

Preparation of primary diamines having a linear main chain for polyamide syntheses

5 The invention relates to the catalytic conversion of diols having a linear main chain and from 4 to 31 carbon atoms into the corresponding diamines. The reaction is carried out in the liquid or supercritical phase using homogeneous ruthenium-containing complexes as catalysts. The advantage of the invention is the production of primary diamines in such a selectivity and purity that they are suitable for polyamide syntheses.

10 The diols used in the process of the invention are converted directly by means of ammonia in one step without the additional presence of molecular hydrogen into the corresponding diamines. The ruthenium-containing catalyst required for this purpose preferably contains one or more coordinating ligands from the group of phosphorus(III) compounds or ligands which contain both P(III)-containing groups and further coordinating sites for the active metal in addition to the active metal.

15 A number of processes in the liquid, gaseous or supercritical phase have been described in science and industry for the conversion of alcohols by means of ammonia into primary amines. The challenge for these processes is to achieve high selectivities to the primary amine. Since alkylamines are more nucleophilic than ammonia and their nucleophilicity increases with the number of alkyl groups on the nitrogen atoms, secondary and tertiary linear amines are preferentially formed. In addition, a limited selectivity to the diamine has been observed when diols are used as starting material in such reactions because appreciable amounts of intermediate amino alcohol have frequently also been isolated.

25 In the case of relatively short-chain diols, cyclization as alternative reaction also plays a significant role (e.g. Fischer et al., Catal. Today 1997, 37, 167-189).

Direct conversion of alcohols into primary amines by means of ammonia over heterogeneous catalysts in a liquid, gaseous or supercritical phase:

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The reaction in the gas phase is possible for readily vaporizable lower alcohols and

diols. It is carried out over heterogeneous catalysts in the presence of NH_3 and H_2 . The high temperatures of up to 400°C and pressures of up to 300 bar which are necessary here frequently bring about the formation of undesirable intermediates, by-products and subsequent products, e.g. secondary and tertiary amines, alkenes and alkanes (by means of dehydration/hydrogenation), cyclic species and in the case of diols also amino alcohols. Direct aminations over heterogeneous catalysts have also been carried out in the liquid phase; in some cases, it is difficult to distinguish between gas and liquid phase on the basis of the available data. Examples of the reaction over heterogeneous catalysts are the patents and literature references mentioned below.

Thus, EP 0963975 describes the direct amination of, inter alia, primary alcohols and 1,2- to 1,6-diols over oxidic ZrO_2 -supported Cu-Ni-Co catalysts in the presence of hydrogen. Depending on the reaction conditions, amino alcohols, cyclic compounds or diamines can be obtained, with the diamine selectivities described being low. In DE 1543377, C4-C8-diols are hydrogenatively aminated to the diamines over Co-Cr-Mn catalysts in the presence of P_4O_{10} , sometimes under hydrogen pressures of up to 300 bar; in this way, 86.5% of hexamethylenediamine can be prepared from 1,6-hexanediol in a single pass. DE 102006061045 (over Ni-Cu/ ZrO_2 catalysts) and DE 102006061042 (over Ni-Cu-Ru/ ZrO_2 catalysts) describe the hydrogenative amination of alcohols or dihydroxy and polyhydroxy compounds in the range from 180°C to 220 - 250°C , but preferably of stearyl alcohols.

WO 9638226 describes the direct hydrogenative amination of, inter alia, C2-C6-alcohols and -diols, also those having further functional groups, by means of ammonia over Re-Cu-Ni-Co catalysts and/or Ru catalysts. WO 2007093514 and WO 2007093552 describe the hydrogenative amination of ethylene glycol over Ru-Co catalysts; ethylenediamine was isolated in yields of up to 57% together with further products. In the examples, only monoethanolamine is used as substrate. Cyclohexanol is reacted with NH_3 and 200 bar of H_2 at 260 - 300°C over Ca aluminosilicates to form cyclohexylamine. The preparation of various primary monoamines is described in DE 19859776 (over Cu-CuO/ TiO_2 catalysts), WO 2008072428 (over Ru/ ZrO_2 catalysts)

and WO 2007077903 (over Ru/Al₂O₃ catalysts) at reaction temperatures of 180-250°C.

