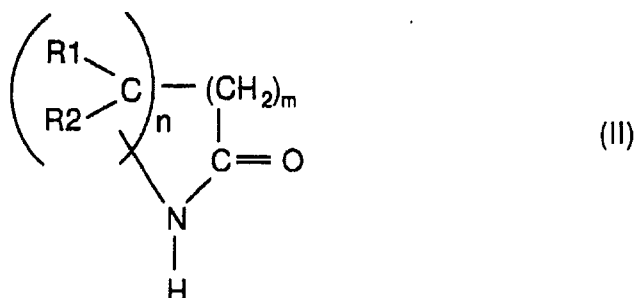
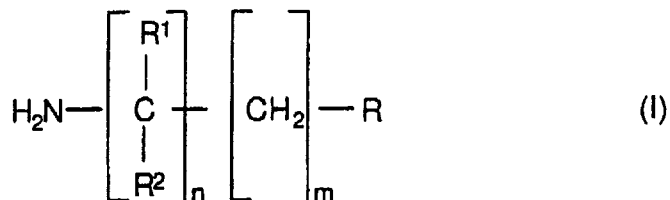


Preparation of cyclic lactams

5



by reacting a compound (I) of the formula



20 with steam in the gas phase, wherein

a) the compound (I) is reacted with steam in the gas phase with the addition, before or after the reaction, of an organic diluent (III) which exhibits a miscibility gap with water under

specific quantity, pressure and temperature conditions,
to give a mixture (IV) containing a lactam (II),

- 5 b) the mixture (IV) is converted, before or after the separation of ammonia, under quantity, pressure and temperature conditions such that the diluent (III) and water are liquid and exhibit a miscibility gap, to give a two-phase system consisting of a phase
10 (V) containing a higher proportion of diluent (III) than water, and a phase (VI) containing a higher proportion of water than diluent (III),
- c) the phase (V) is separated from the phase (VI), and
15
- d) the diluent (III) and optionally by-products selected from the group consisting of low-boiling component [sic], high-boiling component [sic] and unreacted compound (I) are separated from the phase
20 (V) to give a lactam (II).

Processes for the preparation of cyclic lactams by reacting omega-aminocarboxylic acid derivatives with steam in the gas phase in the presence of heterogeneous
25 catalysts, for example the preparation of caprolactam from 6-aminocarboxylic [sic] acid nitrile, are generally known.

Thus WO 96/22974, EP-A-659741, WO 99/47500 and
30 WO 99/28296 disclose the reaction of 6-amino-capronitrile with steam in the gas phase in the presence of heterogeneous catalysts to give caprolactam and ammonia, examples of the heterogeneous catalysts used being aluminum oxide, lanthanum phosphates and
35 zirconium dioxide. WO 96/22974 points out that it is

not excluded to carry out the cyclization using a diluent which is inert under the reaction conditions, for example an alkane, a cycloalkane, an aromatic hydrocarbon or a halogenohydrocarbon, and thus to have
5 a liquid phase in the reaction mixture.

WO 98/05636 describes the work-up of reaction discharges such as those obtained in the gas phase cyclization of 6-aminocapronitrile with steam in the
10 presence of solid catalysts. To effect said work-up:

- a) the bulk of the ammonia formed in the cyclization is separated from the water-containing crude caprolactam, and
15
- b) this crude caprolactam is either subjected to a liquid/liquid extraction with the addition of a solvent containing acidic groups, and/or treated with a cation exchanger.

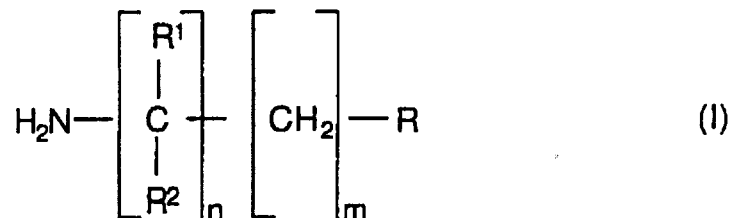
20 Measure b) extracts all the amines or binds them to the cation exchanger. The principal disadvantage of this work-up is that aminocapronitrile which has not reacted in the cyclization is taken up by the ion exchangers and, when the ion exchanger is regenerated, is obtained
25 as the ammonium salt mixed with ammonium salts of amine by-products, so it cannot be returned to the cyclization. Ammonium salts are also formed in the extraction of the aminocapronitrile with extractants
30 containing acidic groups, and create the same problems.

