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(54) Title: METHODS FOR PRODUCING 1,5,7-TRIAZABICYCLO[4.4.0] DEC-5-ENE BY REACTION OF A DISUBSTITUTED CARBODIIMIDE AND DIPROPYLENE TRIAMINE

(57) Abstract: Methods for producing 1,5,7-triazabicyclo[4.4.0]dec-5-ene using a disubstituted carbodiimide, dipropylene triamine and optionally an ethereal solvent and/or an alcohol are disclosed. Use of 1,5,7-triazabicyclo[4.4.0]dec-5-ene produced by this method in an electrodepositable coating composition, and electrophoretic deposition of such coating onto a substrate to form a coated substrate, are also disclosed.

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METHODS FOR PRODUCING 1,5,7-TRIAZABICYCLO[4.4.0]DEC-5-ENE BY REACTION OF A DISUBSTITUTED CARBODIIMIDE AND DIPROPYLENE TRIAMINE

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a continuation-in-part of United States Patent Application Serial Number 13/455,651, filed April 25, 2012.

FIELD OF THE INVENTION

[0002] The present invention relates to methods for producing 1,5,7-triazabicyclo[4.4.0]dec-5-ene.

BACKGROUND OF THE INVENTION

[0003] It is known that bicyclic guanidines, such as 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), are chemically active and can be used to catalyze a variety of chemical reactions. An important consideration in the commercial exploitation of bicyclic guanidines as a catalyst (for any reaction) is that bicyclic guanidines be relatively inexpensive to purchase and/or easy to produce.

[0004] Published methods for synthesizing bicyclic guanidines, however, are often complicated, such as by using a multiple step and/or time consuming synthesis process. Others use prohibitively expensive and/or hazardous starting materials. Further, many published methods do not produce high yields of the desired products, or produce byproducts, such as aniline, that are difficult to separate from the bicyclic guanidines and may themselves be hazardous. Also, many of these methods produce bicyclic guanidines of different types that may be difficult to separate from one another, and/or produce bicyclic guanidines in forms that are difficult to handle.

[0005] There is therefore a need for safe and efficient methods for producing bicyclic guanidines.

SUMMARY OF THE INVENTION

[0006] The present invention is directed to a method for producing 1,5,7-triazabicyclo[4.4.0]dec-5-ene comprising forming a mixture comprising a disubstituted carbodiimide, dipropylene triamine and an ethereal solvent and/or an alcohol; and heating the mixture to cause the disubstituted carbodiimide to react with the dipropylene triamine.

[0007] The present invention is further directed to methods for producing 1,5,7-triazabicyclo[4.4.0]dec-5-ene comprising forming a mixture comprising a disubstituted carbodiimide and dipropylene triamine; and heating the mixture to cause the disubstituted carbodiimide to react with the dipropylene triamine.

DETAILED DESCRIPTION OF THE INVENTION

[0008] The present invention is directed to methods for producing bicyclic guanidines. More specifically, the present invention is directed to methods for producing 1,5,7-triazabicyclo[4.4.0]dec-5-ene comprising reacting a disubstituted carbodiimide with dipropylene triamine ("DPTA"), also known as bis(3-aminopropyl)amine.

[0009] As used herein, the term "disubstituted carbodiimides" refers to a compound having the formula $RN=C=NR^1$, wherein R and R^1 independently comprise an alkyl group, an aryl group or mixtures thereof. R and R^1 can be the same or different. In certain embodiments, the disubstituted carbodiimide comprises a dialkyl carbodiimide and the R/R^1 group is an aliphatic and/or cycloaliphatic alkyl group, for example, having 1 to 10 carbons; particularly suitable dialkylcarbodiimides include, without limitation, N,N'-diisopropylcarbodiimide (DIC) (i.e. when R/R^1 is an isopropyl group), N,N'-dicyclohexylcarbodiimide (DCC) (i.e. when R/R^1 is a cyclohexyl group), N,N'-di-*tert*-butylcarbodiimide (wherein R/R^1 is a *tert*-butyl group), and any combinations thereof.

[0010] In certain embodiments, the disubstituted carbodiimide comprises a diaryl carbodiimide and the R/R^1 group is an aryl group. A particularly suitable diarylcarbodiimide is N,N'-di-*p*-tolylcarbodiimide (wherein R/R^1 is a toluene residue). In certain embodiments, combinations of one or more dialkylcarbodiimides and/or one or more diarylcarbodiimides are used.

[0011] In certain embodiments, the method for producing 1,5,7-triazabicyclo[4.4.0]dec-5-ene includes first dissolving the disubstituted carbodiimide in an ethereal solvent and/or in an alcohol prior to reacting the disubstituted carbodiimide with DPTA. These embodiments are sometimes referred to herein as the "solvent process". In alternative embodiments discussed further below, methods for producing 1,5,7-triazabicyclo[4.4.0]dec-5-ene do not utilize an ethereal solvent or alcohol, and are sometimes referred to herein as the "solventless process".

[0012] In general, the solvent process begins by dissolving a disubstituted carbodiimide in an ethereal solvent and/or in an alcohol. Next, dipropylene triamine is added to the dissolved disubstituted carbodiimide. In some embodiments, the disubstituted

carbodiimide and solvent and/or alcohol mixture is heated, such as to a temperature of 60°C, prior to the addition of the DPTA and in some embodiments the mixture is heated to about 60°C after addition of the DPTA. The mixture is then further heated to an elevated temperature and held for a sufficient period of time to react the disubstituted carbodiimide and dipropylene triamine, first forming an intermediate, (generally an N,N'-disubstituted monocyclic guanidine), and then forming 1,5,7-triazabicyclo[4.4.0]dec-5-ene and an amine. The amine generated by the reaction of the disubstituted carbodiimide and dipropylene triamine depends on the R/R^1 group. For example, the amine will be isopropyl amine if R/R^1 is an isopropyl group, or cyclohexylamine, if R/R^1 is a cyclohexyl group. This amine byproduct can be distilled off during the course of the reaction, such that all that remains in the reaction vessel with the 1,5,7-triazabicyclo[4.4.0]dec-5-ene upon completion of the reaction is the ethereal solvent and/or the alcohol. Alternatively, the amine byproduct can be removed upon completion of the reaction.

[0013] Suitable ethereal solvents that may be utilized in the solvent process of the present invention include, but are not limited to, butyl carbitol formal.

[0014] Suitable alcohols (i.e. alcoholic solvents) that may be utilized in the solvent process of the present invention include, but are not limited to monoalcohols or polyols, such as 2-butoxyethanol (i.e. butyl cellosolve), diethylene glycol monobutyl ether (i.e. butyl CARBITOL), hexaethoxylated bisphenol A polyol and combinations thereof. In certain embodiments, 2-butoxyethanol is used.

[0015] In general, the solventless process of the present invention begins by introducing the disubstituted carbodiimide to a reaction vessel. Next, dipropylene triamine is slowly added to reaction vessel, wherein the resultant mixture begins to react and exotherm. The mixture is then heated to an elevated temperature and held for a sufficient period of time to react the disubstituted carbodiimide and dipropylene triamine, first forming an intermediate and then forming 1,5,7-triazabicyclo[4.4.0]dec-5-ene and an amine. This amine byproduct can be distilled off during the course of the reaction, or removed upon completion of the reaction. A diluent, such as hexaethoxylated bisphenol A polyol, may be added to the formed 1,5,7-triazabicyclo[4.4.0]dec-5-ene in the reaction vessel.

