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(71) Applicant: SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.
Carel van Bylandtlaan 30
NL-2596 HR DEN HAAG(NL)

(72) Inventor: van Tilborg, Wilhelmus Joannes Maria
Westervoortsedijk 67 D
NL-6827 AT Arnhem(NL)

(72) Inventor: Smit, Cornelis Jacobus
Badhuisweg 3
NL-1031 CM Amsterdam(NL)

(72) Inventor: Engels, Rainer
Badhuisweg 3
NL-1031 CM Amsterdam(NL)

(74) Representative: Keuzenkamp, Abraham
P.O. Box 302
NL-2501 CH Den Haag(NL)

(54) **A process for the electroreductive preparation of organic compounds.**

(57) A process for the electroreductive preparation of organic compounds in an undivided cell using at the counter-electrode the oxidation of anions of one or more compounds according to the general formula AB, wherein A represents an alkali or alkaline earth metal moiety, a group of formula $N\overset{\oplus}{R}^1R^2R^3R^4$, wherein each of R^1, R^2, R^3 and R^4, which may be the same or different, represents a hydrogen atom, an alkyl group of up to 8 carbon atoms, or an (alk)aryl group which may be substituted by one or more lower alkyl groups; or a pyridinium ion which may be substituted by one or more lower alkyl groups and B represents an azide group or a group $R^5\text{-}C(=O)\text{-}O^{\ominus}$, wherein R^5 represents a hydrogen atom, a group $-C(=O)\text{-}O\text{-}R^6$, wherein R_6 represents a hydrogen atom, an alkyl group of up to 8 carbon atoms or a group A, or a group $-CH_2OR^7$, wherein R^7 represents a hydrogen atom or an alkyl group of up to 8 carbon atoms or an (alk)aryl group which may be substituted by one or more lower alkyl groups.

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A PROCESS FOR THE ELECTROREDUCTIVE PREPARATION OF ORGANIC COMPOUNDS

The present invention relates to electrochemical reactions which can be carried out suitably in a non-aqueous or aprotic environment. The present invention relates in particular to electrochemical reductions, e.g. electrocarboxylations, which can be carried out in an aprotic environment in undivided cells.

It will be clear that electrochemical processes require the simultaneous occurrence of cathodic and anodic reactions. Since electrochemical processes are normally aimed at the production of preferably one compound at one particular electrode (the working electrode), less or virtually no interest is paid to the process or processes occurring simultaneously at the other electrode (counter electrode). In a number of cases, the reaction at the counter-electrode will not constitute a major problem. For instance, when the reaction at the counter-electrode occurs at a sufficiently low potential the products formed at the working electrode will not be destructed electrochemically at the counter-electrode.

However, if no such reaction at the counter-electrode can be found it will be necessary to separate the anode and the cathode. In protic media diaphragms based on ion-exchange resins can be suitably used, but such diaphragms can not be used satisfactorily in a non-aqueous or an aprotic environment as they become very poorly conducting so that thermal damage may occur even at low current densities. Also diaphragms based on the principle of diffusion limitation are unsuitable for use in non-aqueous, in particular in aprotic environments since the requirements to combine a high electrical conductivity with little diffusion and sufficient mechanical strength appear to be incompatible. Furthermore, the possibility of electrolysis of the

solvent as the reaction at the counter-electrode which can be used nicely for electrochemical processes to be carried out in a protic environment is not available for electrochemical processes to be carried out in a non-aqueous or in an aprotic environment since this would generate highly active species, which would unavoidably lead to the occurrence of a great many undesired side reactions.

It would be of great importance when use could be made in electrochemical processes which have to be carried out in a non-aqueous, and in particular in an aprotic environment in an undivided cell of a reaction at the counter-electrode which not only works at a potential which protects starting materials and products formed at the working electrode from electrochemical destruction at the counter-electrode but also has the advantage that the materials to be converted at the counter-electrode as well as the products obtained do not interfere in an adverse way with the reaction and/or reaction products at the working electrode.

It has now been found that electroreduction processes can be carried out conveniently in a non-aqueous or aprotic environment in an undivided cell when use is made in the electrooxidation step of certain specific compounds which fulfill the requirements set out hereinabove.

The present invention therefore relates to a process for the electroreductive preparation of organic compounds in an undivided cell which comprises as reaction at the counter-electrode the oxidation of anions of one or more compounds according to the general formula AB, wherein A represents an alkali or alkaline earth metal moiety; a group of formula $\overset{\oplus}{N}R^1R^2R^3R^4$, wherein each of R^1, R^2, R^3 and R^4 which may be the same or different, represents a hydrogen atom, an alkyl group of up to 8 carbon atoms, or an (alk)aryl group, which may be substituted by one or more lower alkyl groups; or a pyridinium ion which may be substituted by one or

more lower alkyl groups and B represents an azide group or a group $R^5-C\overset{O}{\underset{O}{<}}\ominus$, wherein R^5 represents a hydrogen atom, a group $-C\overset{O}{\underset{O-R^6}{<}}$, wherein R^6 represents a hydrogen atom, an alkyl group of up to 8 carbon atoms or a group A, or a group $-CH_2OR^7$, wherein R^7 represents a hydrogen atom, an alkyl group of up to 8 carbon atoms, or an (alk)aryl group which may be substituted by one or more lower alkyl groups.

The present invention is of particular interest in that the products obtained at the counter-electrode in the electrooxidation step (i.a. carbon dioxide and nitrogen) in an undivided cell do not interfere adversely with the products obtained in the electroreduction step and are also of no environmental concern. Moreover, in electrocarboxylation reactions use can be made of the electrooxidation of anions of the type $R^5-C\overset{O}{\underset{O}{<}}\ominus$ as defined hereinbefore as (additional) sources for carbon dioxide to be used in the electroreduction step. It should also be noted that the presence of formate ions is of great importance in that they provide the unique system of having both carbon dioxide and protons available in a non-aqueous or even aprotic environment which opens up wide perspectives in preparative organic electrochemistry.