It is therefore an object of the present invention to provide a process which makes it possible to prepare cyclic lactams (II) from compounds (I) in a technically
35 simple and economic manner, produces high yields of

lactam with high conversions of the compound (I) and also minimizes losses of yield in the work-up.

We have found that this object is achieved by the process defined at the outset.

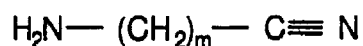
Suitable compounds (I) are aminocarboxylic acids and derivatives thereof, preferably those of general formula I:



in which R is carboxylic acid, nitrile and/or carboxamide groups and n and m can each have the values 0, 1, 2, 3, 4, 5, 6, 7, 8 and 9 and the sum of n + m is at least 3, preferably at least 4.

In principle, R^1 and R^2 can be any kind of substituents, the only proviso being that the desired cyclization reaction is not affected by the substituents. Preferably, R^1 and R^2 independently of one another are C_1 - C_6 -alkyl or C_5 - C_7 -cycloalkyl groups or C_6 - C_{12} -aryl groups.

Particularly preferred starting compounds are aminocarboxylic acid nitriles, preferably those of the general formula



in which m has a value of 3, 4, 5 or 6, especially 5. When m = 5, the starting compound is 6-aminocapronitrile.

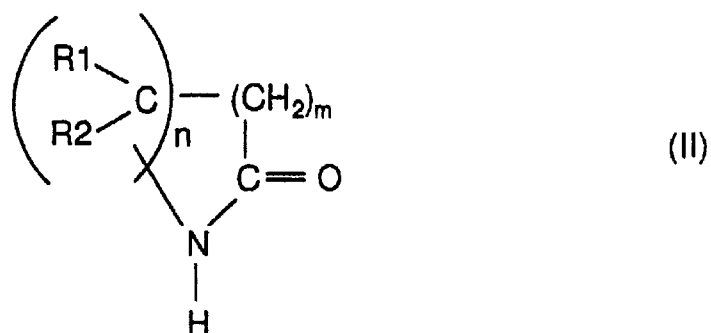
- 5 The compound (I) used can be a single compound (I) or a mixture of different compounds (I). The compound (I) used is preferably a single compound.

10 Omega-aminocarboxylic acid nitriles are obtainable for example by the partial hydrogenation of alpha,omega-dinitriles in the gas or liquid phase, e.g. according to WO 96/20166, WO 96/20916 or WO 96/20165.

15 Omega-aminocarboxylic acids are obtainable for example by the aminating hydrogenation of omega-formylcarboxylic acids or by the hydrolysis of omega-aminocarboxylic acid esters or omega-aminocarboxylic acid nitriles.

20 Omega-aminocarboxamides are obtainable for example by the reaction of omega-aminocarboxylic acids and esters thereof with ammonia or by the reaction of omega-aminocarboxylic acid nitriles with water.

25 The process according to the invention yields the cyclic lactams of formula (II) corresponding to the compound (I):



in which n , m , R^1 and R^2 are as defined above. Particularly preferred lactams are those in which $n = 0$ and m has a value of 3, 4, 5 or 6. When $m = 5$, the product obtained is caprolactam.

5

In step a) of the process according to the invention, the above-described compound (I) is reacted with steam in the gas phase, advantageously in the presence of a heterogeneous catalyst and optionally in the presence
10 of an organic diluent (III), to give a mixture (IV) containing a lactam (II).

Suitable heterogeneous catalysts are any of the catalysts described for the gas phase cyclization of a
15 compound (I) to a lactam (II), such as amorphous titanium dioxide in the form of anatase or rutile, aluminum oxide, lanthanum phosphates, hafnium oxide, zirconium dioxide or mixtures thereof, preferably titanium dioxide, aluminum oxide, lanthanum phosphates,
20 zirconium dioxide or mixtures thereof.