[0016] The term "an elevated temperature", when used in the context of the present processes is the temperature at which the disubstituted carbodiimide reacts with the dipropylene triamine to form the 1,5,7-triazabicyclo[4.4.0]dec-5-ene and the amine. In certain embodiments, the elevated temperature is 160°C or greater, 170°C or greater, or 180°C or greater, and can be as high as 220°C, 230°C, 240°C or even higher. Typically, a

higher temperature results in shorter reaction time. In certain solvent processes, the elevated temperature corresponds to the reflux temperature of the ethereal solvent and/or the alcohol or blend that is used. For example, when 2-butoxyethanol is used, the elevated temperature corresponds to the reflux temperature of 2-butoxyethanol (about 170°C). In a particular embodiment, the disubstituted carbodiimide comprises diaryl carbodiimide and the elevated temperature is 160°C or greater, 170°C or greater or 180°C or greater.

[0017] The term "a sufficient period of time", when used in the context of the present process, is the time needed to cause the disubstituted carbodiimide to substantially or completely react with dipropylene triamine. By "substantially react" is meant 70% conversion or greater; by "completely react" is meant 85% conversion or greater. This time period may vary, depending upon the exact reaction conditions and, in the case of the solvent process, depending upon the ethereal solvent and/or the alcohol used. Typically, the sufficient period of time will be 1 to 6 hours, such as 1 to 4 hours or 2 to 4 hours. The degree of reaction can be determined by analyzing the contents of the reaction vessel using known spectroscopic techniques (IR, ^{13}C NMR, etc.) to confirm the presence or absence of the disubstituted carbodiimide and dipropylene triamine and to confirm the presence of 1,5,7-triazabicyclo[4.4.0]dec-5-ene.

[0018] In certain embodiments, the processes described herein are performed without catalyst. In other embodiments, however, a catalyst is used. Any catalyst that increases the rate of reaction between the disubstituted carbodiimide and dipropylene triamine can be used according to the current methods, such as a weak acid catalyst. Suitable weak acid catalysts include, but are not limited to, thiourea, *t*-dodecylmercaptan, 2-mercaptoethanol, and bisphenol A . In certain embodiments, the catalyst is an additive, and in others a catalyst may be introduced as an impurity in the carbodiimide, possibly generated as a byproduct of the manufacturing process. Even these trace amounts of catalyst can increase the rate of reaction. The catalyst, if used, may be added with the carbodiimide.

[0019] In certain embodiments, the 1,5,7-triazabicyclo[4.4.0]dec-5-ene is isolated from the ethereal solvent and/or the alcohol through distillation at atmospheric pressure. In certain embodiments, after the distillation process, the 1,5,7-triazabicyclo[4.4.0]dec-5-ene may be recovered in powder form. Alternatively, the 1,5,7-triazabicyclo[4.4.0]dec-5-ene may be maintained in solution with the ethereal solvent and/or with the alcohol for subsequent use. As noted above, in both the solvent and solventless processes the amine byproduct can be removed from the reaction vessel via distillation. In certain embodiments, this distillation is performed concurrent with the reaction. By "concurrent" is meant the

distillation is performed during the reaction in which the 1,5,7-triazabicyclo[4.4.0]dec-5-ene is formed. Although the inventors do not wish to be bound by any mechanism, in certain embodiments, distilling off the amine byproduct concurrently with the reaction may result in the reaction occurring more efficiently, that is, more quickly and/or with a higher percent conversion.

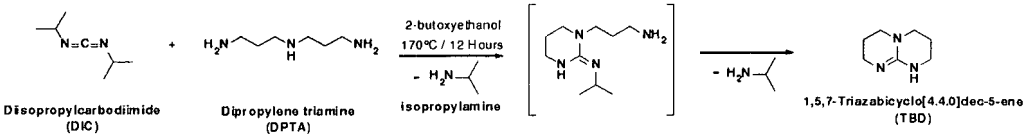
[0020] The isolated bicyclic guanidine (1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD)), formed in either the solvent or solventless processes described above, which is in solution form or powder form, can then be added to any composition in which bicyclic guanidine can be used. For example, in certain embodiments, the bicyclic guanidine formed from the process described herein can be added to an electrodepositable coating composition, such as the electrodepositable coating composition that is described in U.S. Patent No. 7,842,762, which is incorporated in its entirety herein by reference.

[0021] As used herein, unless otherwise expressly specified, all numbers such as those expressing values, ranges, amounts or percentages may be read as if prefaced by the word "about", even if the term does not expressly appear. Any numerical range recited herein is intended to include all sub-ranges subsumed therein. Plural encompasses singular and vice versa. For example, while the invention has been described in terms of "a" disubstituted carbodiimide, "an" alcohol, "the" R/R^1 group, and the like, mixtures of these and other components can be used. Also, as used herein, the term "polymer" is meant to refer to prepolymers, oligomers and both homopolymers and copolymers; the prefix "poly" refers to two or more. When ranges are given, any endpoints of those ranges and/or numbers within those ranges can be combined with the scope of the present invention. "Including", "such as", "for example" and like terms means "including/such as/for example but not limited to".

Examples

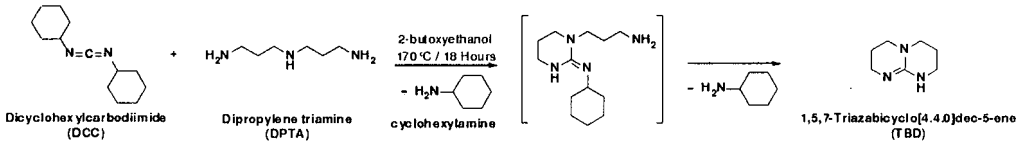
[0022] The following examples are intended to exemplify the invention and are not intended to limit the invention in any way.

Example 1: DIC Route in 2-butoxyethanol



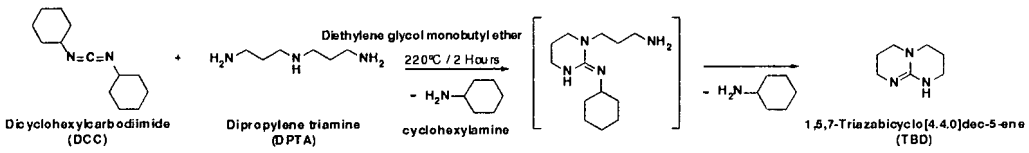
[0023] A 4-neck flask was equipped with a temperature probe, stainless steel mechanical stirrer, and an ice water condenser. Dry nitrogen was swept through the flask, out through the condenser, then through an attached cold trap containing dry ice and ethanol used to trap isopropylamine distillate. The flask was charged with 2-butoxyethanol (220 mL) and *N,N'*-diisopropylcarbodiimide (151.4 g, 1.2 mol), and warmed to 60°C. Then, dipropylene triamine (131.2 g, 1.0 mol) was added slowly. Upon addition of dipropylene triamine, an exotherm of 40°C was observed (~60°C → 100°C). The reaction was warmed slowly to 170°C and refluxed at that temperature for 12 hours. The orange, homogenous solution was then cooled, poured out of the reaction vessel, and used without further purification. The concentration of TBD in the final solution was determined by HPLC (38.8 wt%, 94.6% conversion). ^{13}C NMR analysis indicated that the material consisted solely of 1,5,7-triazabicyclo[4.4.0]dec-5-ene in 2-butoxyethanol. ^{13}C NMR analysis of the distillate confirmed the capture of the byproduct isopropylamine (129 mL) as the sole compound.

