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PROCESS FOR THE MANUFACTURE OF
NITRILES

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The present invention relates to an improved method for manufacturing dinitriles of at least 3 carbon atoms and more particularly to the production of adiponitrile $\text{CN}(\text{CH}_2)_4\text{CN}$ in the liquid phase from adipic acid and gaseous ammonia.

According to a known process for the manufacture of fatty nitriles containing at least six carbon atoms, a current of gaseous ammonia is caused to pass through fatty acids in the liquid state while these are maintained at such a temperature that the water which is formed in the course of the reaction is vaporized as fast as it is formed. It has never been proposed to apply this process to polybasic acids and, as a matter of fact, if it is attempted to prepare adiponitrile by this process, the yields obtained do not exceed 35% of the theoretical.

It has also been proposed to prepare the aliphatic dinitriles by passing a rapid current of ammonia through a liquid mixture of a dibasic aliphatic acid and concentrated aqueous ammonia at an elevated temperature and in the presence of catalysts consisting of oxygenated acids of the metals of Groups V and VI in the periodic system and their salts. In general, such a method of working constitutes an improvement in comparison with that which does not use any catalyst, but in the particular case of adipic acid when ammonium molybdate is used as catalyst it is not possible to obtain a yield of more than 45% of the theoretical.

It is an object of this invention to overcome the disadvantages of the prior art and to provide a new and improved process for dinitrile synthesis.

Other objects and advantages of this invention will be apparent from the following specification in which the preferred embodiments are described.

According to the present invention, yields of dinitriles of at least 3 carbon atoms are obtained, which are superior to those of the known processes, by causing a rapid current of gaseous ammonia to pass through a dicarboxylic compound containing at least 3 carbon atoms and adapted to form an ammoniated carboxylic compound with ammonia, the reaction being carried out in the presence of catalysts which are soluble in the reaction material and which are formed of neutral or acid phosphoric esters or of phosphoric acid itself, the temperature being from 150 to 350° C.

Amongst the phosphoric acid esters which can be employed according to the present invention the following may be mentioned, though the in-

vention is not limited to the use of these particular esters: neutral esters of phosphoric acid with aliphatic alcohols, such as the triethyl-, tributyl-, triamyl-, triethoxyethyl-phosphates; the neutral phosphoric esters of araliphatic alcohols, or cyclo-aliphatic alcohols, such as tribenzyl-, tricyclo-, hexyl-, or trimethyl-phosphates; the neutral phosphoric esters of phenols which may be either mono-nuclear or poly-nuclear, such as triphenyl-, trichlorophenyl-, tricresyl-, trithymyl-, trinaphthyl-, trixenyl-phosphates; the neutral mixed phosphor esters of phenols, such as monophenyl-dixenyl and diphenylmonoxenyl-phosphates; the acid phosphoric esters, such as the dicresyl-, dixenyl- or mono-xenyl-phosphoric acids.

The proportion of catalyst to be employed can vary between wide limits, as for example between 0.1 and 10% of the weight of acid treated. In general a proportion of the order of 5% is suitable, although smaller or larger proportions may be used if desired.

One method of carrying out the invention consists in first melting the acid, such as adipic acid, together with the catalyst and then passing a current of ammonia through the melted mass while gradually increasing the temperature to the neighborhood of 300° C., more or less rapidly according to the catalyst used. This temperature is then maintained until all the water which has been formed in the course of the reaction has been eliminated.

Although the reaction takes place conveniently under atmospheric pressure, it is sometimes advantageous to operate at higher or lower pressures than atmospheric in order to increase the capacity of a given unit of apparatus or to facilitate vaporization of high boiling reactants. In practice, the pressure under which the ammonia reacts on the acid can be regulated somewhat by varying the distance between the inlet for the ammonia and the level of the liquid in the reaction vessel.

The speed at which the ammonia passes through the melted material is preferably regulated in such a way that the gas is not completely absorbed in the reaction, so that a small quantity of gas is evolved through the exit pipe of the apparatus. This quantity of ammonia which has not reacted, is dissolved in the water which is formed in the course of the reaction and is thus recovered in the form of an aqueous solution.