The diluent (III) can be added before the cyclization. In this case the diluent (III) is present during the cyclization of the compound (I) in the gaseous reaction
25 mixture, preferably in amounts of 0.1 to 20 g of diluent (III) per gram of compound (I).

It is preferred to add the diluent (III) to the cyclization discharge, for example by quenching the
30 cyclization discharge.

A further possibility is to add the diluent (III) after the separation of ammonia from the mixture (IV).

The diluents (III) used can be organic compounds which exhibit a miscibility gap with water under specific quantity, pressure and temperature conditions, especially below the reaction temperature in the cyclization.

Suitable diluents (III) are C₄- to C₉-alkanols such as n-butanol, i-butanol or n-pentanol, preferably aliphatic hydrocarbons such as n-hexane, cycloaliphatic hydrocarbons such as cyclopentane or cyclohexane, and especially aromatic hydrocarbons such as benzene, toluene, o-xylene, m-xylene, p-xylene, ethylbenzene, i-propylbenzene or di-i-propylbenzene, and mixtures of such compounds, for example petroleum ethers. The hydrocarbons can carry functional groups such as halogens, for example chlorine, as in chlorobenzene.

Ammonia can also be present in the reaction of step a).

The reaction can advantageously be carried out in the gas phase at temperatures generally of 200 to 450°C, preferably of 250 to 400°C. The pressure should generally range from 0.01 to 20 bar, preferably from 0.1 to 5 bar. The reaction mixture should be predominantly gaseous in this reaction. The residence times generally range from 0.1 to 100 seconds, preferably from 1 to 50 seconds.

The amount of water used in the cyclization should generally be at least 0.5 mol, preferably at least 1 to 50 mol, per mol of compound (I).

The reaction can be carried out in the presence of an inert gas such as nitrogen or a noble gas or mixtures of such gases.

The reaction of step a) gives a mixture (IV) containing a lactam (II).

5 Provided the mixture (IV) contains ammonia, the ammonia can be separated from the mixture (IV) in step b) after or, preferably, before the phase separation, preferably by distillation, to give an ammonia-free or ammonia-poor mixture (IX). The ammonia can also be separated from the phase (V) and/or the phase (VI) after the
10 phase separation, preferably by distillation.

The mixture (IV) can contain ammonia e.g. if ammonia is formed in the reaction of step a) and/or if ammonia has been added to the reaction mixture in the reaction of
15 step a). Ammonia can be formed in the reaction of step a) e.g. if R is a nitrile or carboxamide group.

The separation can advantageously be effected by distillation, especially at bottom temperatures of 60
20 to 220°C and pressures of 1 to 30 bar.

If the mixture (IV) does not contain ammonia - this also being understood as including such small traces of ammonia as would not adversely affect the following
25 process steps - the mixture (IV) and the mixture (IX) are identical.

In step b), according to the invention, the mixture (IX) is converted under quantity, pressure and
30 temperature conditions such that the diluent (III) and water are in liquid form and exhibit a miscibility gap, to give a two-phase system consisting of a phase (V) and a phase (VI).

Preferred quantity, pressure and temperature conditions are such that the constituents of the mixture (VII) are in completely liquid form in the phases (V) and (VI), i.e. no solids precipitate out.

5

If step a) has been carried out in a homogeneous liquid phase, it is generally possible to separate the mixture (VII) into the two phases (V) and (VI) by choosing an appropriate temperature. A further possibility is to
10 choose appropriate proportions, such as the addition of diluent (III), preferably water.

According to the invention, the phase (V) and the phase (VI) are then separated in step c).

15

The phase separation can be effected in a manner known per se in apparatuses described for such purposes, for example those known from Ullmann's Encyclopedia of Industrial Chemistry, vol. B3, 5th ed., VCH
20 Verlagsgesellschaft, Weinheim, 1988, pages 6-14 to 6-22.

The optimum apparatuses and process conditions for the phase separation can easily be determined by a few
25 simple preliminary experiments.