Various diether or polyether diols have likewise been subjected to direct hydrogenative aminations using ammonia. DE 3903367 describes the amination of diethylene glycol
5 over oxidic Zr-Cu-Ni-Co catalysts, giving aminoethoxyethanol and morpholine as main products. Polyether diols are hydrogenatively aminated directly over Raney Ni or Raney Co catalysts at 220-250°C, with 0.06-0.12% of higher amines being formed. The preparation of polyetheramines in US 4153581 is carried out at 140°C over Co-Cu catalysts which contain Zn, Zr or Fe as further active components; here, the proportion
10 of aminated products in the reaction mixture is only 12-60 per cent by weight.

Baiker and coworkers have published a study on the continuous direct amination of propanediol in supercritical ammonia (Angew. Chem. Int. Ed. 1999, 38, 351-354). Here too, the problems of the selectivity to the diamine, which does not exceed 20%, are
15 discussed.

The additional use of hydrogen in a hydrogenative amination in which the use of heterogeneous catalysts is necessary is costly. Such processes are not suitable for relatively long-chain linear aliphatic alcohols and diols because the at least partial
20 decomposition of starting material and product under the reaction conditions required would make the economics questionable. In addition, the achievable selectivities to the diamine are not competitive for applications in the polyamide field.

Direct conversion of alcohols into primary amines by means of ammonia using
25 homogeneous catalysts in the liquid phase:

Only very few examples of the homogeneously catalysed direct amination of primary and secondary alcohols in liquid phase are known in the scientific and patent literature. Here, the use of ruthenium catalysts permits the concept of "borrowing hydrogen"
30 (Williams et al. Adv. Synth. Catal. 2007, 349, 1555-1575), i.e. hydrogen does not have to be additionally introduced since the H₂ equivalent which is initially liberated during the

dehydrogenation of the alcohol in the first reaction step is "parked" on the catalyst and is reintroduced into the cycle in a later phase. Milstein and coworkers (Angew. Chem. Int. Ed. 2008, 47, 8661-8664) report the selective reaction of monohydric, including functionalized, alcohols in the liquid phase in the presence of excess ammonia and the

5 ruthenium-PNP pincer complex carbonylchloro[4,5-bis(diisopropylphosphinomethyl)-acridine]hydridoruthenium(II). The yields of primary amine were 78-96%. The reactions were carried out in a solvent at 7.5 bar, 135-180°C over a period of 12-36 hours.

Polyhydric alcohols were not aminated, nor were secondary alcohols. In addition, WO 2010018570 also describes the use of quinolinyln-based PNP pincer ligands, with

10 comparable results. DE 102010040560 describes the amination of exclusively secondary monoalcohols using carbonylchloro[4,5-bis(diisopropylphosphinomethyl)-acridine]hydridoruthenium(II).

Beller and coworkers (Angew. Chem. 2010, 122, 8303) and Vogt and coworkers (Angew. Chem. 2010, 122, 8307) both describe the preparation of primary amines from

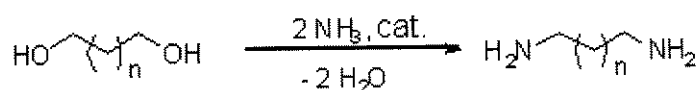
15 secondary alcohols in yields of up to 93% using a catalyst prepared in situ from the Ru and P(III) precursor compounds dodecacarbonyltriruthenium(0) and 2-(dicyclohexylphosphino)-1-phenyl-1*H*-pyrrole (cataCXium®PCy). Here too, no diols were used as starting materials.

20 It cannot be assumed from the abovementioned patent documents and literature references that the catalytic processes described can be applied in the same way to polyhydric alcohols. The abovementioned secondary reactions can play a selectivity-limiting role; in addition, oligomerizations via amino alcohols formed as intermediates are possible in the liquid phase. It is therefore an object of the present invention to

25 provide a single-stage process which gives primary amines having a linear main chain. The advantage of such a process over the prior art is the direct selective production of such diamines in a high purity which allows, after an optional further, simple purification step, direct use of the diamines in the production of polyamides. This results in a substantial technical simplification of such a process.