Example 2: DCC Route in 2-butoxyethanol



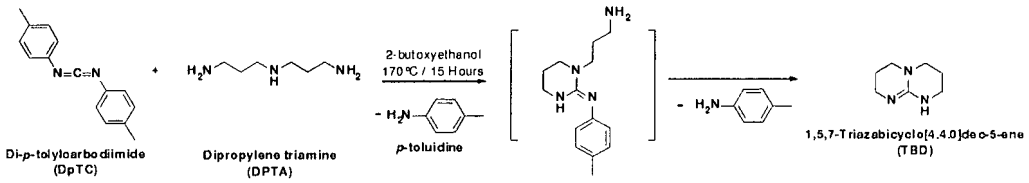
[0024] A 4-neck flask was equipped with a temperature probe, stainless steel mechanical stirrer, and an ice water condenser. Dry nitrogen was swept through the flask and out through the condenser. The flask was charged with 2-butoxyethanol (220 mL) and *N,N'*-dicyclohexylcarbodiimide (247.6 g, 1.2 mol), and warmed to 60 °C. Then, dipropylene triamine (131.2 g, 1.0 mol) was added slowly. Upon addition of dipropylene triamine, an exotherm of 14°C was observed (~58°C → 72°C). The reaction was warmed slowly to 170°C and refluxed at that temperature for 18 hours. The orange, homogenous solution was then cooled, poured out of the reaction vessel, and used without further purification. The concentration of TBD in the final solution was determined by HPLC (32.9 wt%, 80.2% conversion). ^{13}C NMR analysis indicated that the material consisted of 1,5,7-triazabicyclo[4.4.0]dec-5-ene and cyclohexylamine (2.5%) in 2-butoxyethanol.

Example 3: DCC Route in diethylene glycol monobutyl ether



[0025] A 4-neck flask was equipped for total distillation, along with a temperature probe and stainless steel mechanical stirrer. Dry nitrogen was swept through the flask and out through the distillation apparatus. The flask was charged with diethylene glycol monobutyl ether (210 mL) and *N,N'*-dicyclohexylcarbodiimide (247.6 g, 1.2 mol), and warmed to 60 °C. Then, dipropylene triamine (131.2 g, 1.0 mol) was added slowly. Upon addition of dipropylene triamine, an exotherm of 41°C was observed (~61°C → 102°C). The reaction was warmed to 140°C and held for 1 hour, then heated to 220°C and held for 2 hours. The orange, homogenous solution was then cooled, poured out of the reaction vessel, and used without further purification. The concentration of TBD in the final solution was determined by HPLC (35.4 wt%, 81.0% conversion). ^{13}C NMR analysis indicated that the material consisted solely of 1,5,7-triazabicyclo[4.4.0]dec-5-ene in diethylene glycol monobutyl ether. ^{13}C NMR and GC/MS analysis of the distillate confirmed the capture of cyclohexylamine (199 mL).

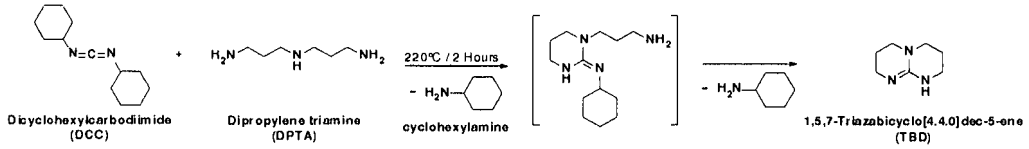
Example 4: DpTC Route in 2-butoxyethanol



[0026] A 4-neck flask was equipped with a temperature probe, magnetic stir bar, and an ice water condenser. Dry nitrogen was swept through the flask and out through the condenser. The flask was charged, at ambient temperature, with 2-butoxyethanol (11 mL), *N,N'*-di-*p*-tolylcarbodiimide (13.5 g, 0.06 mmol), and dipropylene triamine (6.64 g, 0.05 mol). An exotherm of 34°C was observed (~23°C → 57°C). The reaction was warmed slowly to 170°C and refluxed at that temperature for 15 hours. The orange-brown, homogenous solution was then cooled, poured out of the reaction vessel, and used without further purification. The concentration of TBD in the final solution was determined by

HPLC (19.9 wt%, 79.1% conversion). ^{13}C NMR and GC analyses indicated that the material consisted of 1,5,7-triazabicyclo[4.4.0]dec-5-ene and *p*-toluidine (36.8%) in 2-butoxyethanol.

Example 5: DCC Route (100% solids, polyol post-add, 20% DCC excess)



[0027] A 4-neck flask was equipped for total distillation, along with a temperature probe and stainless steel mechanical stirrer. Dry nitrogen was swept through the flask and out through the distillation apparatus. The flask was charged with *N,N'*-dicyclohexylcarbodiimide (247.6 g, 1.2 mol) followed by the slow addition of dipropylene triamine (131.2 g, 1.0 mol). Upon addition of dipropylene triamine, an exotherm of 31°C was observed (~24°C → 55°C). The reaction was warmed to 170°C and held for 1 hour, then heated to 220°C and held for 2 hours. After the final hold, hexaethoxylated bisphenol A polyol (417.0 g, 0.85 mol) was added as a diluent. The orange, homogenous solution was then stirred, cooled, poured out of the reaction vessel, and used without further purification. The concentration of TBD in the final solution was determined by HPLC (21.3 wt%, 94.4% conversion). ^{13}C NMR analysis indicated that the material consisted solely of 1,5,7-triazabicyclo[4.4.0]dec-5-ene in hexaethoxylated bisphenol A polyol. ^{13}C NMR and GC/MS analysis of the distillate confirmed the capture of cyclohexylamine (175 mL).

Example 6: DCC Route (100% solids, polyol post-add, 2% DCC excess)

[0028] A 4-neck flask was equipped for total distillation, along with a temperature probe and stainless steel mechanical stirrer. Dry nitrogen was swept through the flask and out through the distillation apparatus. The flask was charged with *N,N'*-dicyclohexylcarbodiimide (210.5 g, 1.02 mol) followed by the slow addition of dipropylene triamine (131.2 g, 1.00 mol). Upon addition of dipropylene triamine, an exotherm of 32°C was observed (~23°C → 55°C). The reaction was warmed to 170°C and held for 1 hour, then

heated to 220°C and held for 2 hours. After the final hold, hexaethoxylated bisphenol A polyol (319.8 g, 0.65 mol) was added as a diluent. The orange, homogenous solution was then stirred, cooled, poured out of the reaction vessel, and used without further purification. The concentration of TBD in the final solution was determined by HPLC (28.0 wt%, 93.7% conversion). ^{13}C NMR analysis indicated that the material consisted solely of 1,5,7-triazabicyclo[4.4.0]dec-5-ene in hexaethoxylated bisphenol A polyol. ^{13}C NMR and GC/MS analysis of the distillate confirmed the capture of cyclohexylamine (229 mL).