The present invention relates in particular to a process for the electroreductive preparation of organic compounds in an undivided cell in a non-aqueous or aprotic environment which comprises as reaction at the counter-electrode the oxidation of anions of one or more compounds according to the general formula AB, wherein A represents an alkali or alkaline earth metal moiety, a group of formula $\overset{\oplus}{N}R^1R^2R^3R^4$ wherein each of R^1, R^2, R^3 and R^4, which may be the same or different, represents an alkyl group of up to 4 carbon atoms, a phenyl group or a pyridinium ion and B represents a group $R^5-C\overset{O}{\underset{O}{<}}\ominus$, wherein R^5 represents a hydrogen atom, a group

$-C\overset{O}{\underset{O-R^6}{<}}$, wherein R^6 represents a hydrogen atom, an alkyl group of up to 8 carbon atoms or a group A, or a group $-CH_2OR^7$, wherein R^7 represents a hydrogen atom or an alkyl group of up to 8 carbon atoms.

Preferred processes according to the present invention are electroreductive preparations of organic compounds in an undivided cell in non-aqueous or aprotic environments, which comprise as reaction at the counter-electrode the oxidation of anions of one or more compounds according to the general formula AB, wherein A represents a group of formula $\overset{\oplus}{N}R^1R^2R^3R^4$, wherein each of R^1, R^2, R^3 and R^4, which may be the same or different, represents a methyl or ethyl group, and B represents a group $R^5-C\overset{O}{\underset{O}{<}}^{\ominus}$, wherein R^5 represents a hydrogen atom or a group $-C\overset{O}{\underset{OR^6}{<}}$, wherein R^6 represents a hydrogen atom, an alkyl group of up to 4 carbon atoms or a group A. Examples of preferred compounds comprise di-tetraethyl ammonium oxalate (DTEAOx) and tetraethyl ammonium formate (TEAF).

The process according to the present invention is of particular interest for electrocarboxylation reactions, i.e. reactions in which carbon dioxide is reacted with electrogenerated (carb)anions. Suitable electrocarboxylation reactions comprise the carboxylations of activated olefins, imines, and related species such as azo-compounds, ketones as well as of halogen compounds. Preferred electrocarboxylations are those wherein an activated olefin is the compound to be reduced electrochemically.

Activated olefins which can be electrocarboxylated using the process according to the present invention can be represented by the general formula

$$\begin{matrix} R^9 \\ R^{10} \end{matrix}\!\!>\!C = \overset{R^8}{\overset{|}{C}} - A^1 \qquad (I)$$

wherein R^8, R^9 and R^{10}, which may be the same or different, each represents a hydrogen atom, an alkyl group of up to 8 carbon atoms, a phenyl group which may be substituted by one or more halogen atoms and/or lower alkyl groups or a group A^1; and A^1 represents a group -CN or a group $-C\overset{O}{\underset{(O)_n}{<}}R^{11}$, wherein R^{11} represents an alkyl group of up to 8 carbon atoms, or a phenyl group which may be substituted with one or more halogen atoms and/or lower alkyl groups and n is 0 or 1.

Preferred compounds according to the general formula I to be used in the process according to the present invention are those wherein A^1 represents a group -CN, a group $-C\overset{O}{\underset{(O)_n}{<}}R^{11}$, wherein R^{11} represents a methyl group and n is 0 or 1, or a phenyl group and each of R^8, R^9 and R^{10} represents a hydrogen atom or a lower alkyl group or at least one of R^8, R^9 and R^{10} represents a group A^1. Especially preferred compounds according to the general formula I to be used in the process according to the present invention are those which possess two groups A^1. Examples of preferred compounds comprise dimethyl maleate, acrylonitrile, methyl vinyl ketone and alpha-methyl styrene; dimethyl maleate being especially preferred.

It should be noted that the electrocarboxylations according to the present invention can be performed using carbon dioxide generated at the anode as the sole carbon dioxide source. If desired, the electrocarboxylations can also be performed using additional carbon dioxide. Even in those events wherein a large molar excess of non-electrochemically generated carbon dioxide is used, the electrooxidation of the anions according to the general formula AB still generates either potential reactants (carbon dioxide), or harmless co-products (nitrogen). Moreover, the formate and oxalate ions appear to be oxidized at rather low potential (at about +1.2 V vs SCE and +0.2 V vs SCE respectively)

which widens the range of electroreduction reactions applicable.

The products obtained by the electrocarboxylations according to the present invention are (poly)carboxylic acids. The exact nature of the products depends to some extent on the particular reaction conditions and electrodes used.

For instance, starting from dimethyl maleate in a one-compartment (undivided) cell at room temperature in acetonitrile using tetraethyl ammonium oxalate as the compound to be oxidized as well as being the conducting salt, a crude polycarboxylic acid product mixture had been formed (esterified with methyl iodide for product analysis) with a current yield as high as 80 %. After further purification hexamethyl-1,1,2,3,4,4-butane hexacarboxylate was isolated in 40 % yield.

However, when tetraethyl ammonium formate was used as the compound AB as well as conducting salt the product distribution of the polycarboxylic acid esters obtained was significantly changed in that the main products appeared to be trimethyl-1,1,2-ethane tricarboxylate (59 % current yield) and tetramethyl-1,2,3,4-butane tetracarboxylate (20 % current yield); no hexamethyl hexacarboxylate could be detected. Without wishing to be bound to any particular theory, it would appear that the change in product distribution has to be ascribed to an increased protonation versus carboxylation of anionic intermediates due to the production of protons from the anodic oxidation reaction.