In order to obtain the maximum yields care should be taken that the volatile substances

which emerge from the apparatus should consist substantially of water and excess of ammonia. As is known, the action of ammonia on adipic acid can give rise to other substances as well as adiponitrile, such as the ammonium salt, the diamide, adipimide, and omega-cyanovaleamide, which can react further to form adiponitrile. Certain of these substances can be entrained by the water vapor or by the ammonia, and if they are not caused to return to the reaction vessel, their loss naturally leads to a reduction in the yield.

A convenient apparatus for carrying out the process of the present invention consists of a reaction vessel having an inlet tube for the ammonia and an orifice for the escape of the volatile products, this orifice being furnished with a fractionating column and a dephlegmator, the water-circulation of which is arranged so that the temperature of the vapors at the exit is in the neighborhood of 100° C. In this way all the water which is formed in the course of the reaction is eliminated while the intermediate substances mentioned above are returned to the apparatus.

The process can also be operated in a continuous manner by causing both ammonia and molten acid to circulate through one or several vessels. The two reactants can be circulated either in co-current or in counter-current, or alternatively fresh ammonia can be supplied to each vessel individually. The temperature can be chosen differently and conveniently in each vessel.

By a suitable choice of catalyst and apparatus it is possible in this manner by starting with adipic acid and ammonia to obtain yields of adiponitrile of from 85% to 90% of the theoretical.

The following examples illustrate how the invention may be carried out in practice, but the invention is in no way limited to these examples.

Example 1

200 grams of adipic acid are mixed with 2 grams of 85% phosphoric acid and heated to 200° C. in a glass flask surmounted by rectifying column, and a current of ammonia gas is made to bubble through the melted acid at the rate of 90 grams in an hour. The temperature is gradually raised from 200° to 300° and this temperature is maintained as long as water distills, which requires approximately 1½ hours. By distilling the reaction mixture there is obtained a quantity of 87 grams of adiponitrile; yield 59% of the theoretical.

If this preparation is carried out in the same manner but without the addition of the phosphoric acid, there is only obtained a quantity of 52 grams of adiponitrile, which represents a yield of 35% of the theoretical.

Example 2

200 grams of adipic acid are treated in the same manner as in Example 1 except that 16 grams of butyl phosphate are used instead of the phosphoric acid. The amount of adiponitrile obtained is 88 grams giving a yield of 60% of the theoretical.

Example 3

By working in the manner described in Example 1 but using 16 grams of tri-orthocresylphosphate instead of the phosphoric acid the

yield of adiponitrile obtained is 95 grams, corresponding to 64% of the theoretical.

Example 4

By working in the same manner as Example 1 but using instead of phosphoric acid 16 grams of tri-orthoxenylphosphate the amount of adiponitrile obtained is 104 grams, namely, 70% of the theoretical.

Example 5

By working in the same manner as in Example 1 but replacing the phosphoric acid by 8 grams of di-orthoxenylphosphoric acid the amount of adiponitrile obtained is 108 grams, which is 73% of the theoretical.

Example 6

2 kilograms of adipic acid and 80 grams of di-xenylphosphoric acid are placed in a cylindrical vessel of 2 metres height and 6 centimeters diameter constructed of stainless steel and surmounted by a rectifying column and a dephlegmator. The reaction mixture is heated to 250° C. and a current of ammonia gas is passed at the rate of 1800 grams in an hour. The circulation of the water in the dephlegmator is regulated in such a manner that the temperature of the issuing vapors does not exceed 100° C. The temperature of the reaction mixture is gradually increased to 300° C. While gradually diminishing the delivery of ammonia to 200 grams per hour the temperature of the reaction medium is maintained at 300° C. until no water any longer distills, which requires about 2½ hours.

On distilling the contents of the apparatus 1280 grams of adiponitrile are obtained, which represents a yield of 86.6% of the theoretical.

