

Process for preparing cyclododecanone

The present invention relates to a process for preparing cyclododecanone, to a process for preparing laurilactam and to a process for preparing nylon-12.

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Cyclododecanone (CDON) is used for the synthesis of laurilactam. The lactam in turn is suitable for the preparation of nylon-12.

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The preparation of CDON may proceed from cyclododecatriene (CDT). First of all, a selective hydrogenation of cyclododecatriene (CDT) to cyclododecene (CDEN) may be undertaken. This is followed by an epoxidation of CDEN to epoxycyclododecane (CDAN epoxide) and the rearrangement of CDAN epoxide to cyclododecanone (CDON). Proceeding from CDEN, the CDON synthesis comprises the following steps:

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- a. epoxidizing cyclododecene (CDEN) to epoxycyclododecane (CDAN epoxide) and
- b. rearranging the CDAN epoxide to CDON to obtain a mixture comprising cyclododecane (CDAN).

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The mixture (CDON-containing mixture) which is obtained from the rearrangement thus comprises at least CDON and CDAN.

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In this process for preparing CDON, the problem occurs that significant amounts of CDAN or CDEN can arise. This problem is aggravated by the ageing of catalysts which may be used. The amount of by-products obtained may be more than 20% by weight, based on the resulting CDON-containing mixture from the rearrangement.

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The high proportion of CDAN may have adverse effects on the downstream reactions such as the preparation of laurilactam.

In this respect, the problem addressed by the present invention was that of providing a novel process for preparing CDON which reduces the proportion

of CDAN in the CDON end product. In addition, the preparation process was to appear more economically viable overall.

Accordingly, a novel process for preparing CDON comprising the steps a and b cited at the outset has been found, which is referred to hereinafter as reaction route I. The CDAN is separated from the CDON-containing mixture and oxidized to CDON (CDON process of the invention).

The CDON process of the invention can be conducted continuously or batchwise.

The rearrangement is preferably conducted at a maximum hydrogen pressure of 0.9 bar. Preferably, the hydrogen pressure is 0 to 0.9 bar, more preferably 0 to 0.5 bar. The process according to the invention can be conducted without hydrogen, but it is preferable to initially charge at least a small hydrogen content to prevent unsaturated by-products. This hydrogen content may be 0.05 to 0.5 bar, preferably 0.1 to 0.4 bar.

The pressure figures given above relate to the partial pressure of hydrogen in the system. Typically, components of the reaction mixture including the solvent, air or inert gases such as nitrogen or argon are further gaseous constituents of the system.

A rearrangement in the context of the CDON process of the invention is especially understood to mean a reaction in which at least 90% by weight of CDON, based on the total weight of CDON and CDOL formed, is obtained.

Preferably, the CDEN for the epoxidation (step a) is obtained from CDT. The CDT in turn can be obtained from 1,3-butadiene. The selective hydrogenation of CDT can be effected in the gas phase with a low partial pressure of hydrogen and a Pd-containing catalyst (EP 1457476). The step typically gives rise to 5% to 15% by weight of CDAN (cyclododecane) in CDEN.

The epoxidation of CDEN as per step a can be conducted with hydrogen

peroxide, by means of a phase transfer catalyst and a metal salt at acidic pH. The CDAN present in the CDEN acts as a phase separation accelerator (EP 1411050, EP 1411051). After the reaction, CDAN epoxide is obtained, which may further comprise CDAN, unreacted CDEN or both.

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CDAN can be at least partly removed prior to the rearrangement (step b). Preferably, this CDAN is oxidized to CDON.

The oxidation of CDAN to CDON may at least partly give rise to CDOL. The CDOL can then be dehydrogenated to CDON.

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The rearrangement as per step b is preferably effected in the presence of a noble metal catalyst (catalyst system), the catalyst preferably comprising titanium dioxide, zirconium dioxide or both. This reaction step forms CDON containing CDAN as by-product (CDON-containing mixture). In addition, CDEN, CDOL or mixtures thereof may be present as by-products. Further by-products having a higher boiling point than CDON may likewise be present (high boilers). Preferably, the rearrangement is not conducted in the presence of alkali metal hydroxides as catalyst.

