

The title of the invention is:

Method of influencing the cis/trans isomer ratio of
3-aminomethyl-3,5,5-trimethylcyclohexylamine in its preparation
from 3-cyano-3,5,5-trimethylcyclohexanone

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REPLACED SHEETS		SG
☒ Description	: paged 1 to paged 9	
☒ Claim(s)	: paged 10 to paged 11	
☐ Drawing(s)	: paged — to paged —	
☒ Abstract	: paged 12 to paged —	

REPLACED SHEETS		SG
☒ Description	: paged 1 to paged 9	
☒ Claim(s)	: paged 10 to paged 11	
☐ Drawing(s)	: paged — to paged —	
☒ Abstract	: paged 12 to paged —	

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preparation from 3-cyano-3,5,5-trimethylcyclohexanone

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Description

The invention relates to a method of influencing the cis/
trans isomer ratio of 3-aminomethyl-3,5,5-trimethylcyclo-
10 hexylamine (isophoronediamine; IPDA) in its preparation
from 3-cyano-3,5,5-trimethylcyclohexanone
(isophoronenitrile; IPN). The preparation of
isophoronediamine is based on the aminating hydrogenation
of isophoronenitrile with ammonia and hydrogen in the
15 presence of a hydrogenation catalyst.

Isophoronediamine is used as a starting material for the
preparation of isophorone diisocyanate, which is an
isocyanate component for polyurethane systems, as an amine
20 component for polyamides and as a hardener for epoxy
resins. Isophoronediamine is conventionally prepared from
isophoronenitrile, the carbonyl group being converted to an
amino group and the nitrile group to an aminomethyl group
in the presence of ammonia, hydrogen and conventional
25 hydrogenation catalysts. The starting material,
isophoronenitrile, can be obtained in known manner by the
addition of hydrogen cyanide onto isophorone - see
DE-OS 39 42 371.

30 Isophoronediamine can exist in different isomeric forms;
according to Die Angewandte Makromolekulare Chemie, 153
(1987) 1-13 (no. 2502), the isomer present to the extent of
about 75% in commercially available isophoronediamine was
found to have a chair conformation with a cis arrangement
35 of the equatorial amino group on the C¹ atom and the
equatorial aminomethyl group on the C³ atom; the isomer
present to the extent of about 25% is the trans isomer with

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an equatorial amino group and axial methylamino group. The cis and trans isomers of isophoronediamine, and the cis and trans isomers of isophorone diisocyanate obtainable therefrom, have different reactivities, which can be of technical importance for the proposed application. Thus DE-OS 42 11 454 teaches that by using a mixture of isophoronediamine isomers consisting of more than 40% of the trans isomer and less than 60% of the cis isomer as a reaction component in polyaddition resins, such as epoxy resins in particular, the pot life is lengthened and also the maximum hardening temperature is lowered. Conversely, to achieve the fastest possible reaction rate, the preferred mixtures of isophoronediamine isomers are those containing the highest possible proportion of the cis isomer.

Although the preparation of isophoronediamine from isophoronenitrile is described in many documents, they say nothing about the composition of the isomer mixture. Whereas commercially available products have a cis/trans isomer ratio of about 75 to 25, DE-OS 42 11 454 has also disclosed mixtures of IPDA isomers which contain between 50 and 70% of the trans isomer. As regards known processes for the preparation of isophoronediamine by the aminating hydrogenation of isophoronenitrile, reference is made by way of example to US 3,352,913, EP-B 0 042 119, EP-A 0 449 089, EP-A 0 394 967 and JP-A 4-300852. None of these documents gives any information on the isomer ratio.

According to the process described in US 3,352,913, isophoronenitrile is subjected to aminating hydrogenation with ammonia in the presence of cobalt-, nickel-, iron- or noble metal-containing catalysts known per se, at 50 to 150°C and at a pressure of at least 50 bar, for example 120 to 150 bar. The hydrogenation can be carried out in the

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presence or absence of organic solvents, methanol being preferred. The hydrogenation catalyst can be used in the form of a suspension catalyst or fixed bed catalyst.

