. Dhooge, D. E. Stilwell and S.-M. Park, *Ibid.* **129**, 1719 (1982).

[135] F. E. Stenftle, K. M. Patton and I. Heard, Jr., *Fuel* **60**, 1131 (1981).

[136a] J. Haggin, *Chem. Engng News* 17 (9 Aug. 1982); [b] G. A. Harris, C. E. Sinnett and H. E. Swift, *CHEMTECH* **11**, 764 (1981); [c] J. Gibson, *Chem. Br.* **16**, 26 (1980).

[137] S. M. Chakrabartty, *Future Sources of Organic Raw Materials-CHEMRAWN I* (Edited by L. E. St. Pierre and G. R. Brown, pp. 137–153. Pergamon Press, Oxford (1980).

[138] J. H. Wagenknecht, M. M. Baizer and J. L. Chruma, *Synth. Commun.* **2**, 215 (1972).

[139a] R. Liotta and G. Brons, *J. Am. Chem. Soc.* **103**, 1735 (1981); [b] R. Liotta, *Fuel* **58**, 724 (1979); [c] R. Liotta, K. Rose and E. Hippo, *J. Org. Chem.* **46**, 277 (1981).

[140] I. S. Goldstein (Ed.), *Organic Chemicals From Biomass.* CRC Press, Boca Raton, Florida (1981).

[141] Work by H. L. Chum and associates at S. E. R. I., Golden, Colorado.

[142] F. Martigny, M.-A. Michel and J. Simonet, *J. Electroanal. Chem.* **73**, 373 (1976).

[143] D. W. Sopher and J. H. P. Utley, *J. Chem. Soc. Chem. Commun.* 134 (1981).

[144] P. Martigny and J. Simonet, *J. Electroanal. Chem.* **81**, 409 (1977).

[145] T. Shono, Y. Matsumura, K. Tsubata and Y. Sugihara, *Tetrahedron Letters* 2157 (1979).
[146] E.g., J. Casanova and H. R. Rogers, *J. Org. Chem.* **39**, 2408 (1974).
[147] A. N. Dey and B. P. Sullivan, *J. Electrochem. Soc.* **117**, 222 (1970).
[148] T. Shono, Y. Matsumura, S. Kashimura and H. Kyotoku, *Tetrahedron Letters*. 2807 (1978).
[149] T. Nonaka and M. M. Baizer, *Electrochim. Acta* **28**, 661 (1983).
[150] J. W. v. Goethe, *Faust*, Vorspiel auf dem Theater.