30 The present invention provides a process for preparing primary diamines having a

linear main chain from the corresponding diols by reaction with ammonia and/or an ammonia-liberating compound or mixtures thereof in a liquid or supercritical phase in the presence of a homogeneous ruthenium catalyst. The process of the invention preferably provides for the direct reaction of one or more diols having a linear main chain and from 4 to 31 carbon atoms, preferably having a main chain of C5 to C31, and particularly preferably having a main chain of from C6 to C31, with ammonia and/or an ammonia-liberating compound or mixtures thereof as nitrogen source by the method of "borrowing hydrogen", i.e. without an additional external hydrogen source. Reaction equation 1 shows, for the purposes of illustration, a general scheme of the reaction for the illustrated group of straight-chain, α,ω -diols with ammonia, without these specific examples constituting a restriction. Primary diamines which have a linear main chain and are suitable for use as monomers in the production of polyamides can in this way be synthesized directly from the diols.



Reaction equation 1:

General scheme for the reaction of diols having a linear main chain with ammonia to form the corresponding primary diamines for the illustrated reaction of the group of straight-chain, α,ω -diols ($n = 2-29$; cat = Ru catalyst).

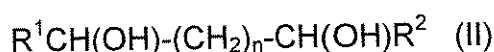
For the purposes of the present invention, "diols having a linear main chain" are diols of the general formula (I),



where R^1 and R^2 are each, independently of one another, hydrogen or substituents having 1-7 carbon atoms, preferably hydrogen or alkyl groups having 1-7 carbon atoms, more preferably hydrogen or methyl, and the unit X is a saturated or unsaturated organic radical which may comprise elements of the boron, carbon, nitrogen and

oxygen groups of the Periodic Table (main groups 3-6 of the Periodic Table), particularly preferably the elements carbon, nitrogen and oxygen. X is preferably a carbon main chain unit having n alkylene units (-CH₂- groups), i.e. the diols are diols of the general formula (II),

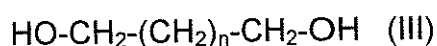
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where R¹ and R² each have, independently of one another, the above meanings, in particular hydrogen or methyl, and n = 0-29, preferably n = 1-29 and particularly

10 preferably n = 2-29.

Very particular preference is given to straight-chain diols of the general formula (III),



15 where n = 2-29, preferably n = 3-29 and particularly preferably n = 4-29.

In the case of mixtures of compounds of the general formulae (I), (II) and (III), the proportion in the mixture of the compound present in the smallest amount is, based on the mixture, less than 50% by weight, preferably less than 10% by weight, even more preferably less than 1% by weight and very particularly preferably less than 0.1% by

20 weight.

Advantages of the process of the invention are the avoidance of multistage processes and the formation of coproducts. No intermediate isolation and purification steps have to be inserted. It is possible to use heat-sensitive substrates, for example ones based

25 on renewable raw materials. This makes it possible to obtain new diamine components for the synthesis of high-quality polyamides, which components have previously not been available or not been available in this quality.

The process of the invention for preparing primary diamines having a linear main chain

30 preferably comprises the following steps:

I. Charging of a reaction vessel with one or more diols having a linear main chain

either a) as fluid phase by dissolution or suspension in a suitable solvent or solvent mixture or b) as fluid phase by melting of the one or more diols or c) as solid phase by dry charging of the one or more diols or d) a combination thereof, optionally with mixing-in of a ruthenium catalyst or precursor compounds thereof to one of the abovementioned procedures a) to d).

II. Addition of a ruthenium catalyst or precursor compounds thereof, if not already done in step 1, and of ammonia and/or an ammonia-liberating compound or mixtures thereof.

III. Setting of the required reaction conditions and carrying-out of the reaction.

IV. Optionally isolation and purification of the diamine or diamines formed.

Suitable reaction vessels for carrying out the reactions are, for example, all conventional types of autoclaves and also all conventional types of apparatuses which operate according to the principle of cocurrent or countercurrent material flow, for instance tube reactors, without this naming representing a restriction; all these can, depending on the specific medium and/or depending on the specific conditions of the respective reaction, be operated under atmospheric pressure or under pressures of 1-1000 bar, preferably 5-500 bar and particularly preferably 5-100 bar. This pressure can be generated by means of the injected ammonia and/or by means of pressurization of the reactor with a further, preferably inert gas such as nitrogen or argon and/or by formation of ammonia in situ from an ammonia-liberating compound or mixtures thereof and/or by setting of the desired reaction temperature.