The electrocarboxylation of acrylonitrile yielded dimethyl cyanosuccinate in 41 % yield after distillation of the methylated product whereas the main products in the electrocarboxylation of methyl vinyl ketone and alpha-methyl styrene were levulinic acid and 2-methyl-2-phenyl-succinic acid, respectively.

Examples of imines which can be suitably electrocarboxylated comprise (substituted) benzalanilines which are converted

into the corresponding alpha-phenyl phenyl glycines. Suitable ketones comprise aromatic ketones, such as acetophenone and substituted acetophenones, benzophenone and related compounds. The electrocarboxylation of aromatic ketones affords alpha-aryl-alpha-hydroxy acids as well as minor amounts of the corresponding pinacols. The process according to the present invention is also of great interest for the preparation of carboxylic acids from the corresponding halogen compounds. For instance, 1-bromo-2-methyl pentane could be converted almost quantitatively into 3-methyl hexanoic acid using tetraethyl ammonium oxalate as the compound AB as well as the conducting salt. Also acid chlorides can be converted using the process according to the present invention. For instance, pivaloyl chloride was converted in a fair yield to pivalic acid (analysed as methyl pivalate).

Apart from electrocarboxylation reactions as discussed hereinbefore, the present invention also relates to non-carboxylating electroreductions. Examples of suitable compounds which can be reduced electrochemically without the introduction of carbon dioxide (whether electrochemically generated or not) into the intermediate to give a carboxylated final product, comprise sulphonium salts, especially aromatic sulphonium salts such as (p-nitro)tosylsulphonium salts, and sulphonamides and 1,2-dihaloalkanes, such as 1,2-dibromo-1,2-diphenyl ethane and related compounds. Without wishing to be bound to any particular theory it would appear that non-carboxylating electroreductions will occur primarily when reactions such as dimerisation, elimination and/or hydrogen abstraction from the solvent become faster reactions than the electrocarboxylation reaction. It is likely that the reduction potential of the intermediary radical species will be a decisive factor in governing the course of the reaction. For instance, 4,4'-dinitrobibenzyl as well as p-nitrotoluene were obtained

when electroreducing dimethyl (p-nitro)tosyl sulphonium chloride in methanol according to the process according to the present invention.

A further example comprises the electroreduction of 1,10-bis(p-toluene sulphonyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane into 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (also known as 1,10-diaza-18-crown-6) in almost quantitative yields using tetraethyl ammonium formate as the compound AB as well as conducting salt. Yet a further example of a non-carboxylating electroreduction is the virtually quantitative pinacolization of acetophenone. However, depending on the reaction conditions electrocarboxylation of acetophenone yielding (after reaction with methyl iodide for product analysis) the methyl ester of alpha-phenyllactic acid may also be achieved.

The process according to the present invention will normally be carried out in the presence of a solvent for the compound to be electroreduced as well as for the compound AB. It will be clear that the choice of the solvent to be applied will depend mainly on the kind of electroreduction envisaged. For instance, when electrocarboxylation reactions are to be carried out, the solvent should be non-aqueous and preferably aprotic. Moreover, the solvent applied should preferably have a fairly high dielectric constant in order to lower the electrical resistance within the cell. Suitable solvents comprise ethers such as dimethoxy ethane, diethyl ether, tetrahydrofuran and macrocyclic polyethers such as for instance the so-called crown ethers (1,4,7,10,13,16-tetraoxacyclooctadecane and related compounds), chlorinated or fluorinated hydrocarbons, such as dichloromethane and carbon tetrachloride, nitriles such as acetonitrile, lower alkanols such as methanol or ethanol, formamides such as dimethyl formamide, sulpholane and alkylsubstituted sulpholanes, organic carbonates such

as ethylene carbonate and propylene carbonate, nitromethane, N-methyl pyrrolidone and hexamethylene phosphortriamide. The optimum choice will depend on the potential to be worked at in the electrochemical reaction. For electrocarboxylations preference is given to the use of acetonitrile, dimethyl formamide and methanol, the use of acetonitrile being particularly preferred.

When non-carboxylating electroreductions are to be carried out according to the process according to the present invention use can be made of aprotic as well as of protic solvents. In general the solvents described hereinabove can be used suitably, preference being given to the use of lower alkanols such as methanol and ethanol. Under those circumstances the presence of water, even in amounts of up to 50 %v, calculated on total solvent, can be tolerated. However, better results will generally be obtained when the amount of water present is rather small, e.g. less than 10 %v.

It will be clear that the compound AB apart from being a reagent also will function as a supporting electrolyte. For this purpose it is not absolutely necessary to have the compound AB completely dissolved in the reaction medium as dissolution of non-dissolved material will occur gradually during the electrochemical process concerned. However, when the compound AB is dissolved at the beginning of the electrochemical process it will have a better supporting function. It is also possible to introduce a further supporting electrolyte. Use can be made of the supporting electrolytes which are well-known in the art. Reference is made to salts of amines or quarternary ammonium salts such as tetraalkyl ammonium, heterocyclic and (alk) aryl ammonium salts, the corresponding anions comprising inorganic as well as organic anions, e.g. phosphates, halides, perchlorates, sulphates, arylsulphonates or alkylsulphonates.

The amount of additional supporting electrolyte present in the reaction mixture may vary within wide limits. Amounts up to 50 %w on solvent/reagent applied can be used, suitable concentrations often being in the range of from 0.5 %w to 15 %w.