In step d), according to the invention, the diluent (III), optionally ammonia and optionally by-products selected from the group consisting of low-boiling
30 component [sic] (VIII), high-boiling component [sic] (VII) and unreacted compound (I) are separated from the phase (V) to give a lactam (II).

In terms of the present invention, low-boiling
35 component [sic] (VIII) are understood as meaning

compounds boiling below the lactam (II) and high-boiling component [sic] (VII) are understood as meaning compounds boiling above the lactam (II).

- 5 This work-up can advantageously be effected by fractional distillation in one or more, such as 2 or 3, distillation apparatuses.

10 Suitable apparatuses are those conventionally used for distillation, for example the ones described in Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd ed., vol. 7, John Wiley & Sons, New York, 1979, pages 870-881, such as sieve-plate columns, bubble-cap columns or packed columns.

15 Preferably, any ammonia and diluent (III) still present are appropriately separated from the phase (V) first. The high-boiling components (VII), the low-boiling components (VIII) and any unreacted compound (I) can
20 then be separated from the lactam (II), individually or together.

Advantageously, all or part of the diluent (III) obtained in step d) can be recycled into step a).

25 Advantageously, all or part of any high-boiling components (VIII) [sic] and/or low-boiling components (VII) [sic] obtained in step d) can be recycled into step a).

30 Advantageously, all or part of any unreacted compound (I) obtained in step d) can be recycled into step a).

35 The phase (VI) obtained in step c) can advantageously be recycled into step a).

Preferably, all or part of the lactam (II) can be separated from the phase (VI) to give a mixture (X), and the low-boiling components (VIII) and/or high-boiling components (VII) can optionally be separated
5 from the resulting lactam (II).

This work-up of the lactam (II) can advantageously be effected by fractional distillation in one or more, such as 2 or 3, distillation apparatuses.

10

Suitable apparatuses are those conventionally used for distillation, for example the ones described in Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd ed., vol. 7, John Wiley & Sons, New York, 1979, pages
15 870-881, such as sieve-plate columns, bubble-cap columns or packed columns.

The high-boiling components (VII) and/or low-boiling components (VIII) can be separated from the lactam (II)
20 individually or together.

Advantageously, all or part of the high-boiling components (VII) and/or low-boiling components (VIII) can be recycled into step a).

25

Particularly preferably, the high-boiling components (VII) are appropriately recleaved before being recycled into step a), as described e.g. in EP-A-793650, EP-A-793651, EP-A-794643 or EP-A-912508.

30 Before the work-up, the lactam (II) obtained from the phase (VI) can also be combined with the crude lactam (II) obtained in step d) and the two worked up together.

The phase (X) can advantageously be recycled into step a).

5 All or part of the lactam (II) can be separated from the phase (VI) by extraction with a liquid extractant (XI) to give a mixture (XII) containing an extractant (XI) and a lactam (II).

10 Suitable extractants (XI) are C₄- to C₉-alkanols such as n-butanol, i-butanol or n-pentanol, preferably aliphatic hydrocarbons such as n-hexane, cycloaliphatic hydrocarbons such as cyclopentane or cyclohexane, and especially aromatic hydrocarbons such as benzene, toluene, o-xylene, m-xylene, p-xylene, ethylbenzene, 15 i-propylbenzene or di-i-propylbenzene, and mixtures of such compounds, for example petroleum ethers. The hydrocarbons can carry functional groups such as halogens, for example chlorine, as in chlorobenzene.

20 In particular, the extractants (XI) and the diluents (III) have the same or a similar composition.

Thus diluent (III) separated off in step d) can advantageously be used as the extractant (XI).

25 The aqueous phase (X) remaining from the extraction can advantageously be recycled into step a).

30 The extractant (XI) and optionally the low-boiling components (VIII), the high-boiling components (VII) and/or unreacted compound (I) can advantageously be separated from the mixture (XII) to give a lactam (II).

This work-up can advantageously be effected by fractional distillation in one or more, such as 2 or 3, distillation apparatuses.

5 Suitable apparatuses are those conventionally used for distillation, for example the ones described in Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd ed., vol. 7, John Wiley & Sons, New York, 1979, pages 870-881, such as sieve-plate columns, bubble-cap columns or
10 packed columns.