Example 7: DCC Route (100% solids, polyol post-add, 2% DCC excess, 98% purity DCC, weak acid catalyst)

[0029] A 4-neck flask was equipped for total distillation, along with a temperature probe and stainless steel mechanical stirrer. Dry nitrogen was swept through the flask and out through the distillation apparatus. The flask was charged, consecutively, with *N,N'*-dicyclohexylcarbodiimide (210.5 g, 1.02 mol, 98% purity - Dalian Harsou Chemical Co., Ltd), bisphenol A (0.570 g, 0.0025 mol), and dipropylene triamine (131.2 g, 1.00 mol). Upon addition of dipropylene triamine, an exotherm of 30°C was observed (24°C → 54°C). The reaction was heated to 140°C and held for 1 hour, then heated slowly to 220°C and held for 2 hours. After the final hold, hexaethoxylated bisphenol A polyol (319.8 g, 0.65 mol) was added as a diluent. The orange, homogenous solution was then stirred, cooled, poured out of the reaction vessel, and used without further purification. The concentration of TBD in the final solution was determined by HPLC (29.3 wt%, 96.7% conversion). ^{13}C NMR analysis indicated that the material consisted solely of 1,5,7-triazabicyclo[4.4.0]dec-5-ene in hexaethoxylated bisphenol A polyol. It should be noted that attempting the above procedure in the absence of bisphenol A gave significantly lower conversion to TBD, as analyzed by HPLC (26.9 wt%, 88.7% conversion). This demonstrates that the use of a weak acid catalyst, like bisphenol A, improves conversion to TBD in the reaction of DPTA with 98% purity DCC.

[0030] Whereas particular embodiments of this invention have been described above for purposes of illustration, it will be evident to those skilled in the art that numerous variations of the details of the present invention may be made without departing from the invention as defined in the appended claims.

What is claimed is:

1. A method for producing 1,5,7-triazabicyclo[4.4.0]dec-5-ene comprising:

(a) forming a mixture comprising a disubstituted carbodiimide, dipropylene triamine and an ethereal solvent and/or an alcohol; and

(b) heating said mixture to cause said disubstituted carbodiimide to react with said dipropylene triamine.

2. The method of Claim 1, wherein said heating is at a temperature of 160°C or greater.

3. The method of Claim 2, wherein said heating is at a temperature of 170°C or greater.

4. The method of Claim 1, wherein said disubstituted carbodiimide comprises dialkylcarbodiimide.

5. The method of Claim 4, wherein said dialkylcarbodiimide comprises N,N'-diisopropylcarbodiimide, N,N'-dicyclohexylcarbodiimide, or combinations thereof.

6. The method of Claim 2, wherein said disubstituted carbodiimide comprises diarylcarbodiimide.

7. The method of Claim 6, wherein said diarylcarbodiimide comprises di-p-tolylcarbodiimide.

8. The method of Claim 1, wherein the mixture of step (a) is formed in alcohol.

9. The method of Claim 8, wherein said alcohol comprises 2-butoxyethanol, diethylene glycol monobutyl ether, hexaethoxylated bisphenol A polyol, or combinations thereof.

10. The method of Claim 1 further comprising:

(c) distilling off byproduct from the reaction of step (b), wherein step (c) and step (b) are concurrent.

11. A method for producing 1,5,7-triazabicyclo[4.4.0]dec-5-ene comprising:

(a) forming a mixture comprising disubstituted carbodiimide and dipropylene triamine; and

(b) heating said mixture to cause said disubstituted carbodiimide to react with said dipropylene triamine.

12. The method of Claim 11 further comprising (c) adding a diluent after step (b)

13. The method of Claim 11, wherein said method is performed in the absence of ethereal solvent and/or alcohol.

14. The method of Claim 13, further comprising (c) distilling off byproduct from the reaction of step (b), wherein step (c) and step (b) are concurrent.

15. The method of Claim 11, wherein said disubstituted carbodiimide comprises dialkylcarbodiimide.

16. The method of Claim 11, wherein said disubstituted carbodiimide comprises diarylcarbodiimide.

17. An electrodepositable coating composition comprising 1,5,7-triazabicyclo[4.4.0]dec-5-ene formed in accordance with the method of Claim 1.

18. An electrodepositable coating composition comprising 1,5,7-triazabicyclo[4.4.0]dec-5-ene formed in accordance with the method of Claim 11.

19. A coated substrate formed by electrophoretically applying and curing the electrodepositable coating composition of Claim 17 onto at least a portion of a substrate.

20. A coated substrate formed by electrophoretically applying and curing the electrodepositable coating composition of Claim 18 onto at least a portion of a substrate.

21. The method of Claim 1, wherein the mixture of step a further comprises a weak acid catalyst.

22. The method of Claim 11, wherein the mixture of step a further comprises a weak acid catalyst.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/037713

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07D487/04
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data, BIOSIS, EMBASE, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	HAO SHEN ET AL: "Ti-amide Catalyzed Synthesis of Cyclic Guanidines from Di-/Triamines and Carbodiimides", ORGANIC LETTERS, vol. 13, no. 17, 2 September 2011 (2011-09-02), pages 4562-4565, XP055078019, ISSN: 1523-7060, DOI: 10.1021/ol201752e the whole document in particular Scheme 1, Table 2, Table 3 - entry 15 and discussion on page 4564	1-22
A	WO 2011/079041 A1 (NOVOMER INC [US]; GRIDNEV ALEXEI [US]) 30 June 2011 (2011-06-30) claim 2; examples 1-8	1-22

-/--

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 September 2013	23/09/2013

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Papathoma, Sofia

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Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/037713

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☒ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/037713

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GELBARD G ET AL: "Polynitrogen Strong Bases : 1 - New Syntheses of Biguanides and their Catalytic Properties in Transesterification Reactions", TETRAHEDRON LETTERS, PERGAMON, vol. 39, no. 18, 30 April 1998 (1998-04-30), pages 2743-2746, XP004113337, ISSN: 0040-4039, DOI: 10.1016/S0040-4039(98)00300-1 figure 2	1-22
X	US 2011/224328 A1 (MCCOLLUM GREGORY J [US] ET AL) 15 September 2011 (2011-09-15) the whole document in particular page 3 and paragraph 45	1-22
X,P	US 2012/220770 A1 (HICKENBOTH CHARLES ROBERT [US] ET AL) 30 August 2012 (2012-08-30) the whole document in particular scheme 1 and claim 1	1-22

1

Form PCT/ISA/210 (continuation of second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2013/037713

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2011079041 A1	30-06-2011	CN 102665406 A	12-09-2012
		EP 2515648 A1	31-10-2012
		JP 2013515728 A	09-05-2013
		KR 20120124419 A	13-11-2012
		US 2012259112 A1	11-10-2012
		WO 2011079041 A1	30-06-2011
US 2011224328 A1	15-09-2011	US 2011224328 A1	15-09-2011
		WO 2011112596 A2	15-09-2011
US 2012220770 A1	30-08-2012	US 2012220770 A1	30-08-2012
		WO 2012116080 A1	30-08-2012

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-10, 17, 19, 21

   Preparation of TBD by reaction of a disubstituted carbodiimide and dipropylene triamine in the presence of an ethereal solvent and/or alcohol and by heating the mixture to react, as well as coating compositions and substrates comprising the TBD as prepared according to the said method.

   ---

2. claims: 11, 13, 16, 18, 20

   Preparation of TBD by reaction of a disubstituted carbodiimide and dipropylene triamine and by heating the mixture to react, as well as coating compositions and substrates comprising the TBD as prepared according to the said method.

   ---

3. claim: 12

   Preparation of TBD by reaction of a disubstituted carbodiimide and dipropylene triamine and by heating the mixture to react, further comprising adding a diluent.

