

1

3,193,479

ELECTROLYTIC COUPLING OF AN OLEFINIC COMPOUND WITH A KETONE

Manuel M. Baizer, St. Louis, Mo., assignor to Monsanto Company, a corporation of Delaware
No Drawing. Filed Aug. 13, 1962, Ser. No. 216,306
14 Claims. (Cl. 204-73)

This invention relates to the manufacture of polyfunctional compounds and more particularly provides a new and valuable electrolytic process for reductive coupling of an alpha,beta-olefinic ketone with an alpha,beta-olefinic carboxylate, nitrile or amide.

A general object of the invention is the provision of a process for the production of carbalkoxy, cyano, and carboxamido ketones. It is a special object to provide a process for preparing keto-nitriles, which are suitable for conversion to lactones and lactams. It is an additional object to provide a process for preparing keto-esters of a type well-known as chemical intermediates. An important object of the present invention is the provision of a process to obtain the reduced, coupled product of an alpha,beta-olefinic ketone with alpha,beta-olefinic esters, nitriles or amides in preference to hydrodimerization products or other reaction products.

These and other objects of the invention are provided by the present process for reductive coupling of alpha,beta-olefinic ketones with alpha,beta-olefinic carboxylates, nitriles and carboxamides in electrolyte under conditions suitable for electrolytic hydrodimerization. In general, the electrolytic reductive coupling is conducted in concentrated solution in an aqueous electrolyte. It is desirable to employ fairly concentrated solutions in order to minimize undesired reactions of intermediate ions with the water of the electrolyte. The olefinic reactants will generally comprise at least 10% by weight of the electrolyte, and preferably at least 20% by weight or more. It is generally desirable to employ fairly high concentrations of salts in the electrolyte, for example constituting 5% and usually 30% or more by weight of the total amount of salt and water in the electrolyte, in order to obtain the desired solubility of the olefinic compounds. To some extent it is possible to obtain the effect of high olefin concentration by lowering the water concentration, for example by employing a co-solvent and having the water constitute less than 5% by weight of the electrolyte salt and co-solvent.

It will be recognized that the term "coupling" as employed herein refers to the joining together of two different compounds and does not include dimerizations of a single compound.

The hydrodimerization of alpha,beta-olefinic carboxylates, nitriles and carboxamides is taught in my copending applications S.N. 145,480 and 145,482, filed October 16, 1961, both of which are now abandoned, and S.N. 75,130, filed December 12, 1960, now forfeited, the disclosures of which are incorporated herein by reference; continuation-in-part applications of the foregoing are S.N. 333,647, filed December 26, 1963, S.N. 337,540, filed January 14, 1964, and S.N. 337,546, filed January 14, 1964. The conditions taught in the referred-to applications for hydrodimerization are suitable for reductive couplings of the present invention, except for such changes as may be indicated desirable herein for the purpose of directing the process to production of reduced, coupled products in preference to hydrodimerization products.

Electrolysis, of course, has been practiced for many

2

years and numerous materials suitable as electrolytes are known, making it within the skill of those in the art in the light of the present disclosure to select electrolytes for reductive coupling according to the present invention. In general, any electrolytes suitable for hydrodimerization of the individual olefinic compounds are suitable for employment in reductive coupling reactions of such compounds. As discussed in my aforesaid copending applications, some olefinic compounds are subject to polymerization or other side reactions if the electrolyte is acidic, or excessively alkaline, and it will be necessary in such cases to conduct the reductive coupling in solutions which are not overly acidic, and also in some cases below a pH at which undesirable side reactions occur, e.g., below about 12 and preferably below about 9.5. To minimize polymerization, simple reduction of the olefinic bond and other side reactions, the pH is usually maintained in the range of about 3 to about 12, preferably 6 to 9.5.

When the catholyte during electrolysis is acidic, it will generally be advisable to conduct the electrolyses under conditions which inhibit polymerization of the reactants involved or in the presence of a polymerization inhibitor, for example, in an atmosphere containing sufficient oxygen to inhibit the polymerization in question, or in the presence of inhibitors effective for inhibiting free radical polymerization. Classes of inhibitors for inhibiting free radical polymerization are well known, e.g., such inhibitors as hydroquinone, p,t-butyl catechol, quinone, p-nitroso dimethylaniline, di-t-butyl hydroquinone, 2,5-dihydroxy 1,4-benzoquinone, 1,4-naphthoquinone, chloranil, 9,10-phenanthraquinone 4-amino-1-naphthol, etc., are suitable.

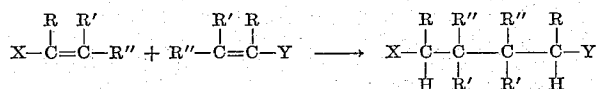
In effecting the reductive coupling of the present invention it is preferred to utilize a cathode having an over-voltage greater than that of copper and to subject to electrolysis in contact with such cathode a concentrated solution of a mixture of the defined olefinic compounds in an aqueous electrolyte under mildly alkaline conditions. In effecting the reductive couplings of the present invention, it is essential to obtain cathode potentials required for such couplings and therefore the salt employed should not contain cations which are discharged at numerically lower, i.e., less negative, cathode potentials, but rather the electrolyte should have a half-wave potential substantially more negative than that at which the desired coupling occurs. It is desirable that the salt employed have a high degree of water solubility to permit use of very concentrated solutions for concentrated salt solutions dissolve greater amounts of the organic olefinic compounds.