Preferably, the extractant (XI) is appropriately separated from the mixture (XII) first. The high-boiling components, the low-boiling components and any
15 unreacted compound (I) can then be separated from the lactam (II) individually or together.

Advantageously, all or part of the extractant (XI) obtained in the work-up can be recycled into step a).
20

Advantageously, all or part of any high-boiling components (VII) and/or low-boiling components (VIII) obtained in the work-up can be recycled into step a).

25 Advantageously, all or part of any unreacted compound (I) obtained in the work-up can be recycled into step a).

The mixture (XII) and the phase (V) can advantageously
30 be used together in step d) of the process according to the invention, it being possible for them to be combined before or during step d).

The lactams obtained in the process according to the invention can be used in a manner known per se for the

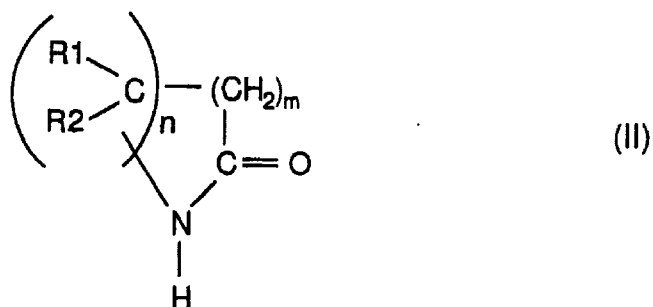
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preparation of industrially important polymers such as polyamides.

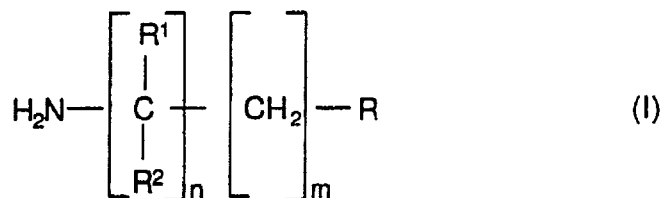
We claim:-

1. A process for the preparation of cyclic lactams of formula (II):



in which n and m can each have the values 0, 1, 2, 3, 4, 5, 6, 7, 8 and 9 and the sum of n + m is at least 3, preferably at least 4, and R¹ and R² are C₁-C₆-alkyl, C₅-C₇-cycloalkyl or C₆-C₁₂-aryl groups,

by reacting a compound (I) of the formula



in which R¹, R², m and n are as defined above and R are [sic] nitrile, carboxamide and carboxylic acid groups,

with steam in the gas phase, wherein

- a) the compound (I) is reacted with steam in the gas phase with the addition, before or after the reaction, of an organic diluent (III) which exhibits a miscibility gap with water

under specific quantity, pressure and temperature conditions, to give a mixture (IV) containing a lactam (II),

5

b) the mixture (IV) is converted, before or after the separation of ammonia, under quantity, pressure and temperature conditions such that the diluent (III) and water are liquid and exhibit a miscibility gap, to give a two-phase system consisting of a phase (V) containing a higher proportion of diluent (III) than water, and a phase (VI) containing a higher proportion of water than diluent (III),

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c) the phase (V) is separated from the phase (VI), and

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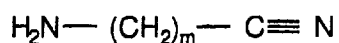
d) the diluent (III) and optionally by-products selected from the group consisting of low-boiling component [sic], high-boiling component [sic] and unreacted compound (I) are separated from the phase (V) to give a lactam (II).

2. A process as claimed in claim 1 wherein the compound (I) used is an aminocarboxylic acid nitrile.

30

3. A process as claimed in claim 1 or 2 wherein the compound (I) used is an aminocarboxylic acid nitrile of the formula

35



in which m is 3, 4, 5 or 6.