- 5 DE-OS 30 11 656 teaches a two-step reaction in which isophoronenitrile is converted to 3-cyano-3,5,5-trimethyl-
iminocyclohexane in the first step and the latter is
hydrogenated to IPDA in the second step. EP-B 0 042 119
also relates to a two-step process for the preparation of
10 IPDA from IPN using a special imine formation reactor.

Another two-step process is the one described in EP-A
0 394 967 for the amination of carbonylnitriles and
iminonitriles, which also includes the preparation of IPDA
15 from IPN. The starting material is initially converted to the aminonitrile under conditions of reductive amination, i.e. in the presence of hydrogen, ammonia and a
hydrogenation catalyst, and conventionally in the presence
of an organic solvent, at moderate temperatures; the
20 nitrile group is then converted to an aminomethyl group at elevated temperature in the presence of a hydrogenation catalyst which is effective in the hydrogenation of nitrile groups. The process can be carried out either in reactors which use suspension catalysts or in reactors which use
25 fixed bed catalysts. As is apparent from the numerous Examples in said document, it was considered necessary to operate a strict temperature profile, the temperature of the first step being increased stepwise in 20°C intervals to the temperature of the second step. The time-consuming
30 temperature programme leads to a lowering of the space-time yield and hence a reduction in the economy of the process. Special promoters were additionally used in order to achieve an adequate product quality.

- 35 In view of the properties of isophoronediamine which are dependent on the cis/trans isomer ratio, the object of the present invention consists in providing a method of

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influencing the cis/trans isomer ratio of 3-aminomethyl-3,5,5-trimethylcyclohexylamine in its preparation from 3-cyano-3,5,5-trimethylhexanone. The measures according to the invention for influencing the isomer ratio should be capable of integration, in a simple manner, into processes known *per se* for the preparation of isophoronediamine from isophoronenitrile in the presence of ammonia and suspension or fixed bed catalysts for aminating hydrogenation, in the presence or absence of an organic solvent.

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A method has been found for influencing the cis/trans isomer ratio of 3-aminomethyl-3,5,5-

trimethylcyclohexylamine (isophoronediamine; IPDA) in its preparation from 3-cyano-3,5,5-trimethylhexanone

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(isophoronenitrile; IPN) by aminating hydrogenation, wherein isophoronenitrile is reacted with hydrogen in the presence of ammonia and a suspension or fixed bed

hydrogenation catalyst from the group comprising cobalt, nickel and noble metal catalysts, at a pressure of 3 to

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20 MPa and at a temperature of up to 150°C, and the resulting reaction mixture is worked up by distillation, said method being characterized in that the hydrogenation is carried out in a first step at 10°C to 90°C and in a subsequent second step at above 90°C to 150°C, the

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temperature difference between the first and second steps being at least 30°C, the reaction time when using a suspension catalyst being 5 to 30 minutes in the first step and 30 to 200 minutes in the second step, and the LHSV value when using a fixed bed catalyst being 2 to 12 h⁻¹ in

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the first step and 0.3 to 2 h⁻¹ in the second step. The LHSV value in the first step is preferably greater than 2 h⁻¹ and in the second step is preferably greater than 0.8 h⁻¹.

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Whereas a cis/trans isomer ratio of 60 to 40 is attained by using for example a cobalt fixed bed catalyst and carrying out the aminating hydrogenation in a trickle bed reactor

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using a starting mixture of isophoronenitrile, ammonia and methanol at a pressure of 60 bar and at a temperature of 120°C, the isomer ratio can be increased to 80 to 20 by carrying out the reaction in the manner according to the invention at about 40°C in the first step and 120°C in the second step. Contrary to the teaching given in EP-A 0 394 967, it is not necessary to raise the temperature stepwise and observe particular temperature jumps and residence times between the temperature of the first step and the temperature of the second step. The cis/trans isomer ratio can thus be influenced in a simple manner by choosing the temperature of the first and second steps. It is possible to achieve a further increase in the cis/trans isomer ratio compared with the abovementioned value by lowering the temperature of the first step even more, for example to room temperature. The measure according to the invention also makes it possible to comply with customers' wishes for a very specific isomer ratio.