In addition to the foregoing considerations, a number of other factors are important in selecting salts suitable for good results. For example, it is undesirable that the salt cation form an insoluble hydroxide at the operating pH, or that it discharge on the cathode forming an alloy which substantially changes the hydrogen overvoltage and leads to poorer current efficiencies. The salt anion should not be lost by discharge at the anode with possible formation of by-products. If a cell containing a separating membrane is used, it is desirable to avoid types of anions which, in contact with hydrogen ions present in the anolyte chamber, would form insoluble acids and clog the pores of the membrane. Alternatively, the use of an ion exchange membrane effectually separates catholyte and anolyte and the use of different anions in the two chambers may minimize any difficulties a particular anion would cause in one of the chambers.

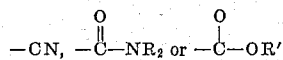
In general amine and quaternary ammonium salts are

suitable for use in the present process. Certain salts of alkali and alkaline earth metals can also be employed to some extent, although they are more subject to interfering discharge at the cathode and the alkaline earth metal salts in general tend to have poor water solubility, making their use inadvisable.

According to the presently provided process, reduced, coupled products of olefinic ketones with other olefinic compounds are produced as follows:



where X is selected from the group consisting of cyano, carboxylate, and carboxamido groups, Y is an acyl group and each R, R' and R'' is selected from the group consisting of hydrogen, alkyl (including cycloalkyl) and aryl radicals, particularly such radicals containing no more than eight carbon atoms. It will be recognized that a wide variance in the substituents is permissible, and each individual R, R' and R'' can be the same as or different from another R, R' or R''. While the illustrative formula show only one functional group, i.e., X or Y in each reactive compound, it will be recognized that each olefinic reactant can have two or more such functional groups, and they can be of the same or different types. X can be further defined as representing:



and Y as representing



in which R represents hydrogen or an alkyl or aryl radical, and R' represents an alkyl or aryl radical, particularly such radicals containing no more than eight carbon atoms.

While the molecular size of the olefinic compounds to be reductively coupled is not controlling, in general olefinic compounds containing more than 20 carbon atoms will be of little or no interest. It is generally preferable that the nitrile, carboxylate or carboxamide group and the carbonyl group be the only functional groups other than the olefinic double bond in the compounds, i.e., that the compounds be saturated hydrocarbon except for the olefinic bond and the nitrile, carboxylate or carboxamide groups, viz. 1-cyano-alk-1-enes, 1-carboxy-alk-1-enes, or 1-carboxamido-alk-1-enes, and the carbonyl group, viz. 1-acyl-alk-1-enes.

The coupled product generally obtained in the present invention is that to be expected from head-to-head addition, i.e., coupling at the carbon atoms beta to the functional groups. It will be realized that the coupled products will be accompanied by varying amounts of hydrodimerization products, depending upon the particular olefin pairs involved and the conditions of the electrolysis. The production of hydrodimerization products is not necessarily detrimental, as many of them are very useful. However, it will often be desired to direct the process toward preferential production of the coupled product. This can be done by regulating the cell voltage so that the electrolysis occurs at a cathode potential close to that for reduction of the monomer requiring the numerically lowest voltage, i.e., the least negative voltage. This is particularly effective if the voltage for the more readily reducible monomer is appreciably lower than that for the other monomer, for example, 0.3 volt or more below that for the other monomer. In such cases, if the electrolysis is conducted at a cathode potential just sufficiently higher than that required for the more easily reducible monomer to achieve a practical reaction rate, there is very little if any hydrodimerization of the more difficultly reducible monomer, and the products are those resulting from coupling of the two monomers, or hydrodimerization of the more easily reducible monomer. It is

possible to minimize the hydrodimerization of the more easily reducible monomer by "swamping" the mixture with the other monomer, employing only enough of the easily reducible monomer to keep the cathode potential at a value near that for reduction of the easily reducible monomer. It may be desirable to utilize small amounts of the easily reducible monomer and continuously or incrementally add such monomer as it is used up.

Examples of some alpha,beta-olefinic compounds suitable for coupling with alpha,beta-olefinic ketones according to the present invention, and their hydrodimerization potential (vs. saturated calomel electrode) are:

	-E vs. S.C.E.
Acrylonitrile	1.9
15 Methacrylonitrile	1.81 to 1.91
Crotonitrile	2.01 to 2.05
2,3-dimethylcrotonitrile	2.15
Cinnamyl nitrile	1.42 to 1.60
Fumaronitrile	1.0 to 1.03
20 1-cyano-1,3-butadiene	1.42 to 1.50
1-cyano-cyclohex-1-ene	2.15 to 2.20
1-cyano-cyclopent-1-ene	2.13
Ethyl acrylate	1.85
25 Ethyl 3-methylcrotonate	2.10 to 2.18
Ethyl cinnamate	1.57 to 1.61
Ethyl 2-ethoxyacrylate	2.22
Diethyl maleate	1.32 to 1.40
Diethyl fumarate	-1.20 to -1.22
30 Dioctyl maleate	1.41
N,N-diethylacrylamide	1.91 to 1.95
N,N-diethylcrotonamide	2.03 to 2.12
Acrylamide	1.82 to 2.00
Methyl cinnamate	1.29
35 Methyl 3-methylcrotonate	1.58 to 1.73

The foregoing compounds can be reductively coupled with various ketones such as—

Ketone:	-E vs. S.C.E.
40 Benzalacetone	1.3
Mesityl oxide	1.58 to 1.73
Methyl vinyl ketone	1.43