If desired, mixtures of two or more compounds according to the general formula AB as well as mixtures comprising at least one compound according to the general formula AB and at least one additional supporting electrolyte can be suitably used. In the event that as compounds according to the general formula AB an oxalate (i.e. a compound wherein B represents a group $R^5-C\overset{O}{\underset{O}{<}}\ominus$, wherein R^5 represents a group $-C\overset{O}{\underset{O-R^6}{<}}$, wherein R^6 is as defined hereinbefore) and a formate (i.e. a compound wherein B represents a group $R^5-C\overset{O}{\underset{O}{<}}\ominus$, wherein R^5 represents a hydrogen atom) are used, advantage can be taken from both a carbon dioxide and a proton source within the same reaction mixture. This is of special importance for electrocarboxylation reactions as the presence of protons may influence the composition of the final products.

Various current densities can be employed in the process according to the present invention. It will be advantageous to employ relatively high current densities in order to achieve high use of electrolysis cell capacity depending on factors such as cost and source of electrical current, resistance of the reaction medium, heat dissipation problems and impact upon yields. It has been found that current densities of from 5-1000 mA/cm^2 can suitably be used for the process according to the present invention. Preference being given to current densities of 25 mA/cm^2 and above.

As disclosed hereinbefore, the process according to the present invention can be carried out in a one-compartment electrolysis cell, i.e. in an electrolysis cell which does not have a cell divider (membrane, diaphragm) to

separate the electrodes. The process can be carried out batch-wise or (semi)-continuously. One-compartment cells especially suited for continuous operation, comprise the so-called capillary gap cells. These cells consist of a stack of circular electrode plates separated from each other by spacers and provided with a central bore. The electrolyte is pumped through the central hole and is forced to flow through the narrow gap between the electrode plates. A constant potential applied over the stack produces a dipolar electrode arrangement, each capillary gap thus serving as a separate cell. Also modifications of the capillary gap cell such as the pump cell (rotation of one of the circular electrode plates causes the electrolyte to flow outwards through the gap, the cell thus acting as its own pump) and the trickle-tower cell (consisting of layers of conducting rings separated from each other by a non-conducting gauze while the electrolyte is sprayed over the top of the column and trickles down over the rings whilst a certain voltage is maintained over the column) can be used to carry out the process according to the present invention.

The electrodes to be used in the process according to the present invention can be of any electrode material which is relatively inert under the reaction conditions. Suitable anodes are those comprising platinum or carbon although other materials (e.g. lead dioxide) can be used as well. Cadmium, lead, mercury and mercurated lead are very good materials for the cathode to be used in the process according to the present invention although other materials can be used as well. Very good results can be obtained using a platinum or carbon anode and a lead or mercurated lead cathode. The choice of the electrodes will also depend to some extent on the electroreduction envisaged taking into account the oxidation of especially oxalate and/or formate anions at the anode. Also impurities present in

one or both electrodes may have some impact on the products obtained.

The process according to the present invention can be carried out in a wide range of temperatures. It has been found that ambient temperatures can be suitably applied but higher as well as lower temperatures (e.g. between +80°C and -20°C) are by no means excluded. It is sometimes found that temperatures less than ambient are to be preferred from a yield point of view. It may then be necessary to cool the reaction medium concerned. Normally, good results are obtained when the electrochemical process is carried out at ambient temperature or slightly below.

With respect to pressure it should be noted that especially electrocarboxylation reactions can be carried out advantageously when carbon dioxide is available at atmospheric or higher pressures. Pressures up to 100 bar can be suitably applied, preference being given to pressures up to 50 bar. As discussed hereinbefore, it is also possible to carry out the electrocarboxylation reactions without the presence of an external carbon dioxide source when oxalates and/or formates are used as the compounds to be electro-oxidized. Non-carboxylating electroreduction reactions are normally carried out at autogeneous pressure, although higher pressures can be used as well.

The products obtained according to the process according to the present invention can be recovered by a variety of procedures. These procedures are well-known in the art and depend on the particular type of product to be recovered. For instance, in electrocarboxylation processes it may be useful to convert the acids produced into the corresponding alkyl esters by treatment with an alkyl halide such as methyl iodide. It may then be easier to separate the esters produced from the starting materials by chromato-

graphic techniques or by distillation, extraction or a combination of such recovery techniques. It is also possible to treat the acids obtained with a suitable base and extracting the salts obtained from the reaction mixture. When macro(hetero) cyclic polyethers are produced according to the electrochemical process according to the present invention use can be made of the well-known complexing aspects of such products for their recovery in a high yield and with a high degree of purity.

It will be clear that the compounds produced according to the present invention can be used in various ways depending on their proper nature, e.g. carboxylic acids can be used in the preparation of the corresponding esters which can be used per se, e.g. as plasticizers or serve as starting materials for the preparation of polyesters by reacting them with the appropriate polyalcohols. Macro(hetero) cyclic polyethers such as 18-crown-6 or 1,10-diaza-18-crown-6 can be used for instance as solvents or as phase transfer agents.

The invention will now be illustrated by means of the following Examples.

The experiments described in the Examples I and III-XIII were carried out in a cylindrical glass cell of 100 ml provided with two electrodes, each having a surface-area of 6 cm^2. A reference electrode was situated within the vessel. The potential of the working electrode was controlled by means of a reference electrode contacted with the solution by a Luggin-capillary. The experiments were carried out in the presence of atmospheric carbon dioxide pressure.

The experiment described in Example II was carried out in a capillary gap cell. The capillary gap cell used comprises a series of cylindrical, bipolar graphite discs with a central orifice through which the electrolyte and the

appropriate substrates enter. They flow radially to the periphery of the discs where they are collected and withdrawn. The carbon dioxide pressure applied was 2 bar and the flow rate of the electrolyte used was 3 l/min^{-1}.

Normally available electrodes were used in the experiments with the exception of mercurated lead electrodes which were prepared by either reducing an aqueous solution of Hg(II) acetate at -0.90 V vs Standard Calomel Electrode (SCE)/ 180 mA for 15 minutes on a lead electrode or by rubbing polarographically pure mercury on a freshly cleaned lead surface.

