Patented Apr. 6, 1948

2,439,308

UNITED STATES PATENT OFFICE

2,439,308

PROCESS FOR SIMULTANEOUS DIMERIZATION AND REDUCTION

Robert M. Leekley, Chicago, Ill., assignor to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

No Drawing. Application July 18, 1946, Serial No. 684,547

6 Claims. (Cl. 260—465.8)

1

This invention relates to a process for the preparation of saturated aliphatic dinitriles from alpha, beta-ethylenically unsaturated aliphatic mononitriles and more particularly to a catalytic process for the preparation of adiponitrile by the reductive dimerization of acrylonitrile.

Although it is well known that certain alpha, beta-unsaturated compounds, such as the acrylates, methacrylates, acrolein, and methylvinylketone, can be dimerized under certain conditions to yield unsaturated dimeric products, the simultaneous dimerization and reduction of such compounds to yield saturated products has heretofore never been accomplished. For example, the U. S. patent to Howk 2,232,785, issued February 25, 1941, shows the dimerization of acrylonitrile by heating in the presence of an inhibitor at a temperature of 200° C. However, an unsaturated dinitrile is produced which on subsequent hydrogenation and hydrolysis yields a dicarboxylic acid which is stated to be presumably methyl glutaric acid. Thus, thermal dimerization of acrylonitrile in the presence of inhibitors has produced branched chain unsaturated dimers but not a linear saturated dimer such as adiponitrile.

It is an object of this invention to provide a new process for the preparation of linear saturated aliphatic dinitriles from alpha, beta-ethylenically unsaturated aliphatic mononitriles. A further object of this invention is the provision of a process for the preparation of linear saturated aliphatic dinitriles from alpha, beta-ethylenically unsaturated aliphatic mononitriles in one stage. A still further object is to provide an economical process for producing adiponitrile from acrylonitrile. Other objects will appear hereinafter.

These objects are accomplished by the following invention of a process for the preparation of a linear saturated aliphatic dinitrile from an alpha, beta-ethylenically unsaturated aliphatic mononitrile which comprises treating the said alpha, beta-ethylenically unsaturated aliphatic mononitrile with active hydrogen, formed by reacting magnesium or a magnesium alloy with a primary aliphatic monohydric alcohol, in the presence of magnesium or magnesium alloy and a promoter, such as mercuric chloride. Thus, acrylonitrile is simultaneously dimerized and reduced to adiponitrile by treating with active hydrogen, formed by reacting a primary aliphatic monohydric alcohol with magnesium in the presence of magnesium and a small amount of mercuric chloride as a promoter.

2

In the preparation of adiponitrile from acrylonitrile there should be used essentially molar equivalent amounts of elemental magnesium and acrylonitrile in an inert solvent, such as benzene. These reactants are placed in a suitable reaction vessel along with the mercuric chloride and the mixture refluxed with stirring. To this mixture is added an amount of a low molecular weight primary aliphatic monohydric alcohol which is more than sufficient to react with all the magnesium and at such a rate as to generate a continuous but slow evolution of hydrogen. After reaction is complete, the adiponitrile is islolated by fractional distillation or other means known to the art.

Although the preferred method for effecting the simultaneous reductive dimerization of alpha, beta-ethylenically unsaturated mononitriles to saturated dinitriles is through the use of magnesium, or one of its alloys, in conjunction with a lower primary aliphatic monohydric alcohol and mercuric chloride, an alternative method for effecting this reaction is through the employment of magnesium, or an organomagnesium compound, such as an alcoholate, in combination with hydrogen and a hydrogenation catalyst, such as nickel.

By alpha, beta-ethylenically unsaturated aliphatic mononitrile as used herein is meant a mononitrile in which the nitrile (—CN) group is attached directly to a carbon atom in the aliphatic chain, which carbon atom is in turn attached to another carbon atom by an ethylenic double bond.

By lower primary aliphatic monohydric alcohol as used herein is meant a primary aliphatic monohydric alcohol having one to five cerbon atoms, such as ethyl and methyl alcohols.

Since magnesium in the form of its alloys with other metals, as well as elemental magnesium, is suitable for the practice of this invention, the use of the term magnesium is intended to include both elemental magnesium and magnesium alloys. However, it is preferred to use elemental magnesium such as metallic magnesium turnings.

Preferred operating temperatures for this process are those lying between 25° and 150° C. However, temperatures in the range of 0° to 225° C. can be used.

The reaction can be carried out in the presence or absence of a volatile organic solvent, such as benzene, diethyl ether, toluene and aliphatic hydrocarbons. Generally it is preferred to operate

in the presence of an organic solvent because this makes reaction easier.

The proportions of ingredients used in the process of this invention should always be adjusted so that about one equivalent of hydrogen is generated or caused to be present for each equivalent of alpha, beta-ethylenically unsaturated aliphatic mononitrile. The use of larger amounts of hydrogen may, under certain conditions, result in the formation of the completely reduced product which in the case of acrylonitrile is hexamethylenediamine. Although it is preferred to add the alcohol to the mixture of alpha, beta-ethylenically unsaturated aliphatic mononitrile and elemental magnesium, this procedure can be varied by adding the elemental magnesium to the mixture of alcohol and nitrile.