It will be recognized that the required cathode potentials will vary somewhat with the conditions employed, but the half-wave potentials of various ketones provide an indication of suitability, e.g., 2-cyclohexenone, -1.55 volts; isopropylidenacetone, -1.61 volts. Various other unsaturated ketones will be suitable for reductive coupling with the above olefinic compounds, e.g., benzalacetophenone, 4-methoxybenzalacetophenone, dibenzalacetone, ethylideneacetophenone, methylionone, heptadiene-3,5-one-2, carvone, etc. The compounds produced by the coupling are ordinarily those to be expected from coupling at the carbon atom beta to the functional group, e.g., 2-cyclohexenone and acrylamide produce 3-(2-oxocyclohexyl)propionamide, benzalacetone and acrylonitrile produce 2-oxo-4-phenyl-6-cyanoheptane, mesityl oxide and acrylonitrile give 2-oxo-4,4-dimethyl-6-cyanoheptane, and methyl vinyl ketone and diethyl fumarate produce 1,2-diethoxycarbonyl-5-hexanone. It will be noted that the reactions herein can employ the alpha,beta-unsaturated ketone either as a donor or as an acceptor, depending upon the cathode voltage required to hydrodimerize the particular ketone and upon the cathode voltage required for hydrodimerization of the other olefinic compound involved in the reductive coupling. Reactions in which acrylonitrile is involved are of particular interest as providing a method of incorporating cyano groups in ketones, and because of the relatively great negative potential required to hydrodimerize acrylonitrile, the acrylonitrile is generally the acceptor while the alpha,beta-olefinic ketone acts as the donor compound.

In general, any alpha,beta-olefinic ketone can be reductively coupled according to the present invention with any alpha,beta-olefinic nitriles, carboxylates, or carbox-

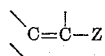
5

amides, so long as they do not contain any reactive groups which would unduly interfere in the reductive coupling reaction, all of the foregoing types of olefinic compounds capable of hydrodimerization by electrolysis being suitable for employment in combination with each other. For the most part the olefinic compounds employed will be mono-olefinic compounds which are hydrocarbon except for the designated functional groups and which contain from 3 to about 12 carbon atoms. While the alpha,beta-olefinic ketones can be combined indiscriminately according to the present invention with the alpha,beta-olefinic esters, nitriles and amides it is often desirable to select monomer pairs differing by at least 0.3 volt in cathode potential in order to effect better control of the coupling by effecting the reaction at or near the lower numerical value, thereby substantially avoiding production of the hydromer of the monomer requiring the higher numerical potential for hydrodimerization.

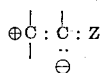
The surprising fact that the coupling reaction occurs at a cathode potential less negative than that required for hydrodimerization of one of the two olefinic compounds is explainable by the proposed mechanism of the electrolytic coupling reaction. It is postulated that one of the olefinic compounds first polarizes to a carbonium ion which then takes up two electrons at the cathode on its beta-carbon atom to form a dicarbanion. The dicarbanion then acts as a donor molecule, while the other olefinic compound has polarized to a carbonium ion which acts as an acceptor molecule. The dicarbanion bearing a negative charge on the beta-carbon atom couples with the carbonium ion bearing a positive charge on its beta-carbon atom. Protons are then extracted from the electrolyte medium to complete the reductive coupling. It can be seen that the proposed mechanism does not require electrolytic reduction of the acceptor molecule, and the coupling reaction can therefore be conducted at cathode potentials less negative than that required for reduction of one of the olefinic compounds involved. While the proposed mechanism of the reductive coupling reaction is considered valid, the present invention is not to be considered as limited to any particular mechanism as the reductive coupling occurs regardless of what the mechanism may be.

It will be recognized that some pairs from the designated classes of olefins will give better results than other pairs, depending upon the abilities of the two compounds to act as donors or acceptors. With regard to acrylonitrile, it should be noted that this compound is a very good acceptor, so better coupling results are obtainable with compounds having a less negative reduction potential than acrylonitrile, preferably substantially less negative than -1.9 volts (vs. saturated calomel electrode), as compared to results obtainable with compounds having a more negative potential which have to compete with acrylonitrile in the acceptor role.

The nature of the electrolytic reductive coupling of the present invention can be illustrated by comparison with the generalized Michael condensation (Organic Reactions, 10, 179). In the Michael condensation a donor molecule, XCH_2Y , in which at least one of X and Y is an activating group, must be capable of furnishing an anion, usually by the agency of an alkaline catalyst, and the "acidity" of a molecule is a rough measure of its efficacy as a donor; while the acceptor molecule



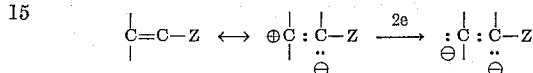
in which Z is an activating group, contains an activated double bond which is capable of polarizing and giving rise to a carbonium ion center:



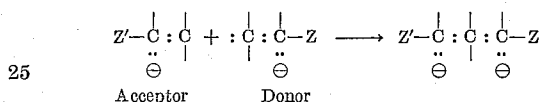
6

The efficacy as an acceptor depends upon the polarization and upon the steric environment about the beta-carbon atom, as well as by the necessity that the product carbanion produced by addition of the donor be stabilized by resonance, as is usually the case because of multiple bonds in the Z group. The efficacy of activating groups (X, Y) in donor molecules decreased in the order $\text{NO}_2 > \text{SO}_3\text{R} > \text{CN} > \text{COOR} > \text{CHO} > \text{COR}$, while the ability of activating groups (Z) to induce polarization in acceptor molecules decreases in the order $\text{CHO} > \text{COR} > \text{CN} > \text{COOR} > \text{NO}_2$ (Arndt et al., Ann., 521, 95, 1936).

