

1

2

3,133,956
DIMERIZATION PROCESS FOR PRODUCING
ADIPONITRILE

Robert E. Robinson, Cincinnati, Ohio, assignor to National Distillers and Chemical Corporation, New York, N.Y., a corporation of Virginia
No Drawing. Filed Dec. 28, 1960, Ser. No. 78,828
3 Claims. (Cl. 260-465.8)

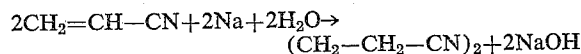
This invention relates to a process for the preparation of dimerized products and, more particularly, to the reductive dimerization of alpha,beta-ethylenically unsaturated mononitriles to produce linear saturated aliphatic dinitriles. Still more particularly, this invention relates to the reductive dimerization of acrylonitrile in the presence of finely dispersed alkali metal to produce adiponitrile.

The dimerization of acrylonitrile to adiponitrile has been reported previously. For example, Leekley, by a process described in U.S. Patent 2,439,308, simultaneously dimerized and reduced acrylonitrile to adiponitrile by the action of magnesium and a promoter, such as mercuric chloride, with active hydrogen. Other known processes dimerize acrylonitrile to adiponitrile in the presence of sodium amalgam in water and of potassium amalgam in hydrochloric acid.

These processes all have the disadvantage of requiring large amounts of mercury which are cumbersome and dangerous to handle, especially when used industrially. Furthermore, commercial use of mercury is expensive.

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 to provide a simple, economical process for producing adiponitrile from acrylonitrile. Other objects will become apparent from the ensuing description.

These objects are accomplished by a process for the preparation of a linear saturated aliphatic dinitrile from an alpha,beta-ethylenically unsaturated aliphatic mononitrile which comprises treating the alpha,beta-ethylenically unsaturated aliphatic mononitrile in aqueous condition with finely dispersed alkali metal. The reaction may be illustrated by the following equation wherein adiponitrile is prepared from acrylonitrile and the alkali metal is sodium:



After reaction is complete, the linear saturated aliphatic dinitrile, for example, adiponitrile, is isolated by fractional distillation or by any other means known to the art.

By alpha,beta-ethylenically unsaturated aliphatic mononitrile as used herein is meant a mononitrile in which the (-CN) group is attached directly to a carbon atom in an aliphatic chain, which carbon atom is in turn attached to another carbon atom by an ethylenic double bond. Examples of such compounds, to which the process of this invention applies, include acrylonitrile, methacrylonitrile, crotonitrile, alpha-propylacrylonitrile, alpha-ethylacrylonitrile, and the like. For convenience, this invention will be described with relation to the reaction of acrylonitrile with finely dispersed sodium, but it is not intended to be limited specifically thereto.

In the preparation of adiponitrile from acrylonitrile there should be used a relatively high proportion of acrylonitrile to alkali metal. In general, a ratio of about 1 to 10 moles of acrylonitrile per gram atom of sodium is used, lower ratios giving considerably lower yields and higher ratios having little effect on the yield. A ratio of about 6.5 moles of acrylonitrile to one gram atom of sodium is preferred.

The process embodied herein comprises reacting aqueous acrylonitrile with an alkali metal in dispersed form in which substantially more than about 50% of the alkali metal particles are not more than about 5 microns in size, and, more preferably, not more than about two microns in size. More preferably, the process embodied herein is carried out by use of the alkali metal in the form of a dispersion in which more than 75% of the alkali metal particles are not more than about 5 microns in size, and preferably not more than about two microns; the average particle size of the dispersion is not more than about 1.5 microns, and the dispersion is devoid of more than about 5% of alkali metal particles larger than about 3 microns in size. Optimum results are obtained by use of an alkali metal dispersion in which all or substantially all of the alkali metal particles do not exceed about two microns in size and the average particle size is 1, and preferably less, micron.

For carrying out the process embodied herein, examples of the alkali metal reactant include sodium, potassium, and lithium, with sodium being preferred since it provides for excellent selectivity and yields of desired dimerized product. Also, it is cheaper and more readily available than the other alkali metals. Chemically pure sodium is not essential, however, since mixtures containing a major proportion of sodium are also useful, as are alloys of sodium and potassium, sodium and calcium, and sodium and lithium. The alkali metal dispersion employed in this invention is most conveniently, but not necessarily, made in an inert hydrocarbon or ether as a separate step preliminary to the reaction with acrylonitrile.

It has been found that yields are improved when the reaction takes place at a pH below about 9. Although satisfactory yields result when no acid is used, the inclusion in the reaction mixture of an acidic material such as hydrochloric acid, sodium bicarbonate, acetic acid, sulfuric acid, or the like has an advantageous effect. The amount of acid used may vary from about 1 to 2 equivalents per gram atom of sodium and is preferably about 1.5 equivalents per gram atom of sodium.

The aqueous acrylonitrile solution may contain from about 25 to about 95 percent of water, and preferably the reaction is run with about 75 to about 80 percent of water in the acrylonitrile-water solution. The use of less than about 25 percent of water would enhance the formation of by-product polyacrylonitrile, while a concentration of water higher than about 95 percent would substantially lower the yield of adiponitrile.

The reaction of acrylonitrile with finely dispersed alkali metal takes place most readily at any temperature between about 5° and 55° C. At lower temperatures it is possible that the reaction medium will freeze. The use of higher temperatures appears to offer no advantages and increases the safety hazard.

