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PROCESS FOR THE PREPARATION OF AN AMINONITRILE
BY PARTIAL HYDROGENATION OF A NITRILE COMPOUND
WITH TWO OR MORE NITRILE GROUPS

The invention relates to a process for the preparation of an aminonitrile by partially hydrogenating a
 5 nitrile compound with two or more nitrile groups in the presence of a catalyst which contains a metal from group 8 of the periodic system of the elements.

Such a process is known from F. Mares, J.E. Galle, S.E. Diamond and F.J. Regina, Journal of Catalysis 112,
 10 (1988), pp. 145-156, according to which publication an alkane dinitrile, such as α,ω -butane dinitrile (succinonitrile), is hydrogenated in the presence of a catalyst consisting of finely divided rhodium halogenide on a magnesium oxide carrier. The catalyst is pretreated with
 15 sodium hydroxide, yielding metallic rhodium on a magnesium oxide carrier. During the hydrogenation reaction NH_3 is supplied in an excess relative to the dinitrile. In the hydrogenation of succinonitrile, at a reaction temperature of 100°C , a pressure of 50 atm (5 MPa) and a reaction time
 20 of 5.5 hours, a conversion of 89.4% and a selectivity to aminobutyronitrile of 87.3% is achieved. This corresponds to an aminobutyronitrile yield of 78%. Although this yield is high, a further increase in the yield is desirable. In addition to this, a large amount of undesirable by-product
 25 is formed (11.9% of the succinonitrile being converted into dimers and oligomers). The article also reports an ϵ -amino capronitrile yield of 66.6% from adiponitrile at 90% conversion. Dimers are formed in an amount of 2.7%.

It is the object of the present invention to
 30 provide a process for the preparation of an aminonitrile by means of a simple method, at a high reaction velocity and

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with a high aminonitrile yield, in which the formation of undesirable byproducts is limited.

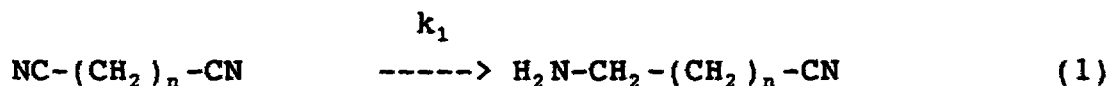
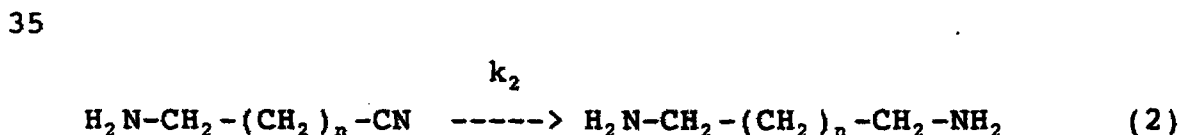
5 The object of the present invention is achieved in that the hydrogenation is carried out under virtually water-free reaction conditions and the catalyst has been treated with an alkanolate.

10 Surprisingly, it has been found that according to the present invention, aminonitrile yields in excess of 80% can be attained. Moreover, in the process of the invention there is no need to supply NH_3 during the reaction. As byproduct virtually only oligoamine is formed, which can be worked up in the chemical industry, as opposed to dimers and
15 oligomers, which are formed according to the process known from the art.

 The process according to the invention is suitable for the partial hydrogenation of any nitrile compound with two or more nitrile groups.

20 Thus, for instance, α,ω -alkane dinitriles are suitable for conversion to their corresponding aminonitriles using the process according to the present invention. These alkane dinitriles are of a general formula $\text{NC}-(\text{CH}_2)_n-\text{CN}$, n being an integer from 0 to 12. Preferably, n is an integer
25 from 1 to 6. Examples are: malonitrile ($n=1$), succinonitrile ($n=2$), adiponitrile ($n=4$) and glutaronitrile ($n=5$). The process according to the present invention is particularly suitable for the hydrogenation of succinonitrile and adiponitrile.

30 The hydrogenation of α,ω -alkane dinitriles can be represented by the following reaction scheme:



In this scheme the product of reaction (1) is the desired ω -aminoalkanenitrile, which can react further to form
 5 diamines in the presence of hydrogen according to reaction (2). k_1 and k_2 denote the rate constants of reactions (1) and (2). In a selective hydrogenation to the ω -amino alkane nitrile the ratio k_1/k_2 is high.