The catalysts used in process step II. in the process of the invention are preferably ruthenium catalysts, in particular ruthenium-ligand complexes having at least one P(III) group. Thus, the catalysts mentioned preferably contain, without this mention representing a restriction, ligands having at least one function which comprises trivalent phosphorus and is capable of coordination, for example phosphane functions. Particular preference is given to using tridentate pincer ligands which contain not only groups comprising trivalent phosphorus but also structural elements which can likewise coordinate to the ruthenium. These can be based on elements of the boron, carbon,

nitrogen and oxygen groups of the Periodic Table (main groups 3-6 of the Periodic Table). Preferred coordinating groups, without this mention representing a restriction, are C, N or O donors.

- 5 To prepare the catalysts used in process step II. in the process of the invention, it is possible, without this mention constituting a restriction, to add ruthenium in the form of precursor compounds. These are ruthenium salts or ruthenium complexes in which weakly coordinated ligands are easily replaced in situ by P(III) groups and/or by groups based on elements of the boron, carbon, nitrogen and oxygen groups of the Periodic
- 10 Table, preferably C, N or O donors, during a possible preforming of the catalyst or during combining of the ruthenium component and the ligand component. Examples of such ruthenium precursor compounds of the ruthenium catalyst to be used, but without the mention thereof constituting a restriction, are ruthenium(III) chloride, ruthenium(III) acetate, ruthenium(III) acetylacetonate, dodecacarbonyltriruthenium(0),
- 15 carbonylchlorohydridotris(triphenylphosphane)ruthenium(II) or di- μ -chlorobis[chloro(p-cymene)ruthenium(II)].

Preferred catalysts for the process are, without the mention thereof constituting a restriction, ruthenium complexes having tridentate pincer ligands or ruthenium

20 complexes having monodentate or bidentate phosphanes. These can be produced, analogously to the abovementioned procedure, in situ from corresponding suitable precursors as mixtures in which they are present; it is likewise possible, without this particular procedure constituting a restriction, to use ruthenium-ligand complexes which have previously been isolated as such by appropriate methods by a person skilled in

25 the art as catalysts for this purpose. Particularly preferred catalysts which may be mentioned by way of example, without this mention constituting a restriction, are ruthenium complexes having tridentate pincer ligands, in particular carbonylchloro[4,5-bis(diisopropylphosphinomethyl)acridine]hydridoruthenium(II), or ruthenium complexes having a monodentate or bidentate phosphane, or a complex

30 prepared in situ from dodecacarbonyltriruthenium(0) and the phosphane 2-(dicyclohexylphosphino)-1-phenyl-1*H*-pyrrole (cataCXium®PCy).

As preferred amount of the ruthenium catalyst or the corresponding Ru- and P(III)-containing precursor compounds, an amount, based on the diol, in the range 0.01-20 mol%, preferably in the range 0.01-6 mol% and particularly preferably in the range 0.25-6 mol%, is added.

As preferred ratio of Ru to P(III) groups in catalysts prepared beforehand in isolated form or prepared in situ from corresponding suitable precursor compounds or mixtures in which they are present, a molar ratio in the range 1:1-1:20, preferably in the range 1:2-1:6 and particularly preferably in the range 1:2-1:3 is selected in the case of ruthenium complexes having tridentate pincer ligands or bidentate phosphanes; while in the case of ruthenium complexes having monodentate phosphanes the preferred molar ratio is in the range 1:1-1:20, preferably in the range 1:1-1:6, and particularly preferably in the range 1:1-1:2.

In the process of the invention, ammonia and/or an ammonia-liberating compound or mixtures thereof is/are added in process step II. Examples of such compounds, without this listing constituting a restriction, are urea, uric acid, ammonium salts and derivatives of a primary amide, for example, without this listing constituting a restriction, symmetrical and unsymmetrical carbamates, carbaminates, semicarbazides and semicarbazoles and also aminium salts or organic or inorganic esters of all these. Preference is given to using ammonia itself, with liquid or gaseous ammonia being able to be used in this embodiment.

As preferred molar ratio of the sum of the hydroxy functions of the one or more diols to the equivalents of ammonia, which can be formed from the ammonia introduced and/or the ammonia-liberating compound or the sum of such compounds, a value in the range 1:2-1:5000, preferably in the range 1:10-1:1000 and particularly preferably 1:20-1:500, is set.

As preferred reaction temperature in process step III. of the process of the invention, a temperature in the range 60-220°C, preferably in the range 90-180°C and particularly

preferably in the range 125-165°C, is set.

As preferred pressure during the reaction in the process of the invention, a pressure in the range 1-1000 bar, preferably 5-500 bar and particularly preferably 5-100 bar, is set.