The process of the present invention can be carried out in the presence or in the absence of a solvent which is preferably an inert volatile organic material. Examples of such a solvent include hexane, benzene, dimethyl ether, toluene, and the like, or mixtures of these.

The invention is further described by the following examples in which all parts are given by weight unless otherwise specified, but it is not intended to limit the invention specifically thereto.

Example 1

A 3-necked flask, fitted with a paddle-type stirrer, a dropping funnel, a thermometer, and a tube leading to a nitrogen bubbler system, was purged with nitrogen and charged with 1.3 moles (69.6 parts) of acrylonitrile, 0.3 mole (25 parts) of concentrated hydrochloric acid, and 200 parts of water. The dropping funnel was charged with 100 parts of n-hexane and 0.2 gram atom (4.6 parts)

of sodium as a 28.2 percent dispersion in mineral spirits (maximum particle size 2 microns). The magnetically agitated dispersion was added dropwise to the stirred aqueous solution over about a 100-minute period while maintaining the reaction temp. at about 5° to 10° C. When the addition was complete, the reaction mixture was steam-distilled until no further organic material was collected. The residue was filtered free of polymer (6.1 parts) and extracted three times with chloroform. Evaporation of the solvent followed by distillation under reduced pressure yielded 2.9 parts (27 percent, based on

that the sodium had a maximum particle size of 30 microns. No adiponitrile was obtained.

Example 8

To show the need for using water with the acrylonitrile, the procedure of Example 1 was repeated, except that 200 parts of glacial acetic acid was substituted for the water. The yield of adiponitrile was less than 5 percent.

The results obtained in these examples are summarized in the following table:

TABLE

Example	Sodium		Acrylonitrile— Amount, Mole	Acid		Sodium Addition		Yield— Adiponitrile, percent, based on Sodium
	Gram atom	Particle size, maxi- mum mi- crons			Amount, Mole	Times, Minutes	Temp., ° C.	
1-----	0.2	2	1.3	HCl-----	0.3	100	5-10	27
2-----	0.2	2	2.6	HCl-----	0.3	95	5-10	23
3-----	0.2	2	1.3	NaHCO ₃ ---	0.3	87	5-10	26
4-----	0.2	2	1.3	NaHCO ₃ ---	0.3	12	5-10	29
5-----	0.2	2	1.3	-----	-----	105	5-10	<11
6-----	0.2	2	1.3	HCl-----	0.3	85	48-52	21
7-----	0.2	30	1.3	HCl-----	0.3	105	5-10	0
8-----	0.2	2	1.3	HCl-----	0.3	100	5-10	<5

sodium) of adiponitrile, B.P. 105–110° C./3 mm. The product was identified by comparison of its infrared spectrum with that of authentic adiponitrile. It was further identified by hydrolyzing it to adipic acid which was then identified by mixed melting point with a commercial specimen of adipic acid.

Example 2

The procedure of Example 1 was repeated, except that 2.6 moles of acrylonitrile was used. The yield of adiponitrile was 23 percent, based on sodium.

Example 3

Substantially the same procedure as described in Example 1 was repeated, except that sodium bicarbonate was used instead of hydrochloric acid. The yield of adiponitrile was 26 percent, based on sodium.

Example 4

The procedure of Example 3 was repeated, except that the sodium was added in 12 minutes. The yield of adiponitrile was 29 percent, based on sodium.

Example 5

To illustrate the desirability of carrying out the reaction in an acid medium, the procedure of Example 1 was repeated, except that no acidic material was used. The yield of adiponitrile was less than 11 percent, based on sodium.

Example 6

The procedure of Example 1 was repeated, except that the temperature was maintained at about 48° to 52° C. The yield of adiponitrile was 21 percent, based on sodium.

Example 7

In order to show the effect of the particle size of the sodium, the procedure of Example 1 was repeated, except

While there are above disclosed but a limited number of embodiments of the process of the invention herein presented, it is possible to produce still other embodiments without departing from the inventive concept herein disclosed, and it is desired therefore that only such limitations be imposed on the appended claims as are stated therein.

What is claimed is:

1. A process for preparation of adiponitrile which comprises treating at a temperature above 5° C. an aqueous solution of acrylonitrile with an alkali metal in dispersed form in which more than about 50 percent of the alkali metal particles are not more than about 5 microns in size, the amount of water in the aqueous solution of acrylonitrile ranging from about 25 to about 95 percent.

2. The process as defined in claim 1 wherein the alkali metal is sodium, the reaction is carried out at a temperature between about 5° and 55° C., and the amount of water in the aqueous solution of acrylonitrile ranges from about 75 to about 80 percent.

3. A process for the simultaneous dimerization and reduction of acrylonitrile to adiponitrile which comprises treating an aqueous solution of acrylonitrile with finely divided sodium in an inert volatile organic solvent, said reaction being carried out at a temperature above about 5° C., the sodium reactant being in the form of finely divided particles of which substantially more than about 50% are not more than about 5 microns in size, and the amount of water in the acrylonitrile-water solution ranging from about 25 to about 95 percent.

References Cited in the file of this patent

UNITED STATES PATENTS

2,773,092 Carley et al. _____ Dec. 4, 1956

OTHER REFERENCES

Bergmann: "Acetylene Chemistry," 1948, page 80.