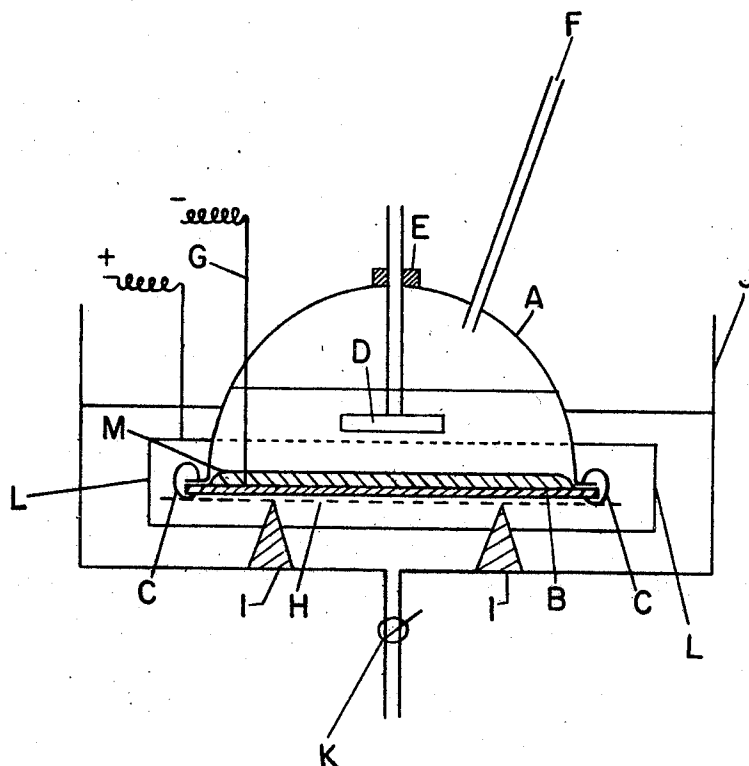


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REDUCTIVE DIMERIZATION OF α,β -UNSATURATED
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REDUCTIVE DIMERIZATION OF α,β -UNSATURATED NITRILES BY MEANS OF AMALGAM

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6 Claims

ABSTRACT OF THE DISCLOSURE

α,β -unsaturated nitriles are reductively dimerized, for example acrylonitrile is converted to adiponitrile, by treating them in an aqueous medium containing an organic cationic agent with an alkali metal or alkaline earth metal amalgam, the amalgam being formed electrolytically during the reduction in a layer of mercury which separates the aqueous medium from an electrolytic cell of which the layer of mercury acts as the cathode.

This invention relates to the reductive dimerisation of α,β -unsaturated nitriles.

An object of the present invention is to provide a process for the reductive dimerisation of α,β -unsaturated nitriles with an amalgam of an alkaline earth metal in an aqueous medium.

In this process we have found that it is advantageous to control the pH of the aqueous medium. The pH is usually maintained between about 5.0 and a higher pH at which undesirable side reactions begin to occur during the reductive dimerisation process. The process may normally be carried out, however, at pH's within the range 2.0 to 13.0. pH values of from 6.0 to 11.0 are preferred. The pH of the aqueous medium may be controlled by the use of salts of polybasic acids such as alkali metal phosphates, borates or carbonates.

The reductive dimerisation may be carried out in an apparatus in the form of an electrolytic cell in which the cathode has as essential parts a layer of mercury supported by a membrane permeable to electrolyte solutions the cathode being interposed between (a) an aqueous solution of an alkali or alkaline earth metal hydroxide or salt containing the anode, and (b) the reaction medium in which reduction is performed. The cell employs as the cathode a mercury layer which may be no thicker than is required to form a continuous barrier between the anode compartment and the medium in which reduction is performed, provided that the layer is bounded on the one side by the reaction medium and on the other by the aqueous medium contained in the anode compartment which forms the source of metal ions responsible for liberating nascent hydrogen in the reaction medium. Employing a support for the mercury layer permeable to electrolyte solutions and interposed between the mercury layer and the anode compartment and/or the reaction medium quite thin continuous mercury layers may be used which provide cathodes of relatively large surface area in contact with the reaction medium and with the aqueous medium in the anode compartment, so that the alkali or alkaline earth metal ions reach the cathode in a substantially uniform manner over the whole area of the cathode. Thus the aqueous medium in the anode compartment is separated from the reaction medium by the thickness of the mercury layer and its supports. The mercury layer is preferably disposed horizontally that is to say with its main plane lying in the horizontal position, the anode medium and the reaction

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medium being on either side above and below. With this arrangement the mercury layer rests on the membrane support and the layer may be held in position at the edge by a further support which need not be permeable to which the permeable membrane may be attached. It is preferable to arrange that the lower surface of the mercury on its support is slightly convex.