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The noble metal in the catalyst system is preferably selected from ruthenium, rhodium, palladium, osmium, iridium and platinum, preference being given to ruthenium, palladium and platinum, and particular preference to palladium. The noble metal may be in the form of powder (unsupported) or in supported form. Elemental noble metals or oxides thereof, for example, are suitable in powder form.

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In addition, at least one metal oxide may be present as a further constituent of the catalyst system. The metal oxide in the catalyst system comprises titanium dioxide, zirconium dioxide or mixtures thereof, or consists of at least one of the aforementioned oxides. These also include titanium dioxide- or zirconium dioxide-doped or -coated substances such as alumina or silica.

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The metal oxide in the catalyst system may function as a support for the noble

metal in the catalyst system. The noble metal may optionally be applied to an alternative support selected, for example, from alumina, silica or activated carbon. Titanium dioxide or zirconium dioxide are preferred supports.

- 5 The metal oxides in the catalyst system and the alternative supports may be in the form of powders or shaped bodies. Suitable shaped bodies are spheres, extrudates, tablets, granules and pellets. It is preferable that the supports of the noble metal are in the form of shaped bodies. It is likewise preferable that the metal oxide in the catalyst system, if it does not function as
10 a support, is in the form of shaped bodies.

The catalyst system may consequently independently be present as one of the following system forms:

- I) The noble metal is unsupported; the metal oxide present in the
15 catalyst system is at least titanium dioxide or zirconium dioxide;
- II) the noble metal is supported, where the support does not comprise or consist of titanium dioxide and/or zirconium dioxide. The system additionally comprises at least one metal oxide selected from titanium dioxide and zirconium dioxide.
- 20 III) The noble metal is supported on a metal oxide selected from titanium dioxide and zirconium dioxide, preferably with no titanium dioxide present.

System forms II and III are preferred, system form III being particularly
25 preferred.

Suitable titanium dioxide as a metal oxide in the catalyst system can be obtained by the sulphate process, the chloride process, or by flame hydrolysis (pyrogenic process) of titanium tetrachloride. All the processes are known to
30 those skilled in the art. Suitable polymorphs are rutile and anatase, and the titanium dioxide used may comprise mixtures of the polymorphs mentioned.

The titanium dioxide prepared by the sulphate or chloride process may give an acidic reaction in water, the compounds typically having a pH of 3 or less

(acidic titanium dioxide). Acidic titanium dioxide likewise usually contains more than 5% by weight, based on the total weight of the titanium dioxide support, of substances such as titanyl sulphate or titanyl hydroxide. A titanium dioxide based on an acidic titanium dioxide is commercially available as
5 Aerolyst 7750 (Evonik, Germany). Acidic titanium oxide is less preferred for the present process. In other words, it is preferable not to use acidic titanium dioxide. Suitable nonacidic titanium dioxide, which is preferred, exhibits a pH of 5 or more in water.

10 Particularly preferred titanium dioxide is obtained by means of flame pyrolysis, as described, for example, in DE-A-830786.

Suitable titanium dioxide is obtainable under the Aeroxide P25 titanium dioxide (powder) or Aerolyst 7711 (shaped bodies) name from Evonik,
15 Germany, and Hombikat M234 (shaped bodies) from Sachtleben, Germany.

Zirconium dioxide (zirconium(IV) oxide) is obtainable, for example, from zirconium hydroxide, by calcining it at more than 200°C, for example at 350°C. The zirconium dioxide may be doped, for example, with yttrium oxide.
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Suitable zirconium dioxide is monoclinic or tetragonal. Mixtures of these polymorphs are possible.

The metal oxide in the catalyst system may have an average bulk density of 0.5 to 2 g/cm³.
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The metal oxide in the catalyst system may have a BET surface area of at least 5 m²/g.

The proportion of noble metal, based on the total weight of noble metal and support, may be 0.01% to 5% by weight, preferably 0.05% to 1.2% by weight
30 and more preferably 0.1% to 0.6% by weight.