The oxalates and formates to be used in the process according to the present invention can be prepared by methods known in the art. For instance, a suitable manner for preparing ditetraethyl ammonium oxalate (DTEAOx) comprises neutralizing a solution of tetraethyl ammonium hydroxide (25 %) in water with the appropriate amount of oxalic acid. Water is then removed using a rotatory evaporator and the residue obtained dried further over a drying agent such as phosphorous pentoxide under reduced pressure. The dry salt obtained appears to be hygroscopic and should therefore be handled in the absence of moisture.

The compounds may also be prepared by reaction of tertiary amines and the appropriate alkyl esters or by cation-exchange of the carboxylic acid or the appropriate carboxylate(s).

The products obtained were identified by one or more of the following techniques: gas/liquid chromatography, mass spectrometry, proton magnetic resonance, ^{13}C magnetic resonance and infrared spectroscopy.

EXAMPLE I - Electrocarboxylation of dimethyl maleate

a) The experiment was performed in the vessel as described hereinbefore. The electrocarboxylation reaction was carried out in dry acetonitrile as the solvent, using a lead cathode and a platinum anode. The reaction was carried out at room temperature using dimethyl maleate in a concentration of 0.46 $mol.l^{-1}$ and ditetraethyl ammonium oxalate as the carbon dioxide source/conducting salt (0.23 $mol.l^{-1}$). The reduction potential applied was -1.60 V vs SCE at a current density of 100 mA/cm^2.

After the reaction had been stopped a crude polycarboxylic acid product mixture had been obtained which was then esterified using methyl iodide to facilitate product analysis in the form of the corresponding methyl esters. The current consumed was 0.95 $F.mol^{-1}$ and the current yield of the crude polycarboxylic acid product mixture was 80 %. From this mixture of polycarboxylic acid methyl esters hexamethyl-1,1,2,3,4,4-butanehexacarboxylate was isolated by crystallization from methanol in 39 % chemical yield (41 % current yield).

b) The experiment described in Example Ia was repeated using a carbon anode. The reduction potential was again -1.60 V vs SCE and the current density applied was 65 mA/cm^2. The current consumed was 0.94 $F.mol^{-1}$. After working-up in the manner as described hereinbefore hexamethyl-1,1,2,3,3,4-butanehexacarboxylate was obtained in 42 % chemical yield (45 % current yield).

c) The experiment described in Example Ib was repeated using tetraethyl ammonium formate (0.46 $mol.l^{-1}$) as the carbon dioxide source/conducting salt. The electrocarboxylation was performed at a reduction potential of -1.60 V vs SCE and at a current density of 38 mA/cm^2.

The current consumed was 1.18 $F.mol^{-1}$. After a working-up procedure similar to that described in Example Ib two main products were identified in the form of the respective methyl esters: trimethyl-1,1,2-ethanetricarboxylate in 35 % chemical yield (59 % current yield) and tetramethyl-1,2,3,4-butanetetracarboxylate in 17 % chemical yield (20 % current yield). No hexamethyl-1,1,2,3,4,4-butanehexacarboxylate could be detected indicating the influence of protons originating from the oxidation of the formate ion on the reaction pattern.

d) The experiment described in Example Ia was repeated using tetraethyl ammonium azide (0.23 $mol.l^{-1}$) as the conducting salt. The electrocarboxylation was performed at a reduction potential of -1.53 V vs SCE at a current density of 25 mA/cm^2. The current consumed was 1.02 $F.mol^{-1}$. After working up in the manner as described hereinbefore polycarboxylic acids were obtainedd in 40 % chemical yield (40 % current yield) of which 11 % appeared to be hexamethyl-1,1,2,3,4,4-butanehexacarboxylate.

e) The experiment described in Example Ia was repeated using methyl triethylmethylammonium oxalate (0.23 $mol.l^{-1}$) as the conducting salt. The electrocarboxylation was performed at a reduction potential of -1.60 V vs SCE at a current density of 40 mA/cm^2. The current consumed was 0.45 $F.mol^{-1}$. After working up in the manner as described hereinbefore tetramethyl-1,2,3,4-butane tetracarboxylate was obtained in 38 % current yield.

EXAMPLE II - Electrocarboxylation of dimethylmaleate in a capillary gap cell

The electrocarboxylation of dimethyl maleate was carried out in a capillary gap cell as described hereinbefore. The electrocarboxylation was carried out in the presence of

gaseous carbon dioxide (pressure 2 bar) at a flow rate of the electrolyte system ditetraethyl ammonium oxalate/ acetonitrile of 3 $l.min^{-1}$. The yield of the crude polycarboxylic acids (isolated as the corresponding methyl esters and identified by gas/liquid chromatography) was 77 %. The addition of methanol caused precipitation of hexamethyl-1,1,2,3,4,4-butanehexacarboxylate (yield 20 %). Distillation of the residue afforded an additional 40 % yield of the following esters:

trimethyl-1,1,2-ethanetricarboxylate (5 %)
tetramethyl-1,1,2,2-ethanetetracarboxylate (24 %) and
pentamethyl-1,1,2,3,4-butanepentacarboxylate (11 %).

EXAMPLE III - Electrocarboxylation of acrylonitrile

The electrocarboxylation of acrylonitrile (0.23 $mol.l^{-1}$) was carried out in the vessel described in Example I using a lead cathode and a platinum anode. The concentration of the carbondioxide source/conducting salt DTEAOx amounted to 0.23 $mol.l^{-1}$. The reduction potential was -2.14 V vs SCE and the current density was 30 mA/cm^2. The current consumed was 1.67 $F.mol^{-1}$. The compound 1-cyano-dimethyl-1,2-ethanedicarboxylate was obtained after distillation in 34 % chemical yield (41 % current yield).