The first step in the electrolytic reductive coupling reaction appears to be the addition of two electrons to form a dicarbanion from a suitably activated olefin:



The unshared electrons on the alpha-carbon atom are delocalized by interaction with the multiple bonds of Z, while those on the beta-carbon atom are available for nucleophilic attack upon an appropriate substrate:



Whereas the acidity of a molecule is a rather imprecise method of expressing the ability of a compound to serve as a donor in the Michael condensation, the half-wave reduction potential of a compound is a precise measure of ability to function as a donor in electrolytic reductive coupling. While the suitability of a compound as a donor molecule will depend upon the contemplated acceptor molecule and to a certain extent upon the electrolyte, in general the compound should not have a half-wave potential more negative than ca. -2.1 volts (measured against a saturated calomel electrode). As in the Michael condensation the adduct then reacts with H^+ (from the aqueous medium) or its equivalent to terminate the process. The coupling and termination reactions appear completely analogous to the corresponding steps in the Michael condensation. In both reactions the donor molecule is in competition with other, usually smaller, anions present in the reaction medium (e.g., OH^- in aqueous electrolyses, OR^- in Michael condensations).

Since an acceptor must be able to accept electrons that are associated with a particular site in a carbanion, the half-wave reduction potential of an acceptor is not a complete criterion of its performance in this role. For example, steric factors which affect only slightly the ability to take up electrons will have a much greater effect on ability to take up a carbanion. However, if the electrolytic reduction of an activated olefin is very difficult (i.e., it has a very negative half-wave potential), the chances that this olefin will act as an acceptor toward an electrolytically generated carbanion are poor. In general those compounds suitable as acceptors in the Michael condensation are also suitable as acceptors in electrolytic reductive couplings.

With some compounds, other factors must be considered. For example, compounds containing groups other than olefinic groups should not be used in reductive couplings, if at the required cathode voltages, the groups other than olefinic groups are attacked electrochemically. However, it is possible to use olefins in which an activating group, e.g., $-\text{NO}_2$ is fairly readily attacked electrochemically, provided it is less readily attacked than the double bond, or if such olefins are used as an acceptor and the donor is reduced at a less electronegative potential than the referred-to activating group.

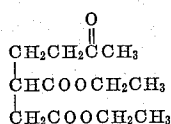
In the mixed reductive coupling competition for the donor anion is more severe than in simple hydrodimerization, since polarized molecules of the donor-to-be molecule are of necessity available to form hydromer and thereby reduce the yield of mixed product. To in-

crease the yield of mixed product, the concentration of donor-to-be may be kept low and of acceptor-to-be high. Also good results can be expected in coupling of a good acceptor, e.g., acrylonitrile, with a donor molecule which more readily accepts electrons but which because of steric effects cannot readily undergo hydrodimerization.

The following examples illustrate the invention:

Example 1

A catholyte was prepared by dissolving 50 g. methyl vinyl ketone (0.71 mole) and 12 g. diethyl fumarate (0.07 mole) in a solution of 50 g. tetraethylammonium p-toluenesulfonate, 2 g. water and 38 g. acetonitrile. A trace of p-nitrosodimethyl aniline was added as stabilizer. A platinum anode was placed in an Alundum cup and immersed in a jacketed glass vessel containing the catholyte and 120 ml. mercury as cathode. The anolyte was prepared by diluting 8 ml. of an aqueous solution containing 92% by weight of methyltributylammonium p-toluenesulfonate with 8 ml. water. The catholyte which was approximately neutral changed to a yellow color as electrolysis was commenced at 0.6 amperes. Electrolysis was continued at cathode potentials circa -1.15 to -1.20 volts (vs. a saturated calomel electrode) for about five hours, the total current being about 3.5 ampere hours. About one hour after the start of the electrolysis, about 10 ml. of an aqueous solution containing 82% by weight of methyltriethylammonium methylsulfate and 5 ml. water was added to the anolyte. Two hours after the start, a milliliter of water was added to the catholyte, and a few drops of water were occasionally added to the anolyte. After the electrolysis, the catholyte was diluted with 200 ml. water, extracted with methylene dichloride, and the extracts were washed with water and dried over calcium sulfate. The methylene dichloride and unreacted methyl vinyl ketone were distilled off, leaving a residue of 24.9 g. Fractional distillation at $100-120^{\circ}\text{C}$., $0.2-0.14$ mm. gave a product of refractive index, n_D^{25} 1.4432 to 1.4438. Redistillation gave material of refractive index n_D^{25} 1.4430, distilling at $103-5^{\circ}$, 0.1 mm. Vapor phase chromatography showed 85% of the product corresponded to a single peak, and analyzed: Calc. (for $\text{C}_{12}\text{H}_{20}\text{O}_5$), C, 59.02; H, 8.25. Found, C, 59.31; H, 8.21. Infrared analysis showed bands at 5.62μ and 5.85μ indicating two types of carbonyl groups. Analysis by nuclear magnetic resonance confirmed the structure as:



While the infrared data obtained were somewhat similar to that for tetraethyl 1,2,3,4-butanetetracarboxylate, the latter compound was ruled out by vapor phase chromatogram retention times, as well as by carbon and hydrogen analysis. The foregoing procedure provides an electrolytic method of obtaining a ketoester.