The noble metal may be distributed on or within the support.

The molar proportion of noble metal, based on the molar amount of CDAN epoxide, may be 0.00001 to 0.1, preferably 0.0001 to 0.01.

5 The molar proportion of metal oxide in the catalyst system, based on the molar amount of the compound E, may be 0.01 to 100, preferably 0.01 to 10.

The CDAN is removed from the reaction mixture and oxidized to CDON.

10 The remaining mixture comprising CDON and high boilers including CDOL can be hydrogenated in the presence of hydrogen and a catalyst in order to remove the unsaturated by-products. Subsequently, the pure CDON product is separated from a high boiler fraction including CDOL by distillation, for example.

15 CDOL can subsequently be distilled out of this high boiler fraction, and CDOL can be converted to CDON within reaction route I by means of a dehydrogenation catalyst. However, it is preferable to send the CDOL removed, prior to the dehydrogenation, to a reaction route II for preparation of CDON.

20 Reaction route II comprises the following steps:

- a. hydrogenation of CDT to CDAN,
- b. oxidation of CDAN to give a mixture comprising CDOL and CDON
- 25 and
- c. dehydrogenation of CDOL to CDON.

Suitable catalysts for the dehydrogenation of CDOL contain copper or copper compounds, for example copper(II) oxide.

30 The CDOL from route I is preferably fed in prior to step c of route II, the dehydrogenation.

In a preferred embodiment of the invention, the CDAN removed from route I is

fed to reaction route II prior to performance of the oxidation. The CDAN comes from the CDON-containing mixture. CDAN which has been removed after the epoxidation can be combined with the CDAN from the CDON-containing mixture.

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The CDAN can be fed in prior to step b of route II, the oxidation. It is preferable here for the CDAN to contain up to 0.5% by weight of CDEN, based on the total weight of CDAN and CDEN.

10 If the CDAN removed from route I contains 0.1% to 99% by weight of CDEN, preferably 0.5% to 99% by weight of CDEN, based on the total weight of CDAN and CDEN, it is preferable to send this mixture to the hydrogenation of CDT as per step a of reaction route II. In this way, CDEN is hydrogenated to CDAN which can be oxidized in step b of route II.

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With regard to the CDEN content, there is a range of overlap within the range from 0.1% to 0.5% by weight. In this case, the person skilled in the art can choose whether to send the CDEN-containing CDAN to step a or step b of route II.

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In this respect, reaction routes I and II can be combined in such a way that CDAN or CDOL obtained are separated and removed from route I and transferred into route II. It is preferable here to conduct both routes continuously. This particular embodiment of the invention utilizes by-products from route I for further processing in route II. This is particularly economically and ecologically beneficial. There is no disposal of by-products from route I.

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The removal of CDEN, CDAN and CDOL and the other high boilers can be undertaken by methods familiar to those skilled in the art. Preference is given here to distillation. More preferably, all removals are effected by means of distillation. It is advantageous to conduct several distillations in succession (multistage distillation).

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The CDAN can be distilled off after the epoxidation.

After the rearrangement, it is advantageous first to distil off the CDAN or a mixture of CDAN and CDEN (low boiler fraction) and to subject the residue comprising CDON, CDOL and further high boilers to another distillation. In this case, it is possible to obtain CDON which is separated from a high boiler fraction comprising CDOL. CDOL in turn can be distilled off from the remaining high boiler products.

Low boilers are substances having a boiling point lower than the boiling point of CDON.

Fig. 1 shows a flow diagram with the corresponding reactions. The compounds in italics are by-products of each reaction.

Proceeding from CDT, via route I, CDEN is obtained by means of hydrogenation (selective hydrogenation) and is epoxidized to CDAN epoxide. This is followed by a rearrangement to CDON, with removal of CDAN present – for example by means of distillation. The CDAN present after the epoxidation can likewise be removed. The CDAN removed may contain CDEN. Preferably, the CDAN, however, is sent to the rearrangement and removed only after the rearrangement. The CDAN removed is preferably transferred into route II, preferably with combination of the individual fractions from route II.