EXAMPLE IV - Electrocarboxylation of methyl vinyl ketone

Methyl vinyl ketone (0.46 $mol.l^{-1}$) was electrocarboxylated under the conditions described in Example III at a reduction potential of -1.92 V vs SCE and at a current density of 25 mA/cm^2. The current consumed was 0.90 $F.mol^{-1}$. After working up in the usual manner the methyl ester of levulinic acid was obtained in 4 % chemical yield (9 % current yield).

EXAMPLE V - Electrocarboxylation of alpha-methylstyrene

The experiment described in Example IV was repeated using alpha-methyl styrene as the compound to be electrocarboxylated. The reduction potential was -2.20 V vs SCE and the current density was 18 mA/cm^2. The current consumed was 1.97 $F.mol^{-1}$. After working up in the usual manner the methyl ester of 2-methyl-2-phenyl succinic acid was obtained in 19 % chemical yield (19 % current yield). Also a trace of the methyl ester of 3-phenyl butanoic acid could be detected.

EXAMPLE VI - Electrocarboxylation of benzalaniline

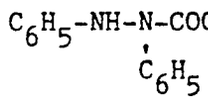
Benzalaniline was electrocarboxylated in the manner as described in Example I using a lead cathode and a platinum anode. The concentration of benzalaniline amounted to 0.20 $mol.l^{-1}$ and that of DTEAOx to 0.23 $mol.l^{-1}$, the solvent being dry acetonitrile. The electrocarboxylation was performed at a reduction potential of -1.80 V vs SCE and at a current density of 20 mA/cm^2. The current consumed was 1.50 $F.mol^{-1}$. After working up in the usual manner methyl-2-phenyl-2-anilino acetate was obtained in 58 % chemical yield (79 % current yield).

EXAMPLE VII - Electrocarboxylation of acetophenone

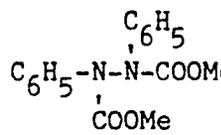
The experiment described in Example VI was repeated using acetophenone (0.23 $mol.l^{-1}$) as the compound to be electrocarboxylated. The reduction potential was -1.80 V vs SCE and the current density was 25 mA/cm^2. The current consumed was 1.06 $F.mol^{-1}$. After working up in the usual manner the methyl ester of alpha-phenyl lactic acid was obtained as the main product (40 % chemical yield, 58 % current yield). Also acetophenone pinacol (2,3-dihydroxy-2,3-diphenylbutane) had been formed in 29 % chemical yield (21 % current yield).

EXAMPLE VIII - Electrocarboxylation of azobenzene

The experiment described in Example VII was repeated using azobenzene (0.23 $mol.l^{-1}$) as the compound to be electrocarboxylated. The reduction potential was -1.31 V vs SCE and the current density was 13 mA/cm^2. The current consumed was 1.06 $F.mol^{-1}$. After working up in the usual manner, a mixture of the methyl esters of the mono- and dicarboxylic acid of azobenzene was obtained:



: 17 % chemical yield (16 % current yield)



: 40 % chemical yield (38 % current yield)

EXAMPLE IX - Electrocarboxylation of halogen-containing compounds

a) The experiment described in Example VIII was repeated using 1-bromo-2-methylpentane (0.23 $mol.l^{-1}$) as the substrate. The reduction potential was -2.15 V vs SCE and the current density amounted to 8 mA/cm^2. The current consumed was 2.03 $F.mol^{-1}$. After working up in the usual manner the methyl ester of beta-methyl hexanoic acid was isolated in a very high yield: 96 % chemical yield and 95 % current yield.

b) The experiment described in Example IXa was repeated using pivaloylchloride (0.23 $mol.l^{-1}$) as the substrate. The reduction potential was -2.20 V vs SCE and the current density was 28 mA/cm^2. The current consumed was 1.61 $F.mol^{-1}$. After the usual working up procedure methyl pivaloate was obtained in 50 % chemical yield (62 % current yield)

c) The experiment described in Example IXa was repeated using 1,1,1,2,3,3,3-heptachloropropane as the substrate. After the usual working up procedure the methyl ester of

alpha-trichloromethyl beta-trichloropropionic acid was isolated in 30 % current yield.

d) The experiment described in Example IXa was repeated using 2,4-dibromo-2,4-dimethylpentan-3-one as the substrate. After the usual working up procedure a mixture of carboxylated products was obtained.

EXAMPLE X - Electroreduction of p-nitrobenzyl dimethyl sulphonium chloride

The electroreduction of p-nitrobenzyl dimethyl sulphonium chloride was performed in the vessel described in Example Ia. The electroreduction was carried out at room temperature using a lead cathode and a platinum anode. Methanol was used as the solvent and the concentration of the sulphonium compound amounted to 0.025 $mol.l^{-1}$ whereas the concentration of the conducting salt DTEAOx amounted to 0.23 $mol.l^{-1}$. The reduction potential was -1.0 V vs SCE and the current density was 3 mA/cm^2. The current consumed was 1.4 $F.mol^{-1}$. The reaction products found were para-nitrotoluene in 22 % yield (55 % current yield) and 4,4'-dinitrobibenzyl in 13 % yield (9 % current yield).

EXAMPLE XI - Electroreduction of 1,10-bis(p-toluene sulphonyl)-1,10-diaza-18-crown-6

The experiment described in the previous Example was repeated using a mercury cathode and a lead anode whilst the compound to be electroreduced was 1,10-bis(p-toluene sulphonyl)-1,10-diaza-18-crown-6 dissolved in dimethyl formamide (0.0044 $mol.l^{-1}$). The conducting salt was tetraethyl ammonium formate (0.20 $mol.l^{-1}$) and the electroreduction was carried out at a reduction potential of -2.26 V vs SCE at a current density of 3 mA/cm^2. The current consumed was 5.4 $F.mol^{-1}$. 1,10-Diaza-18-crown-6 was obtained in 85 % chemical yield (63 % current yield).