4. A process as claimed in any of claims 1 to 3
wherein the compound (I) used is 6-aminocarboxylic
5 [sic] acid nitrile.
5. A process as claimed in any of claims 1 to 4
wherein step a) is carried out in the presence of
a heterogeneous catalyst.
10
6. A process as claimed in claim 5 wherein the
heterogeneous catalyst used is titanium dioxide,
aluminum oxide, lanthanum phosphates or zirconium
dioxide.
15
7. A process as claimed in any of claims 1 to 6
wherein the reaction of step a) is carried out at
a temperature ranging from 200 to 450°C.
- 20 8. A process as claimed in any of claims 1 to 7
wherein the sum of the concentrations of compound
(I) and compound (II) is less than 20% by weight,
based on the mixture (IV).
- 25 9. A process as claimed in any of claims 1 to 8
wherein the diluent (III) used is an aliphatic,
cycloaliphatic or aromatic hydrocarbon.
- 30 10. A process as claimed in any of claims 1 to 9
wherein the diluent (III) used is ethylbenzene,
benzene, toluene, o-xylene, m-xylene or p-xylene.
11. A process as claimed in any of claims 1 to 10
wherein the separation of ammonia from the mixture

(IV) is effected before the separation of the phase (V) in step c).

- 5 12. A process as claimed in any of claims 1 to 11 wherein the reaction of step a) is carried out in a homogeneous liquid phase.
- 10 13. A process as claimed in any of claims 1 to 12 wherein all or part of the phase (VI) separated off in step c) is recycled into step a).
- 15 14. A process as claimed in any of claims 1 to 13 wherein all or part of the lactam (II) is separated from the phase (VI) separated off in step c) to give a phase (X) containing less lactam (II) than the phase (VI), and by-products selected from the group consisting of low-boiling component [sic] (VIII) and high-boiling component [sic] (VII) are optionally separated from the resulting
20 lactam (II).
- 25 15. A process as claimed in any of claims 1 to 14 wherein all or part of the lactam (II) is separated from the phase (VI) by extraction with an extractant (XI) to give a mixture (XII) containing extractant (XI) and lactam (II), and a phase (X) containing less lactam (II) than the phase (VI).
- 30 16. A process as claimed in claim 14 or 15 wherein all or part of the phase (X) is recycled into step a).
- 35 17. A process as claimed in any of claims 5 to 16 wherein the extractant (XI) and optionally by-products selected from the group consisting of

low-boiling component [sic] (VIII) and high-boiling component [sic] (VII) are separated from the mixture (XII) to give a lactam (II).

- 5 18. A process as claimed in any of claims 5 to 17 wherein the mixture (XII) and the phase (V) are used together in step d).
- 10 19. A process as claimed in any of claims 5 to 18 wherein the extractant (XI) and the diluent (III) consist of the same components or have the same composition.
- 15 20. A process as claimed in any of claims 13 to 19 wherein the lactam (II) is separated only from the partial stream of phase (VI) which is not returned to the cyclization step, and all or part of the remainder of phase (VI) is recycled into step a) without recovering the lactam (II).
- 20 21. A process as claimed in any of claims 1 to 20 wherein all or part of the unreacted compound (I) separated off in step d) is recycled into step a).
- 25 22. A process as claimed in any of claims 1 to 21 wherein all or part of the high-boiling components (VII) separated off in step d) is recycled into step a).
- 30 23. A process as claimed in claim 22 wherein the high-boiling components (VII) separated off in step d) contain at least 20% by weight of lactam (II).

24. A process as claimed in any of claims 1 to 23 wherein all or part of the diluent (III) separated off in step d) is recycled into step a).
- 5 25. A process as claimed in any of claims 1 to 24 wherein all or part of the low-boiling components (VIII) separated off in step d) is recycled into step a).
- 10 26. A process as claimed in any of claims 15 to 25 wherein the diluent (III) separated off in step d) is used as the extractant (XI).
- 15 27. A process as claimed in any of claims 1 to 26 wherein all or part of the lactam (II) is extracted from the phase (V) or the phase (XII) with water to give a phase (XIII) impoverished in lactam (II) and a phase (XIV) enriched in lactam (II), and all or part of the phase (XIII) is
20 recycled into step a).
28. A process as claimed in any of claims 1 to 27 wherein the high-boiling stream (VII) recycled into step a) is combined with the recycled stream
25 (VI) or (X) before step a).