The remaining CDON may contain CDOL which can be removed and fed to route II. Alternatively, the CDOL can be dehydrogenated within route I to CDON.

The invention further provides a process for synthesizing laurolactam (lactam process of the invention), in which the aforementioned process of the invention for preparing CDON is employed. In this case, the laurolactam is obtained from CDON, the CDON being prepared by the CDON process of the invention.

The invention further provides a process for synthesising nylon-12 (polyamide process of the invention), in which the aforementioned process of the invention for preparing CDON is employed.

- 5 The CDON produced in the CDON process of the invention can be oximated in the lactam or polyamide process of the invention to obtain cyclododecanone oxime (CDON oxime). In the subsequent step, the Beckmann rearrangement may be effected to give lauro lactam, in which case the rearrangement can be effected by means of sulphuric acid or cyanuric
10 chloride. The lactam may be subjected to further processing by polycondensation to give polyamide.

The oximation, the Beckmann rearrangement and the condensation reaction are known to a person skilled in the art.

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- Even in the absence of further information it is assumed that a person skilled in the art can make very extensive use of the above description. The preferred embodiments and examples are therefore to be interpreted merely as descriptive disclosure, and certainly not as disclosure that is in any way
20 limiting.

The present invention is elucidated in detail hereinafter with reference to an example. Alternative embodiments of the present invention are obtainable analogously.

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Example 1

Epoxide route = reaction route I

5 Conventional route = reaction route II

Selective hydrogenation of CDT:

1000 kg/h of CDT were evaporated continuously in a saturation column as gas/liquid contact apparatus at a pressure of 0.75 bar and a temperature of
10 155°C into a 10 m³/h cycle gas stream that consisted essentially of nitrogen. The resulting gas stream was fed to a fixed bed reactor having a Pd on Al₂O₃ catalyst, in which the reaction with hydrogen was effected at a temperature of 130°C. For this purpose, 25 kg/h of hydrogen were metered into the cycle gas stream at the reactor inlet. At the reactor outlet, the product was condensed
15 out of the cycle gas stream at 35°C. The condensed liquid had a composition of 84.8% CDEN and 15% CDAN. CDDIENE and CDT isomers were present in concentrations of less than 0.2%.

The remaining cycle gas stream was fed via a compressor back to the saturation column (see above).

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Epoxidation of CDEN:

The mixture of CDEN (84.8%) and CDAN (15%) from the selective hydrogenation was epoxidized in a three-stage reactor cascade with H₂O₂.

25 The CDAN/CDEN mixture was first metered continuously into a first 8 l reactor at a metering rate of 2 kg/h. Additionally metered into the 5.5 l biphasic reaction mixture at a temperature of 80°C were a 50% H₂O₂ solution (544 g/h), an aqueous solution of 30% by weight of Na₂WO₄ and 18% by weight of H₃PO₄ (125 g/h), a 50% solution of trioctylamine in CDEN (68 g/h) and water (150 g/h).

30 The biphasic mixture came from the first reactor with a CDEN conversion of 79% and passed over into a second 8 l reactor. For this purpose, a 50% H₂O₂ solution (131 g/h) was metered into the 5.5 l biphasic reaction mixture at a temperature of 78°C.

From this second reactor came a biphasic mixture with a CDEN conversion of

96%, which was passed into a reactor having a fill level of 25 l. The biphasic reaction mixture was stirred in this reactor at a temperature of 76°C.

The two phases of the reaction mixture from the 25 l reactor were separated in a phase separation vessel. The organic phase was subsequently washed with a 5% NaOH solution (0.5 kg/h) in a 5 l vessel. The two phases were subsequently separated in a separation vessel.

The organic phase was sent to a continuous two-stage distillation. In a first column (column with 8 m fabric packing; surface area of 500 m²/m³; top pressure 300 mbar), the residual water was removed as distillate. The bottoms were distilled in a second column (column with 6 m fabric packing; surface area of 500 m²/m³; top pressure 10 mbar), and the desired product comprising 85%-90% CDAN epoxide and 5%-10% CDAN was obtained in the distillate at a rate of 2.1 kg/h. This corresponds to an overall yield of 97% for the epoxidation.