The mercury layer may be subjected to gentle agitation if desired, for example by vibration or by stirring, in order to maintain the reaction conditions as uniform as possible. However, agitation of the layer is not essential. Agitation of the reaction medium may also be used if desired to assist in maintaining steady reduction conditions.

A preferred form of apparatus is shown in the accompanying drawing. The reaction vessel is represented by A the bottom of which is formed and closed by a permeable glass cloth membrane B sealed at the periphery of the bottom of the reaction vessel and firmly attached thereto by the sealing ring C. The reaction vessel is fitted with a stirrer D the shaft of which enters through the seal E, a condenser F, a thermometer (not shown) and a platinum electrode G immersed in the mercury to form the cathode lead. Means for introducing the reaction mixture and withdrawing the products of reaction are also provided (not shown). The reaction vessel is supported at the base preferably by a non-metallic gauze to avoid electrolysis at the gauze when high potentials are used, gauze H resting on suitable supports I, and is placed inside the second vessel J conveniently provided with an outlet tap K. The vessel J is also provided with an anode L formed from a strip of nickel sheet which encircles the vessel A but is spaced from it. The vessel J is provided with cooling coils (not shown). A layer of mercury M is placed inside A so as to cover completely the inner surface of the glass cloth membrane and seal the reaction mixture within A from direct contact with the electrolyte contained in the outer vessel J. The mercury layer M (with its supports) forms the cathode.

When the reductive dimerisation process of our invention is carried out in an apparatus as described the amalgam is formed electrolytically during the reduction in a layer of mercury acting as the cathode of an electrolytic cell which cell is separated from the aqueous medium by a layer of mercury.

We have also found that in the reductive dimerisation of α,β -unsaturated nitriles using such reduction procedures it is advantageous to have an organic cationic agent present in the aqueous medium.

Suitable organic cationic agents for use in the process of the invention are in general those capable of forming organic cations in the aqueous medium under the particular reaction conditions employed. Especially suitable are quaternary ammonium and phosphonium salts and ternary sulphonium salts. If desired the organic cationic agent may be added as the free base, for example a hydroxide such as tetraethyl ammonium hydroxide. It is preferred to employ tetraalkyl ammonium salts in which the alkyl groups contain up to 24 carbon atoms. It is also preferable that the cationic agents should be at least partially soluble in the reaction mixture, and should not decompose during the reductive dimerisation process. Examples of agents which have been particularly effective are tetraethylammonium-p-toluene sulphonate, tetraethylammonium iodide, tetraethylammonium phosphate and cetyl-trimethylammonium bromide.

Although the invention is of great value for the reductive dimerisation of acrylonitrile to given excellent yields of adiponitrile it is also very valuable for carrying out the reductive dimerisation of alkyl substituted acrylonitriles

such as methacrylonitrile to give alkyl substituted adiponitriles.

The invention is illustrated by the following examples—

EXAMPLE 1

The apparatus was of the type described above.

A cylindrical glass reaction vessel 5.6 cm. in diameter and 14 cm. deep was closed at its lower end by a glass cloth membrane sealed around the lower periphery of the vessel. The inner surface of the membrane was completely covered by a layer of mercury; the volume of mercury used was 30 ml. The top of the vessel was provided with an inlet for a glass sheathed platinum wire, the wire emerging from the glass sheath under the surface of the mercury, to form a cathode. The reaction vessel was also provided with a gas inlet tube, an internal cooling coil and a stirrer, all located above the mercury layer.