EXAMPLE XII - Electroreduction of acetophenone

a) The electroreduction described in the previous Example was repeated using a mercury cathode and a platinum anode whilst the compound to be electroreduced was acetophenone dissolved in methanol (0.23 $mol.l^{-1}$). The conducting salt was ditetraethyl ammonium oxalate (0.23 $mol.l^{-1}$) and the electroreduction was carried out at a reduction potential of -1.60 V vs SCE at a current density of 20 mA/cm^2. The current consumed was 1.55 $F.mol^{-1}$. Acetophenone pinacol was obtained in 94 % chemical yield (61 % current yield). No carboxylated product could be detected (cf. Example VII).

b) The experiment described in Example XIIa was repeated using acetonitrile as the solvent. The reduction potential was -1.80 V vs SCE at a current density of 2 mA/cm^2. The current consumed was 1.59 $F.mol^{-1}$ and acetophenone pinacol was obtained in 46 % chemical yield (29 % current yield). Again no carboxylation product could be detected (cf. Example VII).

c) The experiment described in Example XIIa was repeated using tetraethyl ammonium glycolate as the conducting salt (0.23 $mol.l^{-1}$). The electroreduction was carried out at a reduction potential of -1.71 V vs SCE at a current density of 16 mA/cm^2. The current consumed was 1.46 $F.mol^{-1}$. Acetophenone pinacol was obtained in 90 % chemical yield (60 % current yield).

d) The experiment described in Example XIIc was repeated using the methyl ether of tetramethyl ammonium glycolate as the conducting salt (0.25 $mol.l^{-1}$). The electroreduction was carried out at a reduction potential of -1.68 V vs SCE at a current density of 13 mA/cm^2. The current consumed was 1.40 $F.mol^{-1}$. Acetophenone pinacol was obtained in 87 % chemical yield (62 % current yield).

EXAMPLE XIII - Electroreduction of 1,2-dibromo-1,2-diphenyl ethane

a) The electroreduction of 1,2-dibromo-1,2-diphenyl ethane in acetonitrile (0.31 $mol.l^{-1}$) was carried out in the vessel described in Example I using a lead cathode and a platina anode. The concentration of the conducting salt ditetraethyl ammonium oxalate was 0.23 $mol.l^{-1}$. The reduction potential was -1.35 V vs SCE at a current density of 20 mA/cm^2. The current consumed was 1.95 $F.mol^{-1}$. After working up stilbene was obtained in 84 % chemical yield (86 % current yield) in a cis/trans ratio of 38/62.

b) The experiment described in Example XIIIa was repeated using acetonitrile containing 10 %w H_2O as the solvent. Ditetraethyl ammonium oxalate was used as the conducting salt (0.25 $mol.l^{-1}$). The electroreduction was carried out at 80 ^oC and at a reduction potential of -1.50 V vs SCE at a current density of 18 mA/cm^2. The current consumed was 2.04 $F.mol^{-1}$. After working up trans-stilbene was obtained in 93 % chemical yield (91 % current yield).

c) The experiment described in Example XIIIb was repeated using acetonitrile/water (1:1) as the solvent mixture. The electroreduction was carried out at a reduction potential of -1.70 V vs SCE at a current density of 5 mA/cm^2. The current consumed was 2.35 $F.mol^{-1}$. After working up trans-stilbene was obtained in 75 % chemical yield (64 % current yield.

d) The experiment described in Example XIIIc was repeated using dry methanol as the solvent and ammonium-formate (0.2 $mol.l^{-1}$) as the conducting salt. The electro-reduction was carried out at a reduction potential of -1.54 V vs SCE at a current density of 9 mA/cm^2. The current consumed was 5.1 $F.mol^{-1}$. After working up trans-stilbene was obtained in 92 % chemical yield (36 % current yield).

C L A I M S

1. A process for the electroreductive preparation of organic compounds in an undivided cell which comprises as reaction at the counter-electrode the oxidation of anions of one or more compounds according to the general formula AB, wherein A represents an alkali or alkaline earth metal moiety; a group of formula $\overset{\oplus}{N}R^1R^2R^3R^4$, wherein each of R^1, R^2, R^3 and R^4, which may be the same or different, represents a hydrogen atom, an alkyl group of 8 carbon atoms, or an (alk)aryl group which may be substituted by one or more lower alkyl groups; or a pyridinium ion which may be substituted by one or more lower alkyl groups and B represents an azi8e group or a group $R^5\text{-}C\overset{=O}{<_{O}}\ominus$, wherein R^5 represents a hydrogen atom, a group $-C\overset{=O}{<_{O\text{-}R}}6$, wherein R^6 represents a hydrogen atom, an alkyl group of up to 8 carbon atoms or a group A, or a group $-CH_2OR^7$, wherein R^7 represents a hydrogen atom, an alkyl group of up to 8 carbon atoms or an (alk)aryl group which may be substituted by one or more lower alkyl groups.

2. A process according to claim 1, in which the electroreductive preparation of organic compounds is carried out in an undivided cell in a non-aqueous or aprotic environment which comprises as reaction at the counter-electrode the oxidation of anions of one or more compounds according to the general formula AB, wherein A represents an alkali or alkaline earth metal moiety, a group of formula $\overset{\oplus}{N}R^1R^2R^3R^4$, wherein each of R^1, R^2, R^3 and R^4, which may be the same or different, represents an alkyl group of up to 4 carbon atoms, a phenyl group or a pyridinium ion and B represents a group $R^5\text{-}C\overset{=O}{<_{O}}\ominus$, wherein R^5 represents a hydrogen atom, a group $-C\overset{=O}{<_{O\text{-}R}}6$, wherein R^6 represents a hydrogen atom, an alkyl group of up to 8 carbon atoms or a group A, or a group $-CH_2OR^7$, wherein R^7 represents a

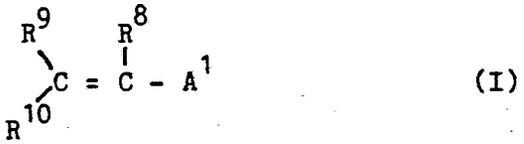
hydrogen atom or an alkyl group of up to 8 carbon atoms.