Rearrangement of CDAN epoxide to CDON:

The CDAN epoxide from the preceding step was converted to CDON by means of a 0.5% Pd/ZrO₂ catalyst in a three-stage reactor cascade.

The mixture of CDAN epoxide (84.8%) and CDAN (15%) from the epoxidation was fed into a first circulation reactor at a metering rate of 2 kg/h. The circulation reactor consisted of a 12 l tubular reactor which was filled with 10 kg of 0.5% Pd/ZrO₂ fixed bed catalyst at a temperature of 200°C and was fed from an 8 l reservoir vessel.

From the first circulation reactor came a mixture of 59% CDON, 18% CDAN epoxide, 16% CDAN, 0.4% CDEN and 1.9% CDOL. This mixture was metered into a second circulation reactor at a metering rate of 2 kg/h. This second circulation reactor likewise consisted of an 8 l reservoir vessel and a 12 l tubular reactor which was filled with 10 kg of 0.5% Pd/ZrO₂ fixed bed catalyst at a temperature of 200°C.

From the second reaction circuit came a mixture of 73% CDON, 4% CDAN epoxide, 16% CDAN, 0.4% CDEN and 2% CDOL. This mixture was metered into a fixed bed reactor filled with 2.7 kg of Pd/ZrO₂ at a metering rate of 2 kg/h. In this tube, the reaction mixture was contacted with N₂ (4 l/h) and H₂ (16 l/h) at a total pressure of 1.7 bar and a temperature of 205°C. From this tube,

a crude mixture of 78% CDON, 17% CDAN and 2.2% CDOL was obtained. The components of this mixture were separated from one another and purified by means of distillation.

5 Distillation of low boiler fraction:

The crude mixture from the rearrangement was freed of a low boiler fraction (components having a lower boiling point than CDON) in a first continuous distillation step. The column used was equipped with 8 m of fabric packing having a surface area of $500 \text{ m}^2/\text{m}^3$ and was operated at a top pressure of 10
10 mbar.

The compounds from this low boiler fraction which contain fewer than or equal to 11 carbon atoms were separated from the CDAN in an additional distillation column. The CDAN obtained with a purity of 99% was conducted into the
15 oxidation with boric acid (conventional route).

Distillation of CDON:

The bottoms from the first distillation were distilled in a further continuous distillation step (column with 6 m fabric packing; surface area of $500 \text{ m}^2/\text{m}^3$),
20 and CDON was obtained as distillate at a top pressure of 10 mbar. Components having a higher boiling point than CDON (for example CDOL) were removed as bottom product. The purity of the CDON obtained was > 99% and the CDON yield achieved in the distillation was 98%.

It was possible to convert this cyclododecanone further to lauro lactam by
25 known methods.

The bottoms from this second distillation were purified further in an additional column: CDOL was separated from other high boilers in an additional column and conducted into the dehydrogenation (conventional route).

30 Utilization of the CDAN obtained in the conventional route:

The CDAN (1 kg/h) from the epoxide route was reacted with boric acid (0.05 kg/h). With a residence time of 2 h, reaction at 155°C with oxygen feed rate 132 l/h, a CDAN conversion of 8.5% and a selectivity for CDON and CDOL of 88% was obtained. This conversion and the composition corresponded to the

conversion and selectivity from the conventional route. It was possible to convert the mixture further to laurolactam analogously to the conventional product.

5 Utilization of the CDOL obtained in the conventional route:

1 kg of CDOL from the epoxide route was mixed with 10 kg of CDOL/CDON (70:30 w:w) mixture from the conventional route in a 30 l dehydrogenation reactor. The reactor was charged with 1.9 kg of Cu-containing catalyst (H10167 from Evonik). After reaction at 240°C for 6 h, a mixture of CDON (10.5 kg) and CDOL (0.5 kg) was obtained. The CDON was distilled off with a purity of more than 99.8% and the CDOL was recycled into the dehydrogenation. The quality of the CDON obtained corresponded to the quality of the cyclododecanone from the conventional route, and it was possible to convert it further to laurolactam by this route.