The process according to the present invention is
 10 also suitable for the partial hydrogenation of compounds containing more than two nitrile groups, for instance for compounds with 3-12 carbon atoms with three or four nitrile groups. The invention is particularly suitable for the hydrogenation of dendritic macromolecules which contain
 15 nitrile groups. A general description of dendritic macromolecules can be found, for instance, in D.A. Tomalia et al. in Angew. Chem. Int. Ed. Engl. 29, (1990) pp. 138-175. These macromolecules as a rule have a weight-average molecular weight (M_w) of 100-100,000 kg/kmol. Examples of
 20 dendritic macromolecules that are suitable for the partial hydrogenation are compounds of the formula:



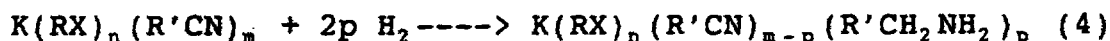
25 where m and n are positive integers, the latter standing for the number of branches of the dendritic macromolecule, while m is higher than or equal to n. The symbols in formula (3) denote the following:

- 30 K a chemical compound that forms the nucleus of the dendritic macromolecule
 RX branches linked to the nucleus which contain carbon atoms and optionally hetero atoms
 R'CN a terminal branch with a nitrile group.

35

According to the present invention the compounds according to formula (3) can be partially hydrogenated according to the reaction equation:





5 where p is a positive integer. The degree of partial hydrogenation Q is defined as:

$$Q=p/m \quad (5)$$

10 According to the invention Q is lower than 1, preferably lower than 0.75. After partial hydrogenation the dendritic macromolecules can be built up further through reaction with compounds that react with the nitrile or amine groups. This may again be followed by partial hydrogenation and the
15 process of alternate buildup or growth and partial hydrogenation can be repeated several times. Since the dendritic macromolecule is built up solely at the location of either the terminal amine groups or the terminal nitrile groups, while according to the invention the degree of
20 hydrogenation can be controlled by changing the reaction conditions, the structure of the dendritic macromolecule can be influenced in any desired way.

The partial hydrogenation according to the invention has to be carried out under almost water-free
25 reaction conditions, which is understood to mean that the reaction medium contains less than 5 wt.% water. The water content is determined by means of a Karl Fischer titration according to the ASTM-E 203 (1971) standard. Preferably, the water content is below 1 wt.%, more preferably below 0.5
30 wt.%, and in particular below 0.1 wt.%.

The nitrile can be dissolved in a suitable solvent prior to the hydrogenation. The solvents that can be used according to the invention should contain almost no water, the water content of the reaction medium, as stated above,
35 being the criterion. Examples of suitable solvents are tetrahydrofuran, dioxane, alkane (di)amines, alcohols and ethers. Solvents that are particularly suitable are the α - ω -alkane diamines or alcohols with 1-10 C atoms. Examples of such particularly suitable solvents are diamino-ethane,



diaminobutane, diaminohexane, methanol, ethanol, n-propanol, i-propanol and n-butanol.

5 The hydrogenation is effected with hydrogen gas (H_2). This is usually present as a gas phase, which is in contact with the solution containing the nitrile, a small portion of the hydrogen gas being dissolved in the solution. The partial pressure of hydrogen is at least 1 atm (0.1
10 MPa), but usually 5-500 atm (0.5-50 MPa). In particular 30-100 atm (3-10 MPa), hydrogen pressure is applied. These and all other pressures are stated as absolute pressures. Other gases may be present during the reaction, but they are usually present in small amounts.

15 During the hydrogenation hydrogen is preferably present in a molar ratio of H_2 : nitrile of at least 1. Hydrogen consumed in the reaction is usually supplied during the reaction. As a rule, the hydrogen pressure is kept constant during the entire reaction.

20 The temperature during the hydrogenation is not critical, but is usually 0-200°C, and in particular 20-100°C.

 The catalyst applied according to the invention is a catalyst that contains a metal from group 8 of the
25 periodic system of the elements which has been treated with an alkanolate. The periodic system of the elements is understood to mean the table as printed on the cover of the Handbook of Chemistry and Physics, 58th Edition, CRC Press, 1977-1978.

30 Metals from group 8 are known to be active in the hydrogenation of nitriles (see, for instance, EP-A-0077911). Nickel, cobalt, platinum, palladium and rhodium are suitable choices. For sufficient catalytic activity, the metal must have a large contact area. The metal can be used as such or
35 on a suitable support.

 US-A-4.362.671 describes a process for the partial hydrogenation of dinitriles to α,ω -aminonitriles using rhodium complexes of the formula $(RR'Rh)A$ as a catalyst, in which R is derived from a non-allenic hydrocarbone diene of



at least 4 carbons, R' is an organitrogen compound and A is a complex monovalent anion serving as counter-anion.