The measure according to the invention for influencing the cis/trans isomer ratio of isophoronediamine can be integrated into the known processes for the preparation of isophoronediamine, provided said processes do not use a special imine formation catalyst. The measures according to the invention can thus be applied in processes such as those disclosed in the documents acknowledged in the introduction, or processes similar thereto.

It is known that the aminating hydrogenation can be carried out in the presence or absence of solvents. The reaction is preferably carried out in the presence of solvents because this usually enables the pressure to be reduced. Preferred organic solvents are C₁- to C₄-alcohols, cyclic ethers such as tetrahydrofuran and dioxane, and glycol monomethyl or monoethyl ether or glycol dimethyl or diethyl ether; methanol has proved to be a particularly good solvent. If a mixture of isophorone, ammonia and organic

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solvent, preferably methanol, is subjected to aminating hydrogenation, the pressure is set in the range 3 to 8 MPa, preferably 5 to 8 MPa. The temperature in such cases will usually be between 20 and 80°C in the first step and
5 between 100 and 140°C in the second step; the temperature difference between the first and second steps is preferably at least 40°C.

The catalysts which can be used for the suspension
10 hydrogenation are those which are generally known for the hydrogenating amination; in particular, they are suspension catalysts containing cobalt, nickel or ruthenium as the active element, such as Raney nickel, Raney cobalt and supported ruthenium catalysts like ruthenium-on- γ -aluminium
15 oxide. The action of the Raney catalysts can be enhanced by the concomitant use of cocatalysts from the group comprising cobalt and nickel salts.

If the aminating hydrogenation is carried out using fixed
20 bed catalysts, the reactor can be operated either as a trickle bed reactor or as a bubble reactor. In the bubble process, the liquid reaction mixture is conveyed from bottom to top so that the reactor is always flooded; in the trickle bed process, the liquid mixture is allowed to
25 trickle over the catalyst bed in the presence of hydrogen.

A trickle bed process is preferred, cobalt or ruthenium fixed bed catalysts being used in particular here. The two temperature steps required according to the invention can
30 be carried out in a single trickle bed reactor with two layers of catalyst arranged therein and with separate devices for adjusting and maintaining the desired temperature in the first and second layers. As an alternative to a single reactor with two layers, two
35 reactors each with one layer can be connected in series. Conveniently, the trickle bed reactor also contains a device for distributing the liquid mixture charged onto the

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upper layer of the reactor. Hydrogen can be fed into the trickle bed reactor either in excess or as required in order to maintain the pressure. It is less preferable to use an excess of hydrogen because it affords no advantages in respect of yield and selectivity and the apparatus is thereby simplified in that no devices are required for separation of the excess hydrogen, for condensation of the ammonia and solvent contained therein and for compression in order to recycle the excess hydrogen.

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When carrying out the method according to the invention using a trickle bed reactor with two layers or using two trickle bed reactors connected in series, it is convenient to charge onto the first catalyst bed a mixture containing 10 to 40% by weight of isophoronenitrile, 10 to 40% by weight of ammonia and methanol as the solvent, and to carry out the hydrogenation at a pressure of 5 to 8 MPa and at a temperature of 10 to 80°C in the first step and 100 to 130°C in the second step. To obtain a high cis/trans isomer ratio, the temperature of the first step is adjusted to low values, i.e. 10 to 40°C in particular.

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In another embodiment of the method according to the invention using one or two trickle bed reactors, a ruthenium fixed bed catalyst, preferably a supported ruthenium catalyst with a ruthenium content of between 0.5 and 10% by weight, is used for the first catalyst bed and a cobalt fixed bed catalyst, preferably a supported cobalt catalyst containing 10 to 70% by weight of cobalt, is used in the second layer. The height of the first and second layers is chosen so as to give the claimed LHSV values for the respective step. As the Applicant has established, ruthenium catalysts favour the formation of cis-isophoronediamine, but detract from the yield. The abovementioned combination of a small layer of a ruthenium catalyst and a larger layer of a cobalt catalyst makes it possible to produce isophoronediamine predominantly of the

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cis configuration, especially if the temperature is kept low in the first step.