Example 2

The catholyte employed consisted of 63.6 g. (1.2 moles) acrylonitrile containing a slight amount of p-nitrosodimethylaniline as a stabilizer and 21.9 g. (0.15 mole) of benzalacetone in 75.0 g. of 80% by weight tetraethylammonium p-toluenesulfonate in water. The cathode was 110 ml. mercury. The current was varied from less than one (1) to four (4) amperes over the one and one-half ($1\frac{1}{2}$) hour reaction period for a total of 4.44 ampere-hours (estimated from the amount of copper deposited in a coulometer). Over the reduction a total of 1.75 ml. acetic acid was added in small increments to control the pH. The cathode voltage (vs. saturated calomel electrode) was maintained at or slightly below -1.50 and the reaction temperature was controlled within the range of $20-29^{\circ}\text{C}$. The end products were worked-up by adding water, removing the mercury, and extracting the re-

maining layer four (4) times with 50 ml. portions of methylene chloride. After back-washing one (1) time with water, the combined extracts were dried over Drierite. Removal of the solvent at the water pump left 24.0 g. oily concentrate. Distillation through a fractionating column gave 1.1 g., B.P. $160-164^{\circ}\text{C}/1.4-0.21$ mm. and 14.5 g. distillate, B.P. $167-174^{\circ}\text{C}/0.10-0.15$ mm. Fraction one was redistilled at $138-150^{\circ}\text{C}/10$ mm. to produce about 1 ml. of a pale yellow liquid, n_D^{25} 1.5043. This gave a strong nitrogen test (potassium hydroxide fusion). Analysis showed 77.97% carbon, 8.21% hydrogen, and 6.96% nitrogen; the calculated values for the 2-oxo-4-phenyl-6-cyanoheptane are 77.58%, 7.51% and 6.96% respectively. The second fraction was slurried in absolute alcohol and a white crystalline product was isolated by filtration. After washing with more alcohol and drying, the M.P. was 163°C ., showing this to be the hydrodimer of benzalacetone (literature M.P. is 161°C . from acetic acid). The cyano group of the 2-oxo-4-phenyl-6-cyanoheptane can be hydrolyzed to form the carboxylic acid (6-oxo-4-phenylheptanoic acid) by ordinary acid or alkali hydrolysis procedures and the carboxylic acid is converted to the corresponding lactone under reduction with hydrogen under conditions to reduce the oxo group to a hydroxyl group. Similarly, the 2-oxo-4-phenyl-6-cyanoheptane can be reduced to the corresponding 6-aminoheptane with sodium and alcohol or by hydrogenation, and the latter can be cyclized to the corresponding lactam by evaporation of an aqueous solution.

Example 3

A catholyte was prepared containing 62.0 g. (1.17 moles) acrylonitrile, 19.1 g. (0.195 mole) mesityloxide, 78.0 g. of 80% tetraethylammonium p-toluenesulfonate and a trace of p-toluenesulfonate and a trace of p-nitrosodimethylaniline as a stabilizer. The cathode was 110 ml. of mercury and, along with the catholyte was contained in a jacketed glass vessel. As the anolyte 12 ml. of the sulfonate solution with an equal volume of water was placed in a porous cup which was immersed in the catholyte. Over the electrolysis the cathode voltage vs. the standard calomel electrode gradually changed from -1.48 to -1.70 . Total reaction time was three and one-half ($3\frac{1}{2}$) hours. Temperature was maintained at $23-28^{\circ}\text{C}$. by means of a cooling bath. The current was increased from 1.1 to 3.0 amperes at the midway point and, subsequently, was reduced again to the starting value for a total of 9.2 ampere-hours. Altogether 1.85 ml. of acetic acid was added to keep the catholyte from becoming excessively basic during the reduction. The reaction mixture was diluted with an equal volume of water and separated from the mercury. Extraction four (4) times with 50 ml. portions of methylene chloride removed the organic components. The combined extracts were back-washed with water and dried over Drierite. Removal of the solvent on a steam bath left 40.1 g. of liquid to which some hydroquinone was added before distillation. Refractionation at 4.7 mm. caused the bulk of the product (about 12 g.) to distill between $122-124^{\circ}\text{C}$. n_D^{25} 1.4485. Carbon, hydrogen and nitrogen quantitative tests confirmed that this liquid was mainly 2-oxo-4,4-dimethyl-6-cyanoheptane; the found values compared against the calculated ones were 71.07/70.54 for carbon, 10.13/9.87 for hydrogen and 8.70/9.14 for nitrogen respectively. The infrared spectrum showed that some self-cyclization probably took place. Higher boiling cuts were characteristic of mesityl oxide hydrodimers. The 2-oxo-4,4-dimethyl-6-cyanoheptane can be converted to lactones or lactams as taught for the 2-oxo-4-phenyl-6 cyanoheptane.