5 According to the present invention, Raney nickel or Raney cobalt are particularly suitable as a catalyst. A description of Raney catalysts and their preparation can be found in US-A-1,628,190 (1927).

 Raney nickel contains mainly nickel and aluminium,
10 the latter in the form of metallic aluminium, aluminium oxides or aluminium hydroxides. Small amounts of other metals in elementary or in chemically bound form, such as iron and/or chromium, may be added to the Raney nickel to increase the activity and selectivity for the hydrogenation
15 of certain groups of compounds. These added metals are usually called promoters, while the catalyst is called promoted Raney nickel. For the use of promoters, see: S.R. Montgomery, Catalysis of Organic Reactions 5, pages 383-409 (1981). According to the invention it is particularly
20 preferred to use chromium and/or iron promoted Raney nickel as catalyst.

 Raney cobalt also contains aluminium and may contain promoters. It is known, for instance, that chromium promoted Raney cobalt is suitable for the hydrogenation of
25 nitriles to primary amines.

 Examples of Raney catalysts that are suitable for the process according to the invention are the Raney nickel types Degussa BLM 112 W^R, Grace 2400^R, Activated Metals A-4000^R and Doduco Ra/Ni^R (Fe-Cr promoted) and Raney cobalt
30 type Grace 2724^R.

 According to the present invention the catalyst is pretreated. Since the hydrogenation is to be carried out under almost water-free reaction conditions, the catalyst has to be freed of water. This can be effected using the
35 methods known from the art, for instance by washing with a water-free solvent. Preferably, the water is removed from the catalyst before the catalyst is treated with the alkanolate.

 According to the invention the catalyst is treated



with an alkanolate. The alkanolate according to the invention is preferably an alkanolate with 1-10 C-atoms, for instance methanolate, ethanolate, n-propanolate, i-propanolate or n-butanolate. The alkanolate is usually available in the form of a metal salt. According to the invention alkali metal alkanolates or earth alkali metal alkanolates are particularly suitable. Examples of extremely suitable alkanolates are potassium and sodium methanolate. The amount of alkanolate applied to the catalyst is usually 0.01-0.5 g per g of catalyst, in particular 0.03-0.2 g/g catalyst, and more in particular 0.05-0.15 g/g catalyst.

The temperature during the treatment with alkanolate is not critical. Usually the treatment takes place at a temperature between 0 and 50°C, in particular at room temperature. The pressure during the treatment is of little importance. Usually the treatment takes place under atmospheric pressure. Preferably, the treatment takes place by mixing the catalyst intensively with a solution of the alkanolate. The solution is preferably a concentrated solution of the alkanolate in an alkanol. The concentration is, for instance, 5-1000 g/l, in particular 10-500 g/l.

The products that can be prepared according to the invention are widely applied as raw materials for the chemical or the pharmaceutical industry. Examples are the use of ω -aminobutane nitrile (aminobutyro nitrile) as a raw material for the preparation of the hydrochloride of γ -aminobutyrylamide (gabamide), with the formula $(\text{H}_2\text{N}-\text{CH}_2)_3-\text{CONH}_2 \cdot \text{HCl}$, which is used for the preparation of antidepressants. In addition, aminobutyro nitrile can be converted into pyrrolidone through saponification and ring closure.

ω -Aminoalkane nitriles can also find application as raw material for the production of nylons. Thus, ϵ -amino-hexane nitrile (ϵ -aminocapronitrile) can be used as a raw material for ϵ -caprolactam, which serves as a raw material for nylon-6. In this route 1,4-dicyano butane (adiponitrile) is subjected to selective hydrogenation according to the

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invention to yield ϵ -amino-capronitrile, which is converted into 6-amino-hexanoic acid (ϵ -amino caproic acid) through saponification, which is subsequently converted into caprolactam by means of a ring closure reaction in which H_2O is split off.

The dendritic macromolecules that can be prepared according to the invention can be used in electronics, for calibration of sieves, in catalyst carriers and for selective membranes and coatings. In addition, the dendritic compounds can be used as impact modifiers or as crosslinking agents in various plastics.

The invention will be further elucidated in the of examples and comparative experiments, without, however, being limited thereto.

The reaction products were analyzed using a gas chromatograph of the type Hewlett Packard HP5890^R, with a column (type No. CP WAX 51) filled with polyethylene glycol, and hydrogen as carrier gas. Succinonitrile was analyzed by means of a separate gas chromatograph, type Chrompack 428A^R, with the following column composition: 5% phenyl, 95% methyl polysiloxane, type CP SIL 8 CB, and nitrogen as carrier gas.