The particular advantages of the method according to the invention are that the cis/trans isomer ratio can be controlled and, in the embodiments described as preferred, isophoronediamine is simultaneously obtained in high yield. The technical measures for controlling the isomer ratio are simple and can be integrated into existing devices. By restricting the process to two temperature steps without a tedious specific heating programme, isophoronediamine can be prepared with a high space-time yield.

Example

Two reaction tubes connected in series, which were each provided with a heating device for separate adjustment of the temperature of each tube, were each filled with 100 ml of hydrogenation catalyst. The feed solution, containing isophorononitrile and methanol, and liquid ammonia were mixed immediately upstream of the reactor and pumped into the first reactor from the top. The pressure was regulated to 60 bar; no excess of H_2 was used. The liquid reaction mixture is collected in a separating vessel arranged underneath the second reaction tube.

The feed solution contained 30% by weight of IPN and 70% by weight of methanol. 5.4%, based on isophorononitrile, of a high-boiling mixture from the distillative working-up of the reaction mixture of a previous batch, containing isophoronediamine residues and 3,5,5-trimethyl-6-imino-7-azabicyclo[3,2,1]octane (amidine) as the main product, was also added to the mixture. 130 ml/h thereof were mixed with 50 ml/h of liquid ammonia and pumped into the reactor. The catalyst used was a commercially available cobalt catalyst (50% of Co on a silicate support). The temperature of the first reactor was varied between 40 and

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140°C. The temperature of the second reactor was constant at 120°C. The results are shown in the Table.

	T (1st reactor) (°C)	Yield (%)	Isomer ratio cis:trans
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	41	91.9	80:20
	80	92.8	76:24
	120	92.3	60:40
10	139	90.3	55:45

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Claims

1. A method of influencing the cis/trans isomer ratio of 3-aminomethyl-3,5,5-trimethylcyclohexylamine (isophoronediamine; IPDA) in its preparation from 3-cyano-3,5,5-trimethylcyclohexanone (isophoronenitrile; IPN) by aminating hydrogenation, wherein isophoronenitrile is reacted with hydrogen in the presence of ammonia and a suspension or fixed bed hydrogenation catalyst from the group comprising cobalt, nickel and noble metal catalysts, at a pressure of 3 to 20 MPa and at a temperature of up to 150°C, and the resulting reaction mixture is worked up by distillation, said method being characterized in that the hydrogenation is carried out in a first step at 10°C to 90°C and in a subsequent second step at above 90°C to 150°C, the temperature difference between the first and second steps being at least 30°C, the reaction time when using a suspension catalyst being 5 to 30 minutes in the first step and 30 to 200 minutes in the second step, and the LHSV value when using a fixed bed catalyst being 2 to 12 h⁻¹ in the first step and 0.3 to 2 h⁻¹ in the second step.
2. A method according to Claim 1, characterized in that the aminating hydrogenation is carried out in the presence of an organic solvent from the group comprising C₁- to C₄- alcohols, cyclic ethers and glycol monomethyl or monoethyl ether or glycol dimethyl or diethyl ether, preferably methanol.
3. A method according to Claim 1 or 2, characterized in that the hydrogenation is carried out at 20 to 80°C in the first step and at 100 to 140°C in the second step.
4. A method according to one or more of Claims 1 to 3, characterized in that the aminating hydrogenation is carried out using one or more fixed bed catalysts under trickle bed conditions, the temperature of the first step



being maintained in a first catalyst bed and the temperature of the second step being maintained in a second catalyst bed.

5 5. A method according to Claim 4, characterized in that a mixture containing 10 to 40% by weight of isophoronenitrile, 10 to 40% by weight of ammonia and methanol as the solvent is charged onto the first catalyst bed and the reaction mixture is allowed to trickle through
10 the first and second catalyst beds arranged in a single trickle bed reactor or in two trickle bed reactors, the hydrogenation being carried out at a pressure of 5 to 8 MPa and at a temperature of 10 to 80°C in the first step and 100 to 130°C in the second step.

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6. A method according to Claim 4 or 5, characterized in that a ruthenium-containing fixed bed catalyst is used in the first step and a cobalt-containing fixed bed catalyst is used in the second step.

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