The reaction vessel was immersed to a depth of about 3 cm. in an aqueous solution of sodium hydroxide (30% by weight) contained in an outer cylindrical glass vessel, this outer vessel being filled to a depth of about 10 cm. with the said sodium hydroxide solution. A cylindrical anode, 9 cm. in diameter and 4 cm. deep, made from nickel strip, was inserted in the outer vessel so as to surround the reaction vessel.

A reaction mixture consisting of acrylonitrile (22.0 g.), tetraethylammonium p-toluene sulphonate (17.4 g.) and water (10.0 g.) was placed in the reaction vessel. The mixture was vigorously stirred and carbon dioxide gas was bubbled slowly through it, while a current of 10 amp. was passed between the anode and the cathode. The temperature of the reaction mixture was maintained at 25° C. to 35° C.

After the current had been passed for 30 minutes the mixture was removed from the reaction vessel and the vessel was washed out with water. The reaction mixture and washings were combined and steam-distilled. The distillate contained 8.7 g. of acrylonitrile.

The aqueous residue from the steam distillation was extracted with chloroform (two portions of 50 ml., four portions of 25 ml.). The chloroform extracts were combined, the chloroform was distilled under reduced pressure to give 10.1 g. of crude adiponitrile, shown by analysis to contain 8.8 g. of adiponitrile. This represents a yield of 65% adiponitrile on acrylonitrile consumed and a current efficiency to adiponitrile of 87%.

EXAMPLE 2

A similar reduction of that of Example 1, but using potassium amalgam and a phosphate buffer, was performed in the same cell.

The electrolyte placed in the outer vessel was an aqueous solution of potassium hydroxide (40% by weight), and the reaction mixture, which was placed in the inner vessel, consisted of acrylonitrile (20.3 g.), and aqueous solution of tetraethylammonium hydroxide (30.6 g. of 25% by weight), potassium dihydrogen phosphate (27.1 g.), potassium hydroxide (3.0 g.) and water (36.9 g.). The pH of this mixture was 7.0.

The reaction mixture was vigorously stirred while

a current of 4 amp. was passed between the anode and cathode. The temperature of the reaction mixture was maintained at 50° C. to 64° C.

After the current had been passed for 40 minutes the mixture, which now had a pH of 9.5, was removed from the reaction vessel and worked up by the procedure described in Example 1. The weight of adiponitrile obtained was 4.3 g., and 13.0 g. of acrylonitrile were recovered. This represents a yield of 61% adiponitrile on acrylonitrile consumed and a current efficiency to adiponitrile of 80%.

We claim:

1. In a process for the reductive dimerization of a nitrile selected from the group consisting of acrylonitrile and alkyl-acrylonitriles to obtain adiponitrile and alkyl-adiponitriles, respectively, wherein a solution of the nitrile in water containing a cation selected from the group consisting of quaternary ammonium, quaternary phosphonium and ternary sulphonium cations is contacted with an alkali metal or alkaline earth metal amalgam at a pH of 2 to 13 and at a reductive dimerization temperature, the improvement which comprises forming the amalgam electrolytically during the reductive dimerization in a layer of mercury by maintaining one face of said mercury layer in contact with the solution of nitrile, providing an aqueous electrolyte solution containing cations of said metal in contact with the other face of said mercury layer, maintaining the mercury layer as a continuous barrier between the electrolyte and the solution of nitrile so that said electrolyte and nitrile solution are kept separated from each other and passing current through said electrolyte using said mercury layer as cathode whereby the metal cations in said electrolyte form the amalgam in said layer for contact with said nitrile solution and resultant reductive dimerization of said nitrile.

2. The process of claim 1 in which the pH is controlled within the range 6.0 to 11.0.

3. The process of claim 1 in which the pH of the aqueous medium is controlled by the use of a salt of a polybasic acid selected from the group consisting of alkali metal phosphates, borates and carbonates.

4. The process of claim 1 in which the cation is a tetraalkyl ammonium cation in which the alkyl groups contain from 1 to 24 carbon atoms.

5. The process of claim 1 in which the cation is a tetraethyl ammonium cation.

6. The process of claim 1 in which the nitrile is acrylonitrile and the product is adiponitrile, the reaction temperature being in the range 25° C to 64° C.

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