The invention is further illustrated by the following example, in which parts are by weight unless otherwise specified.

Example

A mixture of 15 parts of mercuric chloride and 106 parts of acrylonitrile was placed in a flask and stirred at room temperature until solution was complete. This solution was added to a mixture of 160 parts of dry benzene and 15 parts of magnesium turnings and refluxed with stirring for one hour. At the end of this time, 35 parts of methyl alcohol was added over a period of 1.5 hours, the resulting reaction mixture allowed to stand overnight, and then treated with 98 parts of concentrated sulfuric acid dissolved in 300 parts of water. The benzene layer was separated, washed in turn with 50 parts of water, 50 parts of 10% sodium carbonate solution, and 50 parts of water. After removal of the benzene, distillation of the residue gave 6.4 parts crude adiponitrile boiling at 118–128° C./3.5 mm.

The adiponitrile was identified by conversion to adipic acid as follows: Hydrolysis of the fraction boiling at 118–128° C./3.5 mm. was carried out by boiling in 20 parts of concentrated hydrochloric acid for one hour. The crude adipic acid which precipitated on cooling was recrystallized from 50 parts of water to yield 2.2 parts of adipic acid; M. P. 149–150° C. (M. P. of an authentic adipic acid sample was 150.5-151.5° C.). The mixed melting point of the above product with the authentic sample of adipic acid was 149.5–150.5° C.

A second run was carried out exactly as described above with the exception that the final reaction mixture was refluxed for 20 hours after the addition of methanol. In this run 3.2 parts of adipic acid, melting at 149.5–151° C., was obtained upon hydrolysis of the adiponitrile obtained.

Although the invention has been illustrated with respect to acrylonitrile specifically, it is to be understood that the process of this invention is generally applicable to alpha, beta-ethylenically unsaturated aliphatic mononitriles. Examples of such nitriles, besides acrylonitrile, are methacrylonitrile, alpha-ethylacrylonitrile, alpha-propylacrylonitrile, crotonitrile, and the like.

Lower primary aliphatic monohydric alcohols useful in the practice of this invention are methanol, ethanol, propanol, butanol and pentanol. It is preferred to use methyl or ethyl alcohol in this invention because of their availability, low cost and ease with which they react with magnesium to liberate active hydrogen.

This invention is of particular value as a route to adiponitrile for conversion to adipic acid and hexamethylenediamine which are nylon intermediates. In addition, adiponitrile is of considerable interest as an intermediate for the synthesis of various other organic compounds.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that I do not limit myself to the specific embodiments thereof except as defined in the appended claims.

I claim:

1. A process for the simultaneous dimerization and reduction of acrylonitrile to adiponitrile which comprises treating acrylonitrile in the presense of magnesium and mercuric chloride with active hydrogen produced by the reaction of said magnesium with a primary aliphatic monohydric alcohol.

2. A process for the simultaneous dimerization and reduction of acrylonitrile to adiponitrile which comprises treating acrylonitrile in an inert volatile organic solvent and in the presence of magnesium and mercuric chloride with active hydrogen produced by the reaction of said magnesium with a primary aliphatic monohydric alcohol containing not more than five carbon atoms.

3. A process for the simultaneous dimerization and reduction of acrylonitrile to adiponitrile which comprises treating acrylonitrile in benzene and in the presence of magnesium and mercuric chloride with active hydrogen produced by the reaction of said magnesium with methanol.

4. A process for the simultaneous dimerization and reduction of an acrylonitrile containing from 3 to 6 carbon atoms to a saturated aliphatic dinitrile which comprises treating said acrylonitrile in the presence of magnesium and a promoter with active hydrogen produced by the reaction of said magnesium with a primary aliphatic monohydric alcohol.

5. A process for the simultaneous dimerization and reduction of an acrylonitrile containing from 3 to 6 carbon atoms to a saturated aliphatic dinitrile which comprises treating said acrylonitrile in an inert volatile organic solvent and in the presence of magnesium and mercuric chloride with active hydrogen produced by the reaction of said magnesium with a primary aliphatic monohydric alcohol containing not more than five carbon atoms.

6. A process for the simultaneous dimerization and reduction of acrylonitrile containing from 3 to 6 carbon atoms to a saturated aliphatic dinitrile which comprises treating said acrylonitrile in benzene and in the presence of magnesium and mercuric chloride with active hydrogen produced by the reaction of said magnesium with methanol.

ROBERT M. LEEKLEY.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,891,055	Reppe et al.	Dec. 13, 1932
2,232,785	Howk	Feb. 25, 1941
2,244,645	Jacobson	June 3, 1941
2,334,140	Winans	Nov. 9, 1943