The amount of water in the reaction mixture was determined by means of a Karl Fischer titration according to ASTM-E 203 (1971).

Example I

Raney nickel of the type Degussa BLM 112W^R was used as a catalyst; according to the producer the composition was 85 wt.% Ni, 2.0 wt.% Fe, 2.5 wt.% Cr and 9.7 wt.% Al (Al and Al_2O_3). 8 g (dry weight) of catalyst was washed five times with 25 ml water-free methanol, prepared by drying methanol with a type 3A molecular sieve. After sedimentation of the slurry, the methanol was decanted. The slurry was subsequently contacted with a solution of 0.8 g $NaOCH_3$ in 20 ml methanol, intensive stirring being applied. After sedimentation of the slurry, the liquid was decanted and the treated catalyst was washed with 25 ml diaminoethane,



followed by decantation of the washing liquid.

As reactor a 160 ml Parr autoclave provided with a
5 drain valve with a filter to trap the catalyst particles,
was used. The reactor was further equipped with a 50 ml
dosing vessel, connected to the autoclave via a dosing line
with a valve. Both the reactor and the dosing valve have
adjustable heating and pressure control. The reactor
10 contents can be mixed by means of a stirrer.

The treated catalyst was introduced into the
autoclave as a slurry in 80 g diamino-ethane. The water
content of this catalyst slurry was 0.77 wt.%. Subsequently
the autoclave was purged three times with H_2 , the H_2
15 pressure was raised to 70 atm, and the temperature was
raised to 80°C while stirring (1500 rpm). 8 g succinonitrile
was dissolved in 10 g diamino-ethane and introduced into the
dosing vessel. Subsequently the dosing vessel was purged
with H_2 twice and the pressure was raised to 80 atm with H_2 .
20 After this, the valve shutting off the dosing vessel was
opened, so that the content of the dosing vessel are
transferred to the autoclave, after which the reaction took
place in the autoclave, under stirring (1500 rpm).

After 300 s the reaction was stopped, by opening
25 the valve in the reactor drain so that the reactor contents,
apart from the catalyst, flew out of the reactor. The
product was analyzed by means of gas chromatography. The
succinonitrile conversion was 100%. The reaction product
consisted of: 85 mol % pyrrolidine, 14 mol % diaminobutane
30 and 1 mol % pyrrolidine. The aminobutyronitrile yield was
85%.

Comparative experiment A

8 g of the Raney nickel catalyst as in Example I
35 was washed with 25 ml distilled water five times. After
sedimentation of the slurry, the water was decanted. The
slurry was subsequently contacted with a solution of 0.8 g
NaOH in 20 ml distilled water, while stirring intensively.
After sedimentation of the slurry, the liquid was decanted



and the treated catalyst was washed with 25 ml
diaminoethane. The water content of the catalyst slurry was
5 7.7 wt.%.

The catalyst thus treated was used in the
hydrogenation of succinonitrile, as described in Example I.
After 300 s 100% of the succinonitrile was converted. The
reaction product consisted of 96 mol % diaminobutane and 2.5
10 mol % pyrrolidine and a residual amount of tarry product.
The aminobutyro nitrile yield was 0%. Gas chromatographic
analysis proved that the tarry product consisted mainly of
diaminobutane dimers.

15 Example II

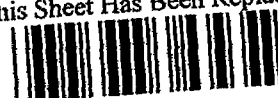
The hydrogenation was carried out as described in
Example I, but now 1.1 g KOCH₃ was used instead of NaOCH₃,
and diaminobutane was used as solvent instead of diamino-
ethane. After 300 s the succinonitrile conversion was 100%.
20 The reaction product consisted of 85 mol % aminobutyro
nitrile, 14 mol % diaminobutane and 1 mol % pyrrolidine. The
aminobutyronitrile yield was 85%.

Example III

25 The hydrogenation was carried out as described in
Example II, but now hexamethylene diamine was used as
solvent in stead of diaminobutane. After 300 s the
succinonitrile conversion was 100%. The reaction product
consisted of 86.5 mol % aminobutyro nitrile, 13 mol %
30 diaminobutane and < 1 mol % pyrrolidine. The aminobutyro
nitrile yield was 86.5%.

To study the hydrogenation kinetics, during the
reaction a small sample was drawn from the reactor every 15
s and was analyzed. For reactions (1) and (2) first-order
35 kinetics were observed, with $k_1 = 0.013$ and $k_2 = 8.1 \cdot 10^{-4}$
s⁻¹. The k_1/k_2 ratio was 16.