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Example 2

The CDAN (or the mixture of CDAN and CDEN) can be utilized in an alternative way. Instead of transferring the CDAN into the oxidation with boric acid, it can be used in the preceding stage (hydrogenation of CDT to CDAN). This applies particularly when the CDAN from the epoxide route contains a significant amount of CDEN.

Utilization of the mixture of CDAN and CDEN in the CDT hydrogenation:

25 The mixture of CDAN and CDEN (0.04 kg/h) from the epoxide route was mixed with CDT (0.36 kg/h) in a 0.4 l hydrogenation reactor. The hydrogenation reactor was charged with 0.284 kg of 0.5% Pd/Al₂O₃. At 160°C and 15 bar of hydrogen, CDAN was obtained with a purity of 98.5%. This purity corresponded to the purity of the cyclododecanone in the conventional route under the corresponding reaction conditions, and it was possible to convert it further to laurolactam by this route.

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Claims

1. Process for preparing cyclododecanone (CDON) by means of a reaction route I, comprising the steps of
 - 5 a. epoxidizing cyclododecene (CDEN) to epoxycyclododecane (CDAN epoxide) and
 - b. rearranging the CDAN epoxide to CDON to obtain a mixture comprising cyclododecane (CDAN),characterized in that CDAN is separated from the CDON-containing mixture and oxidized to CDON.
- 10 2. Process according to Claim 1, characterized in that the rearrangement (step b) is effected in the presence of a noble metal catalyst.
- 15 3. Process according to Claim 2, characterized in that the catalyst for the rearrangement (step b) comprises titanium dioxide, zirconium dioxide or both.
4. Process according to any of the preceding claims, characterized in that
 - 20 the CDAN epoxide from step a comprises CDAN which is at least partly removed prior to the rearrangement (step b).
5. Process according to Claim 4, characterized in that the CDAN removed prior to the rearrangement is oxidized to CDON.
- 25 6. Process according to any of the preceding claims, characterized in that the CDON-containing mixture comprises cyclododecanol (CDOL) which is dehydrogenated to CDON.
- 30 7. Process according to Claim 6, characterized in that the CDOL is separated from the CDON-containing mixture prior to the dehydrogenation and is sent to a reaction route II for preparation of CDON, comprising
 - 35 a. hydrogenation of CDT to CDAN,

- b. oxidation of CDAN to give a mixture comprising CDOL and CDON and
 - c. dehydrogenation of CDOL to CDON.
- 5 8. Process according to any of the preceding claims, characterized in that the CDAN removed, prior to performance of the oxidation, is sent to a reaction route II for preparation of CDON, comprising
 - a. hydrogenation of CDT to CDAN,
 - 10 b. oxidation of CDAN to give a mixture comprising CDOL and CDON and
 - c. dehydrogenation of CDOL to CDON.
- 9. Process according to Claim 8, characterized in that the CDAN removed is
15 sent to the oxidation of CDAN as per step b of reaction route II.
- 10. Process according to Claim 9, characterized in that the CDAN contains up to 0.5% by weight of CDEN, based on the total weight of CDAN and CDEN.
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- 11. Process according to Claim 8, characterized in that the CDAN removed is sent to the hydrogenation of CDT as per step a of reaction route II, the CDAN containing 0.1% to 99% by weight of CDEN, based on the total weight of CDAN and CDEN.
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- 12. Process according to any of the preceding claims, characterized in that at least one removal is conducted, preferably all the removals are conducted, by means of distillation.
- 30 13. Process for synthesizing lauro lactam from CDON, wherein the CDON is prepared according to any of the preceding claims.
- 14. Process according to Claim 13, characterized in that the CDON is converted to cyclododecanone oxime (CDON oxime).

15. Process for preparing nylon-12 from CDON, wherein the CDON is prepared according to any of the preceding claims.