The electrolytic reductive couplings of the present invention are conducted in solution in electrolyte, generally in fairly concentrated solution in an aqueous electrolyte. It will be recognized that as used herein an electrolyte is considered aqueous even if the amount of water is small. Many electrolytes can be employed in the present inven-

tion but some are less suitable than others. The salts employed, either to provide conductivity or to increase solubility of the reactants have an important bearing on the electrolysis and will be discussed at length below. The acidity or basicity is also significant, neutral or mildly alkaline solutions generally being preferred. Many of the olefinic compounds employed in the present invention tend to polymerize when electrolyzed in strongly acidic solution, such as solutions of mineral acids, and it is desirable or necessary in such cases to avoid excessive acidity, making it desirable to operate at pH's above about 5 or 6, such as provided by solutions of salts of strong bases. Moreover, the hydrogen ion has a cathode discharge potential of about -1.5 volts, making it desirable to avoid high concentrations of hydrogen ion in the catholyte if the reductive coupling occurs at similar or more negative cathode potentials. The reductive couplings can suitably be conducted at pH's higher than those at which substantial polymerization of olefinic compound occurs, or higher than pH's at which there is undue generation of hydrogen, for example pH's at which more than half the current is expended in discharging hydrogen ions. The pH's referred to are those obtaining in the bulk of the catholyte solution, such as determinable by a pH meter on a sample of the catholyte removed from the cell. The electrolysis in effect generates acid at the anode and base at the cathode; it will be recognized that in an undivided cell the pH in the immediate vicinity of the cathode may differ considerably from that near the anode, particularly if good stirring is not employed. To some extent the effects of acidity can be counteracted by high current density to cause more rapid generation of hydroxyl ions. However, high current densities also require good stirring or turbulence to move the reactants to the cathode.

During electrolysis in a divided cell, alkalinity increases in the catholyte. However, the anolyte becomes acidic. When a porous diaphragm is used to separate the catholyte from the anolyte, the alkalinity of the catholyte will depend upon the rate of diffusion of acid from the anolyte through the porous barrier. Control of alkalinity in the catholyte, when employing a diaphragm, may thus be realized by purposely leaking acid from the anolyte into the catholyte. It can also be achieved, of course, by extraneous addition to the catholyte of an acid material, e.g., glacial acetic acid, phosphoric acid or p-toluenesulfonic acid. Alkalinity may also be controlled, whether or not a diaphragm is used in the cell, by employing buffer systems of cations which will maintain the pH range while not reacting at the reaction conditions.

When the olefinic compounds include a carboxylate, the pH of the catholyte solution should not be allowed to rise to the point where substantial hydrolysis of the ester occurs. Since the lower alkyl esters, i.e., the methyl or ethyl esters, are usually more readily hydrolyzed than the higher alkyl esters, the optimum pH will vary with the nature of the ester. When the olefinic compounds include acrylonitrile, it will be desirable to maintain the pH sufficiently low to avoid or substantially minimize cyanoethylation, for example substantially below 9.5. Otherwise, substantial quantities of bis-(beta-cyanoethyl)ether are obtained. Similarly, when other olefinic nitriles are employed, it will be necessary to maintain the pH low enough to substantially minimize addition of water to the double bond. Good agitation or turbulence, may counteract excess alkalinity to some extent by minimizing local concentrations of hydroxyl ions at the cathode.

When a divided cell is employed, it will often be desirable to use an acid as the anolyte, any acid being suitable, particularly dilute mineral acids such as sulfuric or phosphoric acid. Hydrochloric acid can be employed but would have the disadvantage of generating chlorine at the anode, and of being more corrosive with respect to some anode materials. When an acid is employed as anolyte, it is advantageous to use an ion exchange membrane to separate the anolyte from the catholyte. If desired, a salt

solution can be used as anolyte, those useful as catholyte also being suitable as anolyte, although there are many other salt solutions suitable for such use.

Materials suitable for constructing the electrolysis cell employed in the present process are well known to those skilled in the art. The electrodes can be of any suitable cathode and anode material. The anode may be of virtually any conductor, although it will usually be advantageous to employ those that are relatively inert or attacked or corroded only slowly by the electrolytes; suitable anodes are, for examples, platinum, carbon, gold, nickel, nickel silicide, Duriron, lead and lead-antimony and lead-copper alloys, and alloys of various of the foregoing and other metals.

Any suitable material can be employed as cathode, various metals and alloys being known to the art. It is generally advantageous to employ metals of fairly high hydrogen overvoltage in order to promote current efficiency and minimize generation of hydrogen during the electrolysis. In general it will be desirable to employ cathodes having overvoltages at least about as great as that of copper, as determined in a 2 N sulfuric acid solution at current density of 1 milliamp/square centimeter (Carman, Chemical Constitution and Properties of Engineering Materials, Edward Arnold and Co., London, 1949, page 290). Suitable electrode materials include, for example, mercury, cadmium, tin, zinc, bismuth, lead, graphite, aluminum, nickel, etc., in general those of higher overvoltage being preferred. It will be realized that overvoltage can vary with the type of surface and prior history of the metal as well as with other factors; therefore the term overvoltage as used herein with respect to copper as a gauge has reference to the overvoltage under the conditions of use in electrolysis.

Among the salts which can be employed according to the invention for obtaining the desired concentration of dissolved olefinic compound, the amine and quaternary ammonium salts are generally suitable, especially those of sulfonic and alkyl sulfuric acids.