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4. claim: 14

   Preparation of TBD by reaction of a disubstituted carbodiimide and dipropylene triamine and by heating the mixture to react, further comprising distilling of the by-product in a concurrent manner to the heating of the mixture.

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5. claim: 15

   Preparation of TBD by reaction of a dialkylcarbodiimide and dipropylene triamine and by heating the mixture to react.

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6. claim: 22

   Preparation of TBD by reaction of a disubstituted carbodiimide and dipropylene triamine and by heating the mixture to react, further comprising a weak acid catalyst.

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(19)中华人民共和国国家知识产权局

(12)发明专利申请

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C07D 487/04(2006.01)

权利要求书1页 说明书6页

(54)发明名称

用二取代碳二亚胺和二亚丙基三胺生产1,5,7-三氮杂双环[4.4.0]癸-5-烯

(57)摘要

公开了使用二取代的碳二亚胺，二亚丙基三胺和任选地醚属溶剂和/或醇，生产1,5,7-三氮杂双环[4.4.0]癸-5-烯的方法。海公开了在可电沉积的涂料组合物中使用通过这一方法生产的1,5,7-三氮杂双环[4.4.0]癸-5-烯，和在基底上电泳沉积这一涂层，形成涂布的基底。

CN 104254536 A

1. 生产 1,5,7- 三氮杂双环 [4.4.0] 癸 -5- 烯的方法，该方法包括：

(a) 形成含二取代的碳二亚胺、二亚丙基三胺和醚属溶剂和 / 或醇的混合物；和

(b) 加热所述混合物，引起所述二取代的碳二亚胺与所述二亚丙基三胺反应。

2. 权利要求 1 的方法，其中所述加热是在大于或等于 160℃的温度下。

3. 权利要求 2 的方法，其中所述加热是在大于或等于 170℃的温度下。

4. 权利要求 1 的方法，其中所述二取代的碳二亚胺包括二烷基碳二亚胺。

5. 权利要求 4 的方法，其中所述二烷基碳二亚胺包括 N,N' - 二异丙基碳二亚胺、N,N' - 二环己基碳二亚胺或其组合。

6. 权利要求 2 的方法，其中所述二取代的碳二亚胺包括二芳基碳二亚胺。

7. 权利要求 6 的方法，其中所述二芳基碳二亚胺包括二 - 对甲苯基碳二亚胺。

8. 权利要求 1 的方法，其中在醇中形成步骤 (a) 的混合物。

9. 权利要求 8 的方法，其中所述醇包括 2- 丁氧基乙醇、二甘醇单丁醚、六乙氧基化双酚 A 多元醇或其组合。

10. 权利要求 1 的方法，进一步包括：

(c) 从步骤 (b) 的反应中蒸馏掉副产物，其中步骤 (c) 和步骤 (b) 是同时的。

11. 生产 1,5,7- 三氮杂双环 [4.4.0] 癸 -5- 烯的方法，该方法包括：

(a) 形成含二取代的碳二亚胺和二亚丙基三胺的混合物；和

(b) 加热所述混合物，引起所述二取代的碳二亚胺与所述二亚丙基三胺反应。

12. 权利要求 11 的方法，进一步包括 (c) 在步骤 (b) 之后添加稀释剂。

13. 权利要求 11 的方法，其中在醚属溶剂和 / 或醇不存在的情况下进行所述方法。

14. 权利要求 13 的方法，进一步包括 (c) 从步骤 (b) 的反应中蒸馏掉副产物，其中步骤 (c) 和步骤 (b) 是同时的。

15. 权利要求 11 的方法，其中所述二取代的碳二亚胺包括二烷基碳二亚胺。

16. 权利要求 11 的方法，其中所述二取代的碳二亚胺包括二芳基碳二亚胺。

17. 一种可电沉积的涂料组合物，它包括根据权利要求 1 的方法形成的 1,5,7- 三氮杂双环 [4.4.0] 癸 -5- 烯。

18. 一种可电沉积的涂料组合物，它包括根据权利要求 11 的方法形成的 1,5,7- 三氮杂双环 [4.4.0] 癸 -5- 烯。

19. 通过在至少一部分基底上电泳施加并固化权利要求 17 的可电沉积的涂料组合物形成的涂布的基底。

20. 通过在至少一部分基底上电泳施加并固化权利要求 18 的可电沉积的涂料组合物形成的涂布的基底。

21. 权利要求 1 的方法，其中步骤 a 的混合物进一步包括弱酸催化剂。

22. 权利要求 11 的方法，其中步骤 a 的混合物进一步包括弱酸催化剂。

用二取代碳二亚胺和二亚丙基三胺生产 1,5,7- 三氮杂双环 [4.4.0] 癸 -5- 烯

[0001] 相关申请的交叉参考

[0002] 本申请是 2012 年 4 月 25 日提交的美国专利申请序列号 13/455,651 的部分继续申请。

发明领域

[0003] 本发明涉及生产 1,5,7- 三氮杂双环 [4.4.0] 癸 -5- 烯的方法。

[0004] 发明背景

[0005] 已知双环胍类，例如 1,5,7- 三氮杂双环 [4.4.0] 癸 -5- 烯 (TBD) 是化学活性的且可被用于催化各种化学反应。商业利用双环胍类作为催化剂（用于任何反应）的重要考虑因素是，双环胍类的购买相对便宜和 / 或容易生产。

[0006] 然而，已经公布的合成双环胍类的方法常常复杂，例如通过使用多步和 / 或耗时的工艺。其他方法使用非常昂贵和 / 或危险的起始材料。进一步地，许多公布的方法没有产生高产率的所需产物，或者产生难以与双环胍类相分离且本身可能危险的副产物，例如苯胺。此外，这些方法中的许多方法产生可能难以彼此分离的不同类型的双环胍类，和 / 或产生难以处理形式的水合胍类。

[0007] 因此，需要安全且有效的生产双环胍类的方法。

[0008] 发明概述

[0009] 本发明涉及生产 1,5,7- 三氮杂双环 [4.4.0]-5- 烯的方法，该方法包括形成含二取代的碳二亚胺，二亚丙基三胺和醚属溶剂 (ethereal solvent) 和 / 或醇的混合物；和加热该混合物，引起二取代的碳二亚胺与二亚丙基三胺反应。

[0010] 本发明进一步涉及生产 1,5,7- 三氮杂双环 [4.4.0] 癸 -5- 烯的方法，该方法包括形成含二取代的碳二亚胺和二亚丙基三胺的混合物；和加热该混合物，引起二取代的碳二亚胺与二亚丙基三胺反应。

[0011] 发明详述

[0012] 本发明涉及生产双环胍类的方法。更具体地，本发明涉及生产 1,5,7- 三氮杂双环 [4.4.0]-5- 烯的方法，该方法包括使二取代的碳二亚胺与也称为双 (3- 氨丙基）胺的二亚丙基三胺（“DPTA”）反应。

[0013] 本文中所使用的术语“二取代的碳二亚胺”是指具有化学式 $RN=C=NR^1$ 的化合物，其中 R 和 R^1 独立地包括烷基，芳基或其混合物。R 和 R^1 可以相同或不同。在某些实施方案中，二取代的碳二亚胺包括二烷基碳二亚胺，和 R/R^1 基是脂族和 / 或脂环族烷基，例如具有 1-10 个碳的脂族和 / 或脂环族烷基；尤其合适的二烷基碳二亚胺没有限制地包括 N,N'- 二异丙基碳二亚胺 (DIC)（即，当 R/R^1 是异丙基时），N,N'- 二环己基碳二亚胺 (DCC)（即，当 R/R^1 是环己基时），N,N'- 二叔丁基碳二亚胺（当 R/R^1 是叔丁基时），及其任何组合。