3. A process according to claim 2, which comprises as reaction at the counter-electrode the oxidation of anions of one or more compounds according to the general formula AB, wherein A represents a group of formula $\overset{\oplus}{N}R^1R^2R^3R^4$, wherein each of R^1, R^2, R^3 and R^4, which may be the same or different, represents a methyl or ethyl group and B represents a group $R^5-C\overset{O}{\underset{O}{\leq}}e$, wherein R^5 represents a hydrogen atom or a group $-C\overset{O}{\underset{O-R^6}{\leq}}$, wherein R^6 represents a hydrogen atom, an alkyl group of up to 4 carbon atoms or a group A.

4. A process according to claim 3, which comprises as reaction at the counter-electrode the oxidation of oxalate and/or formate ions.

5. A process according to any one of the preceding claims, which comprises as electroreduction reaction the electrocarboxylation of activated olefins, imines, ketones or halogen compounds.

6. A process according to claim 5, which comprises the electrocarboxylation of an activated olefin according to the general formula:



(I)

wherein R^8, R^9 and R^{10}, which may be the same or different, each represent a hydrogen atom, an alkyl group of up to 8 carbon atoms, a phenyl group which may be substituted by one or more halogen atoms and/or lower alkyl groups or a group A^1; and A^1 represents a group -CN or a group $-C\overset{O}{\underset{(O)_n-R^{11}}{\leq}}$, wherein R^{11} represents an alkyl group of up to 8 carbon atoms, or a phenyl group which may be substituted with one or more halogen atoms and/or lower alkyl groups and n is 0 or 1.

7. A process according to claim 6, which comprises the electrocarboxylation of compounds according to the general formula I, wherein A^1 represents a group -CN, a group $-C\overset{O}{\underset{(O)_n}{}}-R^{11}$, wherein R^{11} represents a methyl group and n is 0 or 1, or a phenyl group and each of R^8, R^9 and R^{10} represents a hydrogen atom or a lower alkyl group or at least one of R^8, R^9 and R^{10} represents a group A^1.

8. A process according to claim 7, which comprises the electrocarboxylation of dimethyl maleate, acrylonitrile, methyl vinyl ketone or alpha-methyl styrene.

9. A process according to claim 5, in which a (substituted) benzalaniline or a bromo or chloro compound such as 1-bromo-2-methyl pentane or pivaloyl chloride is electrocarboxylated.

10. A process according to any one of claims 5-9, in which the electrocarboxylation is carried out in the presence of non-electrochemically generated carbon dioxide.

11. A process according to any one of claims 1-4, which comprises the electroreduction of sulphonium salts, especially aromatic sulphonium salts, sulphonamides or 1,2-dihaloalkanes.

12. A process according to claim 11, which comprises the electroreduction of a bis(substituted) sulphonamide of a macrocyclic (heterocyclic) polyether, especially of 1,10-bis(p-toluene sulphonyl)-1,10-diaza,4,7,13,16-tetraoxacyclooctadecane.

13. A process according to claim 11, which comprises the electroreduction of an 1,2-dihaloalkane, especially of 1,2-dibromo-1,2-diphenyl ethane.

14. A process according to any one of the preceding claims, in which the electroreduction is performed in the presence of an inert solvent.

15. A process according to claim 14, in which the solvent applied is an ether, a chlorinated or fluorinated hydro-

carbon, a nitrile, a lower alkanol, a formamide, an (alkyl)substituted sulpholane, an organic carbonate, nitromethane, N-methyl pyrolidone or hexamethylphosphortriamide.

16. A process according to claim 15, in which the solvent applied is acetonitrile, dimethylformamide or methanol.

17. A process according to any one of the preceding claims, in which the electroreduction is carried out in the presence of an additional conducting salt, preferably in a concentration in the range of from 0.5 %w to 15 %w.

18. A process according to any one of the preceding claims, in which the reaction is carried out at a current density in the range of from 5-1000 mA/cm^2, preferably at a current density of at least 25 mA/cm^2.

19. A process according to any one of the preceding claims, in which the electroreduction is performed in a one-compartment cell of the capillary-gap type.

20. A process according to any one of the preceding claims, in which the electroreduction is carried out using a platinum or carbon anode and a lead or mercurated lead cathode.

21. A process according to any one of the preceding claims, in which the electroreduction is carried out at ambient temperature or slightly below.

European Patent Office

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Application number

EP 80 20 0992

EUROPEAN SEARCH REPORT

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
A	US - A - 4 022 673 (J.F. CONNOLLY et al.)	
A	US - A - 3 864 225 (D.A. TYSSEE)	
A	US - A - 3 379 627 (J.A.M. LEDUC)	
A	US - A - 3 344 045 (W.C. NEIKAM)	
A	MANUEL M. BAIZER: "Organic Electrochemistry",1973 Marcel Dekker Inc. pages 469-471 New York US	
A	JOURNAL OF THE ELECTROCHEMICAL SOCIETY, vol. 123, no. 6 1976, M.M. BAIZER and R.C. HALLCHER: "Paired Electro-organic Syntheses"	

CLASSIFICATION OF THE APPLICATION (Int. Cl.³)

C 25 B 3/00
C 25 B 3/04

TECHNICAL FIELDS SEARCHED (Int. Cl.³)

C 25 B 3/00
C 25 B 3/04

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	10-02-1981	DEL PIERO