It will be understood that the present invention is not limited to the synthesis of the specific nitrile, adiponitrile, mentioned in the examples, but may be employed equally as well in the synthesis of dinitriles generally of at least 3 carbon atoms, such as sebaconitrile from sebacic acid, and the like.

Various changes may be made in the details of this invention without sacrificing the advantages thereof or departing therefrom.

We claim:

1. A process for the production of aliphatic dinitriles of at least 3 carbon atoms which comprises passing a rapid current of ammonia through a liquid dicarboxylic compound containing at least 3 carbon atoms and adapted to form an ammoniated carboxylic compound with ammonia, the reaction being carried out at a temperature of from 150 to 350° C. in the presence of a catalyst soluble in the reaction material and selected from the group consisting of phosphoric acids and neutral and acid esters of phosphoric acids.

2. A process for the production of aliphatic dinitriles of at least 3 carbon atoms which comprises passing, at a temperature of 150 to 350° C., a rapid current of ammonia through a liquid dicarboxylic compound containing at least 3 carbon atoms and adapted to form an ammoniated carboxylic compound with ammonia, the reaction being carried out in the presence of from 0.1 to 10% by weight of a catalyst soluble in the reaction material and selected from the group consisting of phosphoric acids and neutral and acid esters of phosphoric acids.

3. A process for the production of aliphatic dinitriles of at least 3 carbon atoms which com-

prises passing, at a temperature of 150 to 350° C., a rapid current of ammonia through a liquid dicarboxylic compound containing at least 3 carbon atoms and adapted to form an ammoniated carboxylic compound with ammonia, the reaction being carried out in the presence of about 5% by weight of a catalyst soluble in the reaction material and selected from the group consisting of phosphoric acids and neutral and acid esters of phosphoric acids.

4. A process for the production of aliphatic dinitriles of at least 3 carbon atoms which comprises passing, at a temperature of 150 to 350° C., a rapid current of ammonia through a liquid dicarboxylic compound containing at least 3 carbon atoms and adapted to form an ammoniated carboxylic compound with ammonia, the reaction being carried out in the presence of a phosphoric acid catalyst soluble in the reaction material.

5. A process for the production of adiponitrile which comprises passing, at a temperature of 150 to 350° C., a rapid current of ammonia through molten adipic acid, the reaction being carried out in the presence of a catalyst soluble in the reaction material and selected from the group consisting of phosphoric acids and neutral and acid esters of phosphoric acids.

6. A process for the production of adiponitrile which comprises passing, at a temperature of 150 to 350° C., a rapid current of ammonia through molten adipic acid, the reaction being carried out in the presence of from 0.1 to 10% by weight of a catalyst soluble in the reaction material and selected from the group consisting of phosphoric acids and neutral and acid esters of phosphoric acids.

7. A process for the production of adiponitrile which comprises passing, at a temperature of 150 to 350° C., a rapid current of ammonia through molten adipic acid, the reaction being carried out in the presence of from about 5% by weight of a catalyst soluble in the reaction material and selected from the group consisting of phosphoric acids and neutral and acid esters of phosphoric acids.

8. A process for the production of adiponitrile which comprises passing, at a temperature of 150 to 350° C., a rapid current of ammonia through molten adipic acid, the reaction being carried out in the presence of a phosphoric acid catalyst.

9. A process for the production of adiponitrile which comprises passing, at a temperature of 150 to 350° C., a rapid current of ammonia through molten adipic acid, the reaction being carried out in the presence of a dixenyl phosphoric acid catalyst.

10. A process for the production of adiponitrile which comprises passing, at a temperature of 150 to 350° C., a rapid current of ammonia through molten adipic acid, the reaction being carried out in the presence of about 0.1 to 10% by weight of a phosphoric acid catalyst.

11. A process for the production of adiponitrile which comprises passing, at a temperature of 150 to 350° C., a rapid current of ammonia through molten adipic acid, the reaction being carried out in the presence of about 0.1 to 10% by weight of a dixenyl phosphoric acid catalyst.

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