[0014] 在某些实施方案中，二取代的碳二亚胺包括二芳基碳二亚胺，和 R/R^1 基是芳基。尤

其合适的二芳基碳二亚胺是N,N'-二对甲苯基碳二亚胺（其中R/R^1是甲苯残基）。在某些实施方案中，使用一种或更多种二烷基碳二亚胺和/或一种或更多种二芳基碳二亚胺的组合。

[0015] 在某些实施方案中，生产1,5,7-三氮杂双环[4.4.0]癸-5-烯的方法包括首先在醚属溶剂中和/或在醇中溶解二取代的碳二亚胺，之后使二取代的碳二亚胺与DPTA反应。这些实施方案在本文中有时称为“溶剂法”。在以下进一步讨论的备选的实施方案中，生产1,5,7-三氮杂双环[4.4.0]癸-5-烯的方法没有利用醚属溶剂或醇，和在本文中有时称为“无溶剂法”。

[0016] 一般地，溶剂法始于在醚属溶剂中和/或在醇中溶解二取代的碳二亚胺。接下来，将二亚丙基三胺加入到已溶解的二取代的碳二亚胺中。在一些实施方案中，加热二取代的碳二亚胺和溶剂和/或醇混合物，例如到60℃的温度，之后添加DPTA，和在一些实施方案中，在添加DPTA之后，加热该混合物到约60℃。然后进一步加热该混合物到升高的温度，并保持充足的时间段，使二取代的碳二亚胺和二亚丙基三胺反应，首先形成中间体（通常N,N'-二取代的单环胍类），然后形成1,5,7-三氮杂双环[4.4.0]癸-5-烯和胺。通过使二取代的碳二亚胺和二亚丙基三胺反应生成的胺取决于R/R^1基团。例如，若R/R^1是异丙基，则胺将是异丙基胺，或者若R/R^1是环己基，则胺将是环己基胺。这一胺副产物可在反应过程中蒸馏掉，使得当反应完成时，在反应容器内与1,5,7-三氮杂双环[4.4.0]癸-5-烯一起残留的所有物质是醚属溶剂和/或醇。或者，胺副产物可以在反应完成时除去。

[0017] 可在本发明的溶剂法中使用的合适的醚属溶剂包括，但不限于丁基卡必醇缩甲醛(butyl carbitol formal)。

[0018] 可在本发明的溶剂法中使用的合适的醇（即，醇类溶剂）包括，但不限于，一元醇或多元醇，例如2-丁氧基乙醇（即，丁基溶纤剂），二甘醇单丁醚（即，丁基CARBITOL），六乙氧基化双酚A多元醇及其组合。在某些实施方案中，使用2-丁氧基乙醇。

[0019] 一般地，本发明的溶剂法始于引入二取代的碳二亚胺到反应容器中。接下来，将二亚丙基三胺缓慢地加入到反应容器中，其中所得混合物开始反应并放热。然后加热该混合物到升高的温度，并保持充足的时间段，使二取代的碳二亚胺和二亚丙基三胺反应，首先形成中间体，然后形成1,5,7-三氮杂双环[4.4.0]癸-5-烯和胺。这一胺副产物在反应过程中可以蒸馏掉，或者当反应完成时被除去。稀释剂，例如六乙氧基化双酚A多元醇可加入到反应容器内形成的1,5,7-三氮杂双环[4.4.0]癸-5-烯中。

[0020] 当在本发明方法的上下文中使用时，术语“升高的温度”是二取代的碳二亚胺与二亚丙基三胺反应形成1,5,7-三氮杂双环[4.4.0]癸-5-烯和胺时的温度。在某些实施方案中，升高的温度是大于或等于160℃，大于或等于170℃，或者大于或等于180℃，且可以高达220℃，230℃，240℃或甚至更高。典型地，较高温度导致较短的反应时间。在某些溶剂法中，升高的温度对应于所使用的醚属溶剂和/或醇或共混物的回流温度。例如，当使用2-丁氧基乙醇时，升高的温度对应于2-丁氧基乙醇的回流温度（约170℃）。在特别的实施方案中，二取代的碳二亚胺包括二芳基碳二亚胺和升高的温度是大于或等于160℃，大于或等于170℃，或者大于或等于180℃。

[0021] 当在本发明方法的上下文中使用时，术语“充足的时间段”是引起二取代的碳二亚胺与二亚丙基三胺基本上或完全反应所需的时间。“基本上反应”是指转化率大于或等于

70%；“完全反应”是指转化率大于或等于85%。这一时间段可以随确切的反应条件而变化，和在溶剂法的情况下，随所使用的醚属溶剂和/或醇而变化。典型地，充足的时间段为1-6小时，例如1-4小时或者2-4小时。可使用已知的光谱技术（IR，^{13}C NMR等），通过分析反应容器的内容物，确定反应程度，以证实二取代的碳二亚胺和二亚丙基三胺存在与否，并证实1,5,7-三氮杂双环[4.4.0]癸-5-烯的存在。

[0022] 在某些实施方案中，在没有催化剂的情况下，进行本文中描述的方法。然而，在其他实施方案中，使用催化剂。根据目前的方法，可使用增加二取代的碳二亚胺和二亚丙基三胺之间反应速率的任何催化剂，例如弱酸催化剂。合适的弱酸催化剂包括，但不限于，硫脲，叔十二烷基硫醇，2-巯基乙醇和双酚A。在某些实施方案中，催化剂是添加剂，和在其他实施方案中，催化剂可作为碳二亚胺内的杂质（可能地作为制造工艺的副产物形式生成）引入。甚至这些痕量的催化剂可增加反应速率。若使用的话，则催化剂可与碳二亚胺一起添加。

[0023] 在某些实施方案中，通过在大气压下蒸馏，将1,5,7-三氮杂双环[4.4.0]癸-5-烯与醚属溶剂和/或醇相分离。在某些实施方案中，在蒸馏工艺之后，可以以粉末形式回收1,5,7-三氮杂双环[4.4.0]癸-5-烯。或者，1,5,7-三氮杂双环[4.4.0]癸-5-烯可与醚属溶剂和/或与醇维持在溶液内以供随后使用。如上所述，在溶剂和无溶剂法二者中，可借助蒸馏，从反应容器中除去胺副产物。在某些实施方案中，这一蒸馏与反应同时进行。“同时（concurrent）”是指在其中在形成1,5,7-三氮杂双环[4.4.0]癸-5-烯的反应过程中进行蒸馏。尽管发明人不希望束缚于任何机理，但在某些实施方案中，蒸馏掉副产物与反应同时进行可导致更加有效地，亦即更加快速地和/或在更高转化率百分比下发生反应。

[0024] 在以上所述的或者溶剂或者无溶剂法中形成的分离的双环胍（1,5,7-三氮杂双环[4.4.0]癸-5-烯（TBD））（它为溶液形式或者粉末形式）然后可加入到双环胍可在其内使用的任何组合物中。例如，在某些实施方案中，由本文描述的方法形成的双环胍可加入到可电沉积的涂料组合物，例如在美国专利No.7,842,762中描述的可电沉积的涂料组合物中，在此通过参考将其全文引入。