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Comparative experiment B

Comparative example A was repeated, now the
5 reaction kinetics being determined as described in Example
III. First-order kinetics were observed for reactions (1)
and (2), with $k_1 = 0.013$ and $k_2 = 2.2 \times 10^{-3} \text{ s}^{-1}$. The k_1/k_2
ratio was 5.6.

10 Example IV

The hydrogenation was carried out as described in
Example I, but now adiponitrile was hydrogenated. In place
of NaOCH_3 , 1.2 g KOCH_3 was added. The water content of the
catalyst slurry was 0.46 wt.%. After 180 s the adiponitrile
15 conversion was 95%. The reaction product consisted of 77 mol
% ϵ -aminocapronitrile and 23 mol % diaminoheptane. The
 ϵ -aminocapronitrile yield was 73%.

To study the hydrogenation kinetics, after every 15
s of the reaction time a small sample was drawn from the
20 reactor, which was analyzed. For reactions (1) and (2)
first-order kinetics were observed, with $k_1 = 0.017$ and $k_2 =$
 $2.18 \times 10^{-3} \text{ s}^{-1}$. The k_1/k_2 ratio was 6.

Comparative experiment C

25 The hydrogenation was carried out as described in
Example IV. Use was made of a catalyst in water, which
resulted in a water content of 11.2 wt.% in the reaction
mixture. After 90 s the adiponitrile conversion amounted to
99%. The reaction product consisted of 51 mol %
30 ϵ -aminocapronitrile and 49 mol % hexamethylene diamine. The
 ϵ -aminocapronitrile yield was 51%.

To study the hydrogenation kinetics, during the
reaction a small sample was drawn from the reactor, every 15
s and analyzed. For reactions (1) and (2) first-order
35 kinetics were observed, with $k_1 = 0.051$ and $k_2 = 0.016 \text{ s}^{-1}$.
The k_1/k_2 ratio was 3.2.

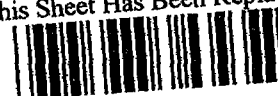
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C L A I M S

- 5 1. Process for the preparation of an aminonitrile by
partially hydrogenating a nitrile compound with two or
more nitrile groups in the presence of a catalyst
containing a metal from group 8 of the periodic system
of the elements, characterized in that the hydrogenation
10 is carried out under almost water-free reaction
conditions and the catalyst has been treated with an
alkanolate.
2. Process according to claim 1, characterized in that the
alkanolate is chosen from a methanolate or an
15 ethanolate.
3. Process according to claim 1 or 2, characterized in that
the alkanolate is an alkali metal alkanolate or an earth
alkali metal alkanolate.
4. Process according to claim 3, characterized in that the
20 alkanolate is sodium or potassium methanolate.
5. Process according to any one of claims 1-4,
characterized in that the amount of alkanolate applied
to the catalyst is 0.01-0.5 g per g of catalyst.
6. Process according to claim 5, characterized in that the
25 amount of alkanolate applied to the catalyst is 0.05-
0.15 g per g of catalyst.
7. Process according to any one of claims 1-6,
characterized in that the catalyst is a Raney nickel or
Raney cobalt catalyst.
- 30 8. Process according to any one of claims 1-7,
characterized in that the catalyst is rendered water-
free before being treated with the alkanolate.
9. Process according to any one of claims 1-8,
characterized in that the water-free reaction conditions
35 are such that the water content of the reaction medium
is below 1 wt.%.

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10. Process according to any one of claims 1-9,
characterized in that the partial hydrogenation is
5 carried out in a solvent chosen from the group
consisting of tetrahydrofuran, dioxane, alkane
(di)amines, alcohols and ethers.
11. Process according to claim 10, characterized in that the
solvent is chosen from α,ω -alkane diamines or alcohols
10 with 1-10 C-atoms.
12. Process according to claim 11, characterized in that the
solvent is chosen from the group consisting of diamino-
ethane, diaminobutane, diaminohexane, methanol, ethanol,
n-propanol, i-propanol and n-butanol.
- 15 13. Process according to any one of claims 1-12,
characterized in that the nitrile compound is an
 α,ω -alkane dinitrile.
14. Process according to claim 13, characterized in that the
 α,ω -alkane dinitrile is succinonitrile or adiponitrile.
- 20 15. Process according to any one of claims 1-12,
characterized in that the nitrile compound is a
dendritic macromolecule.
16. Process as contained in the description and elucidated
in the experiments.

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