- 5 This pressure can be generated by means of the injected ammonia and/or by pressurizing the reactor with a further, preferably inert gas such as nitrogen or argon and/or by means of ammonia formed in situ from an ammonia-liberating compound or mixtures thereof and/or by setting the desired reaction temperature.
- 10 As preferred concentration of the diol or diols used in a solvent or a supercritical medium during the reaction in the process of the invention, a concentration in the range 0.1-10 000 mmol/l, preferably in the range 5-1000 mmol/l and particularly preferably in the range 10-500 mmol/l, is set. As supercritical medium, preference is given to using supercritical ammonia.

- 15 It is possible to use solvents or solvent mixtures. Organic solvents selected from the group consisting of tertiary and neopentyl alcohols, ethers, arenes and aliphatics can preferably be used. Particular preference is given to using, without this mention representing a restriction, tert-butanol, 2-methyl-2-butanol, toluene, xylene, mesitylene, dioxane, tetrahydrofuran, cyclohexane, methyl tert-butyl ether and anisole or mixtures thereof. There are no particular requirements regarding the purity of the solvents.
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- The diamines having a linear main chain which are formed in process step III. can optionally be isolated and purified in a process step IV. For example, the reaction mixture obtained can be filtered and subjected to a distillation in order to isolate the diamine or diamines formed. Further purification methods known to those skilled in the art are likewise possible. For example, it is possible, without this mention implying a restriction, to feed a primary diamine having a linear main chain which has been prepared by the reaction according to the invention after purification or directly to a subsequent polycondensation by preparing the diaminium dioate ("nylon salt") to be used in this polycondensation in situ by addition of an approximately stoichiometric
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amount of the appropriate dicarboxylic acid, purifying or isolating it by methods known to those skilled in the art and subsequently using it in the polycondensation.

The invention is illustrated below by examples which are not to be interpreted as a
5 restriction of the invention.

Example 1

Reaction of 1,19-nonadecanediol

3.01 g (10.0 mmol) of 1,19-nonadecanediol and 151 mg (0.25 mol%) of
10 carbonylchloro[4,5-bis(diisopropylphosphinomethyl)acridine]hydridoruthenium(II) are
dissolved under protective gas in 25 ml of 2-methyl-2-butanol and transferred to an
autoclave provided with stirrer, heating and temperature measuring facility. 6 ml of
liquid ammonia are subsequently introduced into the autoclave by means of a spindle
press. The autoclave is closed and the contents are stirred at 140°C for 48 hours. This
15 results in an increase in the internal pressure from 22 to 40 bar. After cooling, the
contents of the reactor are filtered through kieselguhr, the filtrate is evaporated to
dryness and the residue is subjected to a bulb tube distillation. Yield of linear primary
diamine: 2.02 g (68% of theory; $bp_{0.8\text{ mbar}} = 170-185^{\circ}\text{C}$), conversion of the linear
diol: > 99%.

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Example 2

Reaction of 1,12-dodecanediol

Reaction and work-up were carried out under the same conditions as in Example 1
using 10.0 mmol of 1,12-dodecanediol. Yield of linear primary diamine: 1.36 g (68% of
25 theory; $bp_{0.8\text{ mbar}} = 115-125^{\circ}\text{C}$), conversion of the linear diol: >99%.

Example 3

Reaction of 1,8-octanediol

The reaction was carried out under the same conditions as in Example 1 using
30 10.0 mmol of 1,8-octanediol. Yield and conversion were determined by gas
chromatography using commercially available reference compounds. Yield of linear

primary diamine: 78%, conversion of the linear diol: >99%.

Example 4

Reaction of 1,6-hexanediol

- 5 The reaction was carried out under the same conditions as in Example 1 using 10.0 mmol of 1,6-hexanediol. Yield and conversion were determined by gas chromatography using commercially available reference compounds. Yield of linear primary diamine: 55%, conversion of the linear diol: >99%.