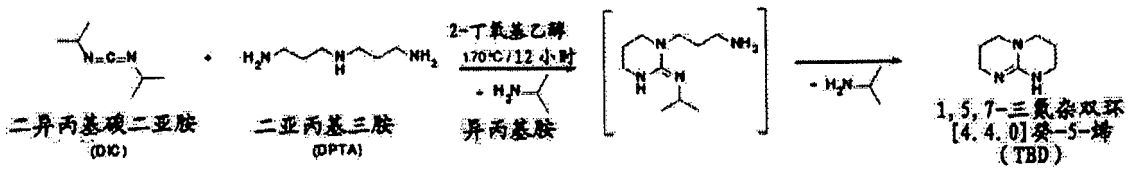
[0025] 除非另外明确说明，本文中所使用的所有数值，例如表达值、范围，用量或百分比的那些数值可以如同冠以措辞“约”来阅读一样，即使该术语没有明确地出现。本文中引证的任何数值范围拟包括本文中包含的所有子范围。复数包括单数和相反。例如，尽管就“一种”二取代的碳二亚胺，“一种”醇描述了本发明，“该（the）”R/R^1基团和类似基团，但可使用这些和其他组分的混合物。此外，本文中所使用的术语“聚合物”拟指预聚物，低聚物，和均聚物与共聚物二者；前缀“聚”是指两个或更多个。当给出范围时，在这些范围内，这些范围和/或数值的任何终点可与本发明的范围组合。“包括”，“例如”和类似术语是指“包括/例如/例如，但不限于”。

实施例

[0026] 下述实施例拟例举本发明且绝不打算限制本发明。

[0027] 实施例1：在2-丁氧基乙醇内的DIC路线

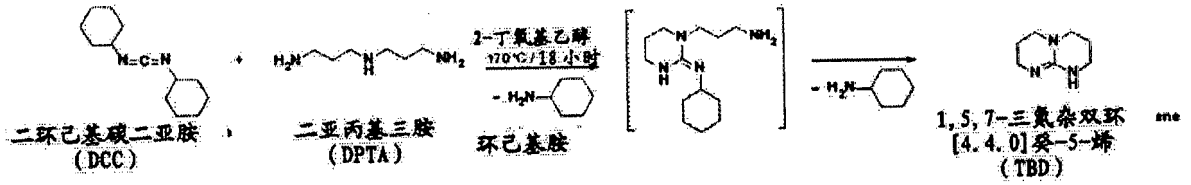
[0028]



[0029] 四颈烧瓶配有温度探针，不锈钢机械搅拌器，和冰水冷凝器。干燥氮气吹扫通过该烧瓶，经冷凝器出来，然后通过含有干冰与乙醇的附着的冷阱，以捕获异丙基胺蒸馏物。向该烧瓶中引入 2- 丁氧基乙醇 (220mL) 和 N,N' - 二异丙基碳二亚胺 (151.4g, 1.2mol)，并温热到 60℃。然后，缓慢地添加二亚丙基三胺 (131.2g, 1.0mol)。一旦添加二亚丙基三胺，则观察到 40℃的放热 (～ 60℃→ 100℃)。反应被缓慢地温热到 170℃，并在该温度下回流 12 小时。然后冷却橙色的均匀溶液，倾倒出反应容器，并在没有进一步纯化的情况下使用。通过 HPLC，测定最终溶液内的 TBD 浓度 (38.8wt%，94.6%转化率)。^{13}C NMR 分析表明该物质仅仅由在 2- 丁氧基乙醇内的 1,5,7- 三氮杂双环 [4.4.0] 癸 -5- 烯组成。蒸馏物的 ^{13}C NMR 分析证实了捕获副产物异丙基胺 (129mL) 作为唯一的化合物。

[0030] 实施例 2 :在 2- 丁氧基乙醇内的 DCC 路线

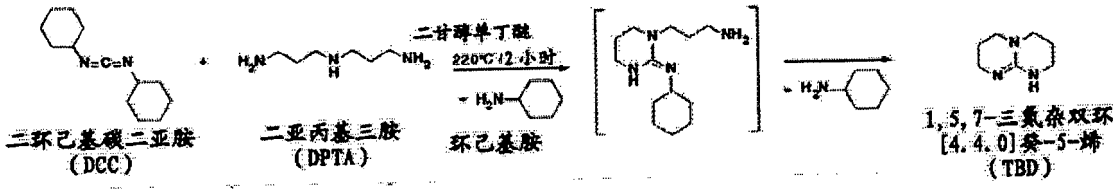
[0031]



[0032] 四颈烧瓶配有温度探针，不锈钢机械搅拌器，和冰水冷凝器。干燥氮气吹扫通过该烧瓶，并经冷凝器出来。向该烧瓶中引入 2- 丁氧基乙醇 (220mL) 和 N,N' - 二环己基碳二亚胺 (247.6g, 1.2mol)，并温热到 60℃。然后，缓慢地添加二亚丙基三胺 (131.2g, 1.0mol)。一旦添加二亚丙基三胺，则观察到 14℃的放热 (～ 58℃→ 72℃)。反应被缓慢地温热到 170℃，并在该温度下回流 18 小时。然后冷却橙色的均匀溶液，倾倒出反应容器，并在没有进一步纯化的情况下使用。通过 HPLC，测定最终溶液内的 TBD 浓度 (32.9wt%，80.2%转化率)。^{13}C NMR 分析表明该物质仅仅由在 2- 丁氧基乙醇内的 1,5,7- 三氮杂双环 [4.4.0] 癸 -5- 烯和环己基胺 (2.5%) 组成。

[0033] 实施例 3 :在二甘醇单丁醚内的 DCC 路线

[0034]

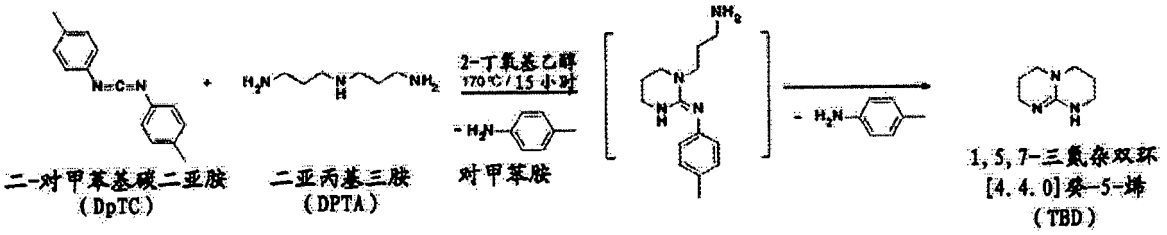


四颈烧瓶配有全蒸馏装置以及温度探针，和不锈钢机械搅拌器。干燥氮气吹扫通过该烧瓶，并经蒸馏装置出来。向该烧瓶中引入二甘醇单丁醚 (210mL) 和 N,N' - 二环己基碳二亚胺 (247.6g, 1.2mol)，并温热到 60℃。然后，缓慢地添加二亚丙基三胺 (131.2g, 1.0mol)。一旦添加二亚丙基三胺，则观察到 41℃的放热 (～ 61℃→ 102℃)。反应被温热到 140℃，并保持 1 小时，然后加热到 220℃，并保持 2 小时。然后冷却橙色的均匀溶液，倾倒出反