Such salts can be the saturated aliphatic amine salts or heterocyclic amine salts, e.g., the mono-, di- or trialkylamine salts, or the mono-, di- or tri-alkanolamine salts, or the piperidine, pyrrolidine or morpholine salts, e.g., the ethylamine, dimethylamine or triisopropylamine salts of various acids, especially various sulfonic acids. Especially preferred are aliphatic and heterocyclic quaternary ammonium salts, i.e., the tetraalkylammonium or the tetra-alkanolammonium salts or mixed alkyl alkanol ammonium salts such as the alkyltrialkanolammonium, the dialkyltrialkanolammonium, the alkanotrialkylammonium or the N-heterocyclic N-alkyl ammonium salts of sulfonic or other suitable acids. The saturated aliphatic or heterocyclic quaternary ammonium cations in general have suitably high cathode discharge potentials for use in the present invention and readily form salts having suitably high water solubility with anions suitable for use in the electrolytes employed in the present invention. The saturated, aliphatic or heterocyclic quaternary ammonium salts are therefore in general well adapted to dissolving high amounts of olefinic compounds in their aqueous solutions and to effecting reductive couplings of such olefinic compounds. It is understood, of course, that it is undesirable that the ammonium groups contain any reactive groups which might interfere to some extent with the reductive coupling reaction. In this connection it should be noted that aromatic unsaturation as such does not interfere as benzyl substituted ammonium cations can be employed; (as also can aryl sulfonate anions).

Among the anions useful in the electrolytes, the aryl and alkaryl sulfonic acids are especially suitable, for example, salts of the following acids: benzenesulfonic acid, o-, m- or p-toluenesulfonic acid, o-, m- or p-ethylbenzenesulfonic acid, o-, m- or p-cumenesulfonic acid, o-, m- or p-tert-amybenzenesulfonic acid, o-, m- or p-hexylbenzenesulfonic acid, o-xylene-4-sulfonic acid, p-xylene-2-sulfonic

acid, m-xylene-4 or 5-sulfonic acid, mesitylen-2-sulfonic acid, durene-3-sulfonic acid, pentamethylbenzenesulfonic acid, o-dipropylbenzene-4-sulfonic acid, alpha- or beta-naphthalenesulfonic acid, o-, m- or p-biphenylsulfonic acid, and alpha-methyl-beta-naphthalenesulfonic acid. Alkali metal salts are useful in the present invention with certain limitations, and the alkali metal salts of such sulfonic acids can be employed, i.e., the sodium, potassium, lithium, cesium or rubidium salts such as sodium benzenesulfonate, potassium p-toluenesulfonate, lithium o-biphenylsulfonate, rubidium beta-naphthalenesulfonate, cesium p-ethylbenzenesulfonate, sodium o-xylene-3-sulfonate, or potassium pentamethylbenzenesulfonate. The salts of such sulfonic acids may also be the saturated, aliphatic amine or heterocyclic amine salts, e.g., the mono-, di- or trialkylamine salts, or the mono-, di- or trialkanolamine salts, or the piperidine, pyrrolidine, or morpholine salts, e.g., the ethylamine, dimethylamine or triisopropylamine salt of benzenesulfonic acid or of o-, p- or m-toluenesulfonic acid; the isopropanolamine, dibutanolamine or triethanolamine salt of o-, p- or m-toluenesulfonic acid or of o-, p- or m-biphenylsulfonic acid; the piperidine salt of alpha- or beta-naphthalenesulfonic acid or of the cumenesulfonic acids; the pyrrolidine salt of o-, m- or p-aminobenzenesulfonate; the morpholine salt of benzenesulfonic acid, of o-, m- or p-toluenesulfonic acid, or of alpha- or beta-naphthalenesulfonic acid, etc. In general, the sulfonates of any of the ammonium cations disclosed generically or specifically herein can be employed in the present invention. The aliphatic sulfonates are prepared by reaction of the correspondingly substituted ammonium hydroxide with the sulfonic acid or with an acyl halide thereof. For example, by reaction of a sulfonic acid such as p-toluenesulfonic acid with a tetraalkylammonium hydroxide such as tetraethylammonium hydroxide there is obtained tetraethylammonium p-toluenesulfonate, use of which in the presently provided process has been found to give very good results. Other presently useful quaternary ammonium sulfonates are, e.g., tetraethylammonium o-, or m-toluenesulfonate or benzenesulfonate; tetraethylammonium o-, m- or p-cumenesulfonate or o-, m- or p-ethylbenzenesulfonate, tetramethylammonium benzenesulfonate, or o-, m- or p-toluenesulfonate; N,N-di-methylpiperidinium, o-, m- or p-toluenesulfonate or o-, m- or p-biphenylsulfonate; tetrabutylammonium alpha- or beta-naphthalenesulfonate or o-, m- or p-toluenesulfonate; tetrapropylammonium o-, m- or p-aminobenzenesulfonate or alpha-ethyl-beta-naphthalenesulfonate; tetraethanolammonium o-, m- or p-cumenesulfonate or o-, m- or p-toluenesulfonate; tetrabutanolammonium benzenesulfonate or p-xylene-3-sulfonate; tetrapentylammonium o-, m- or p-toluenesulfonate or o-, m- or p-hexylbenzenesulfonate, tetrapentanolammonium p-cymene-3-sulfonate or benzenesulfonate; methyltriethylammonium o-, m- or p-toluenesulfonate or mesitylene-2-sulfonate; trimethylethylammonium o-xylene-4-sulfonate or o-, m- or p-toluenesulfonate; triethylpentylammonium alpha- or beta-naphthalenesulfonate or o-, m- or p-butylbenzenesulfonate, trimethylethanolammonium benzenesulfonate or o-, m- or p-toluenesulfonate; N,N-di-ethylpiperidinium or N-methyl-pyrrolidinium o-, m- or p-hexylbenzenesulfonate or o-, m- or p-toluenesulfonate, N,N-di-isopropyl or N,N-di-butylmorpholinium o-, m- or p-toluenesulfonate or o-, m- or p-biphenylsulfonate, etc.