10 Example 5

Reaction of 1,8-octanediol

- A mixture of 10.0 mmol of 1,8-octanediol, 12 mol% of 2-(dicyclohexylphosphino)-1-phenyl-1*H*-pyrrole (cataCXium®PCy) and 4 mol% of Ru₃(CO)₁₂ is dissolved under protective gas in 25 ml of 2-methyl-2-butanol and transferred to an autoclave provided with stirrer, heating and temperature measuring facility. 6 ml of liquid ammonia are subsequently introduced into the autoclave by means of a spindle press. The autoclave is closed and the contents are stirred at 170°C for 48 hours. This resulted in an increase in the internal pressure from 22 to 40 bar. After cooling, the contents of the reactor are filtered through kieselguhr. Yield and conversion are determined by gas chromatography using commercially available reference compounds. Yield of linear primary diamine: 17%, conversion of the linear diol: 96%.
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Claims:

1. Process for preparing primary diamines having a linear main chain from the
5 corresponding diols by reaction with ammonia and/or an ammonia-liberating
compound or mixtures thereof in a liquid or supercritical phase in the presence of a
homogeneous ruthenium catalyst.
2. Process according to Claim 1, characterized in that one or more diols having a
10 linear main chain and from 4 to 31 carbon atoms are used.
3. Process according to Claim 1 or 2, characterized in that a ruthenium-ligand complex
having at least one P(III) group is used as ruthenium catalyst.
- 15 4. Process according to Claim 3, characterized in that an Ru precursor compound of
the ruthenium catalyst to be used selected from the group consisting of
ruthenium(III) chloride, ruthenium(III) acetate, ruthenium(III) acetylacetonate,
dodecacarbonyltriruthenium(0), carbonylchlorohydridotris(triphenylphosphane)-
ruthenium(II) and di- μ -chlorobis[chloro(p-cymene)ruthenium(II)] is used for possible
20 preforming of the catalyst or preparing it in situ.
5. Process according to Claim 3, characterized in that ruthenium catalysts having
tridentate pincer ligands or ruthenium catalysts having monodentate or bidentate
phosphanes are used.
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6. Process according to Claim 5, characterized in that
carbonylchloro[4,5-bis(diisopropylphosphinomethyl)acridine]hydridoruthenium(II) is
used as ruthenium catalyst having a tridentate pincer ligand.
- 30 7. Process according to Claim 5, characterized in that a complex prepared in situ from
dodecacarbonyltriruthenium(0) and the phosphane 2-(dicyclohexylphosphino)-

1-phenyl-1*H*-pyrrole (cataCXium®PCy) is used as ruthenium catalyst.

8. Process according to one or more of Claims 1 to 7, which comprises the process steps:

- 5 I. Charging of a reaction vessel with one or more diols having a linear main chain either a) as fluid phase by dissolution or suspension in a suitable solvent or solvent mixture or b) as fluid phase by melting of the one or more diols or c) as solid phase by dry charging of the one or more diols or d) a combination thereof, optionally with mixing-in of a ruthenium catalyst or precursor compounds thereof,
10 to one of the abovementioned procedures a) to d).
II. Addition of a ruthenium catalyst or precursor compounds thereof, if not already done in step 1, and of ammonia and/or an ammonia-liberating compound or mixtures thereof.
III. Setting of the required reaction conditions and carrying-out of the reaction.
15 IV. Optionally isolation and purification of the diamine or diamines formed.

9. Process according to Claim 8, characterized in that the reaction temperature is set in the range 60-220°C in process step II.

20 10. Process according to one or more of Claims 1 to 9, characterized in that ammonia is used in the form of liquid or gaseous ammonia.

11. Process according to one or more of Claims 1 to 10, characterized in that the molar ratio of the sum of the hydroxy functions of the one or more diols to the equivalents
25 of ammonia which can be formed from the ammonia used and/or the ammonia-liberating compound or the sum of such compounds is set in the range 1:2-1:5000.

12. Process according to one or more of Claims 1 to 11, characterized in that the reaction is carried out at reaction pressures in the range 1-1000 bar.

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13. Process according to Claim 12, characterized in that the reaction pressure is

generated by means of ammonia and/or by introduction of a further, preferably inert gas such as nitrogen or argon into the reactor and/or by ammonia formed in situ from an ammonia-liberating compound or mixtures thereof and/or by setting of the desired reaction temperature.

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14. Process according to one or more of Claims 8 to 13, characterized in that organic solvents selected from the group consisting of tertiary and neopentyl alcohols, ethers, arenes and aliphatics are used.

10 15. Process according to Claim 14, characterized in that the organic solvent is selected from among tert-butanol, 2-methyl-2-butanol, toluene, xylene, mesitylene, dioxane, tetrahydrofuran, cyclohexane, methyl tert-butyl ether and anisole and mixtures thereof.