应容器，并在没有进一步纯化的情况下使用。通过 HPLC，测定最终溶液内的 TBD 浓度（35.4wt%，81.0%转化率）。^{13}C NMR 分析表明该物质仅仅由在二甘醇单丁醚内的 1,5,7-三氮杂双环 [4.4.0] 癸 -5- 烯组成。蒸馏物的 ^{13}C NMR 和 GC/MS 分析证实了捕获环己基胺（199mL）。

[0035] 实施例 4 :在 2- 丁氧基乙醇内的 DpTC 路线

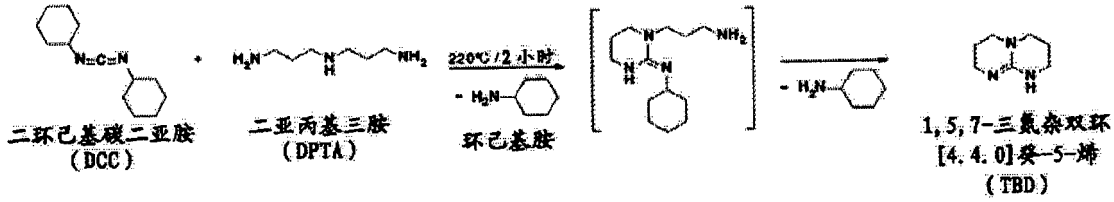
[0036]



[0037] 四颈烧瓶配有温度探针，磁搅拌棒，和冰水冷凝器。干燥氮气吹扫通过该烧瓶，并经冷凝器出来。在环境温度下向该烧瓶中引入 2- 丁氧基乙醇（11mL），N,N'- 二 - 对甲苯基碳二亚胺（13.5g,0.06mmol），和二亚丙基三胺（6.64g,0.05mol），观察到 34℃的放热（～ 23℃→ 57℃）。反应被缓慢地温热到 170℃，并在该温度下回流 15 小时。然后冷却橙 - 棕色的均匀溶液，倾倒出反应容器，并在没有进一步纯化的情况下使用。通过 HPLC，测定最终溶液内的 TBD 浓度（19.9wt%，79.1%转化率）。^{13}C NMR 和 GC 分析表明该物质仅仅由在 2- 丁氧基乙醇内的 1,5,7- 三氮杂双环 [4.4.0] 癸 -5- 烯和对甲苯胺（36.8%）组成。

[0038] 实施例 5 :DCC 路线（100%固体，后添加的多元醇，DCC 过量 20%）

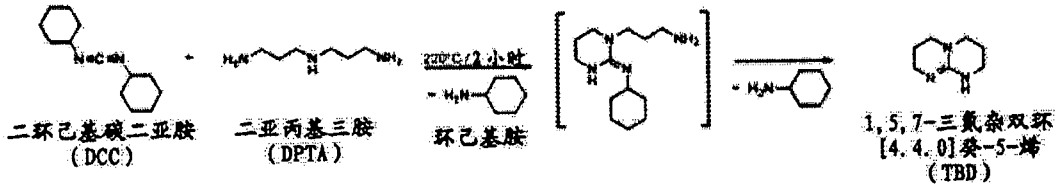
[0039]



[0040] 四颈烧瓶配有全蒸馏装置以及温度探针，和不锈钢机械搅拌器。干燥氮气吹扫通过该烧瓶，并经蒸馏装置出来。向该烧瓶中引入 N,N'- 二环己基碳二亚胺（247.6g,1.2mol），接着缓慢添加二亚丙基三胺（131.2g,1.0mol）。当添加二亚丙基三胺时，观察到 31℃的放热（～ 24℃→ 55℃）。反应被温热到 170℃，并保持 1 小时，然后加热到 220℃，并保持 2 小时。在最后的保持之后，添加六乙氧基化双酚 A 多元醇（417.0g,0.85mol）作为稀释剂。然后搅拌、冷却橙色的均匀溶液，倾倒出反应容器，并在没有进一步纯化的情况下使用。通过 HPLC，测定最终溶液内的 TBD 浓度（21.3wt%，94.4%转化率）。^{13}C NMR 分析表明该物质仅仅由在六乙氧基化双酚 A 多元醇内的 1,5,7- 三氮杂双环 [4.4.0] 癸 -5- 烯组成。蒸馏物的 ^{13}C NMR 和 GC/MS 分析证实了捕获环己基胺（175mL）。

[0041] 实施例 6 :DCC 路线（100%固体，后添加多元醇，DCC 过量 2%）

[0042]



[0043] 四颈烧瓶配有全蒸馏装置以及温度探针，和不锈钢机械搅拌器。干燥氮气吹扫通过该烧瓶，并经蒸馏装置出来。向该烧瓶中引入N,N'-二环己基碳二亚胺(210.5g,1.02mol)，接着缓慢添加二亚丙基三胺(131.2g,1.00mol)。当添加二亚丙基三胺时，观察到32℃的放热(～23℃→55℃)。反应被温热到170℃，并保持1小时，然后加热到220℃，并保持2小时。在最后的保持之后，添加六乙氧基化双酚A多元醇(319.8g,0.65mol)作为稀释剂。然后搅拌、冷却橙色的均匀溶液，倾倒出反应容器，并在没有进一步纯化的情况下使用。通过HPLC，测定最终溶液内的TBD浓度(28.0wt%，93.7%转化率)。^{13}C NMR分析表明该物质仅仅由在六乙氧基化双酚A多元醇内的1,5,7-三氮杂双环[4.4.0]癸-5-烯组成。蒸馏物的^{13}C NMR和GC/MS分析证实了捕获环己基胺(229mL)。

[0044] 实施例7:DCC路线(100%固体，后添加的多元醇，DCC过量2%，98%纯度的DCC，弱酸催化剂)

[0045] 四颈烧瓶配有全蒸馏装置以及温度探针，和不锈钢机械搅拌器。干燥氮气吹扫通过该烧瓶，并经蒸馏装置出来。向该烧瓶中连续引入N,N'-二环己基碳二亚胺(210.5g,1.02mol,98%纯度-Dalian Harsou Chemical Co.,Ltd)，双酚A(0.570g,0.0025mol)和二亚丙基三胺(131.2g,1.00mol)。当添加二亚丙基三胺时，观察到30℃的放热(24℃→54℃)。反应被温热到140℃，并保持1小时，然后缓慢地加热到220℃，并保持2小时。在最后的保持之后，添加六乙氧基化双酚A多元醇(319.8g,0.65mol)作为稀释剂。然后搅拌、冷却橙色的均匀溶液，倾倒出反应容器，并在没有进一步纯化的情况下使用。通过HPLC，测定最终溶液内的TBD浓度(29.3wt%，96.7%转化率)。^{13}C NMR分析表明该物质仅仅由在六乙氧基化双酚A多元醇内的1,5,7-三氮杂双环[4.4.0]癸-5-烯组成。应当注意，尝试在不存在双酚A情况下的上述工序得到显著较低的TBD转化率，这通过HPLC来分析(26.9wt%，88.7%转化率)。这证明在DPTA与98%纯度的DCC反应中，使用弱酸催化剂，例如双酚A改进了TBD的转化率。

[0046] 尽管为了阐述的目的，以上描述了本发明的特别的实施方案，但对于本领域技术人员来说，明显的是可在没有脱离所附权利要求定义的本发明的情况下，作出本发明细节的许多改变。