The tetraalkylammonium salts of the aryl or alkaryl sulfonic acids are generally preferred for use as the salt constituents of the electrolysis solution because the electrolyses in the tetraalkylammonium sulfonates are exclusively electrochemical processes.

Among the ammonium and amine sulfonates useful as electrolytes in the present invention are the alkyl, aralkyl and heterocyclic amine and ammonium sulfonates, in which ordinarily the individual substituents on the nitrogen atom contain no more than 10 atoms, and usually the amine or ammonium radical contains from 3 to 20

carbon atoms. It will be understood, of course, that di- and poly-amines and di- and poly-ammonium radicals are operable and included by the terms amine and ammonium. The sulfonate radical can be from aryl, alkyl, alkaryl or aralkyl sulfonic acids of various molecular weights up to for example 20 carbon atoms, preferably about 6 to 20 carbon atoms, and can include one, two or more sulfonate groups. Any of the quaternary ammonium sulfonates disclosed and claimed in my copending application S.N. 75,123, filed December 12, 1960, can suitably be employed.

Another especially suitable class of salts for use in the present invention are the alkylsulfate salts such as methosulfate salts, particularly the amine and quaternary ammonium methosulfate salts. Methosulfate salts such as the methyltriethylammonium, tri-n-propylmethylammonium, triamylmethylammonium, tri-n-butylmethylammonium, etc., are very hygroscopic, and the tri-n-butylmethylammonium in particular forms very concentrated aqueous solutions which dissolve large amounts of organic materials. In general the amine and ammonium cations suitable for use in the alkylsulfate salts are the same as those for the sulfonates.

Various other cations are suitable for use in the present invention, e.g., tetraalkylphosphonium and trialkyl sulfonium cations, particularly as sulfonate salts formed from sulfonic acids as described above, or as methosulfate salts.

What is claimed is:

1. The method of producing a reduced, coupled product which comprises subjecting a solution of alpha,beta-olefinic ketone and olefinic compound selected from the group consisting of alpha,beta-olefinic nitriles, esters and carboxamides to electrolysis in a cell in which both anode and cathode are in actual physical contact with electrolysis medium, the solution being in contact with a cathode having a hydrogen overvoltage greater than that of copper and containing water, at least about 10% by weight of olefinic compound and at least 5% by weight of salt to make the solution conductive and separating the reduced coupled product from the electrolyte.

2. The method of claim 1 in which the olefinic ketone and other olefinic compound have cathode potentials for hydrodimerization which differ by more than 0.3 volt, and the cathode potential during the electrolysis is slightly more negative than the less negative of the said cathode potentials for hydrodimerization.

3. The method of claim 1 in which the olefinic compound is acrylonitrile.

4. The method of claim 1 in which the electrolyte comprises a salt selected from the group consisting of amine and ammonium sulfonates and alkyl sulfates.

5. The method of producing a reduced coupled product which comprises subjecting a solution of alpha,beta-olefinic ketone and olefinic compound selected from the group consisting of alpha,beta-olefinic nitriles, esters and carboxamides to electrolysis in a cell in which both anode and cathode are in actual physical contact with electrolysis medium, the solution being in contact with a cathode having a hydrogen overvoltage greater than that of copper, causing development of the cathode potential required for hydrodimerization of at least one of the said ketone and olefinic compound, the said solution containing at least about 10% by weight of each of the selected compounds and at least 5% by weight salt which discharges at numerically lower cathode potentials than the olefinic compound and having a pH above about 6, and recovering the reduced coupled product.

6. The method of claim 5 in which the olefinic compound is an alpha,beta-olefinic nitrile and the product recovered is a beta-(2-cyanoalkyl) alkyl ketone.

7. The method of claim 5 in which the olefinic compound is an alkyl ester of an alpha, beta-olefinic acid and the recovered product is a beta-(2-carbalkoxy) alkyl ketone.

13

8. The method of claim 5 in which the electrolysis is conducted of a current of at least 0.5 ampere and the salt cation discharges at the cathode only at potentials substantially more negative than the potential at which the electrolysis is conducted.

9. The method of claim 5 in which the pH is maintained between about 7 and about 9.5 during substantially all of the electrolysis.

10. The method of claim 1 in which a substantial excess of the less easily reducible reactant is employed to direct the reaction toward the reduced, coupled product.

11. The method of forming cyano derivative of ketones which comprises reductively coupling acrylonitrile with an alpha,beta-olefinic ketone which is reducible at cathode voltages substantially less negative than -1.9 volts, by subjecting a solution of such compound and acrylonitrile in aqueous electrolyte to electrolysis and removing the reduced, coupled product from the electrolyte.

14

12. The method of claim 1 in which mesityl oxide is reductively coupled with acrylonitrile.

13. The method of claim 1 in which benzalacetone is reductively coupled with acrylonitrile.

14. The method of claim 1 in which methyl vinyl ketone is reductively coupled with diethyl fumarate.

References Cited by the Examiner

UNITED STATES PATENTS

2,632,729	3/53	Woodman	204—72
2,726,204	12/55	Park et al.	204—72

FOREIGN PATENTS

566,274 11/58 Canada.

JOHN H. MACK, *Primary Examiner*.

MURRAY TILLMAN, WINSTON A. DOUGLAS,
Examiners.