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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.

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.

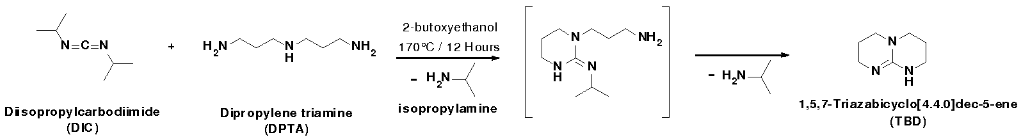
[0020] The isolated bicyclic guanidine (1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD)), formed in either the solvent or solventless processes described above, which is in solution form or powder form, can then be added to any composition in which bicyclic guanidine can be used. For example, in certain embodiments, 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

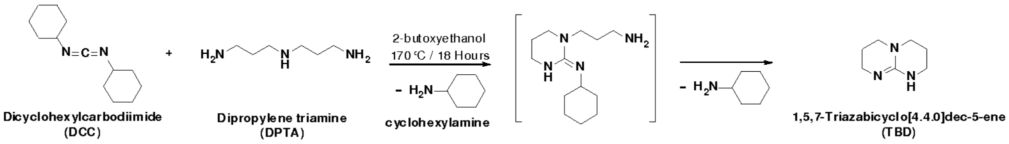
[0022] The following examples are intended to exemplify the invention and are not intended to limit the invention in any way.

Example 1: DIC Route in 2-butoxyethanol



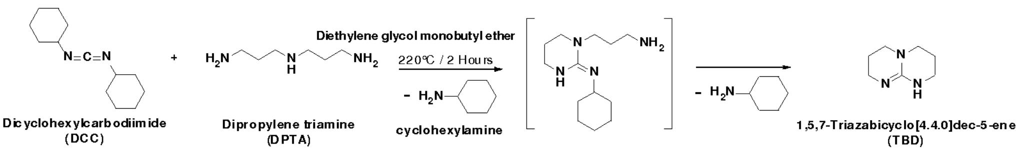
[0023] A 4-neck flask was equipped with a temperature probe, stainless steel mechanical stirrer, and an ice water condenser. Dry nitrogen was swept through the flask, out through the condenser, then through an attached cold trap containing dry ice and ethanol used to trap isopropylamine distillate. The flask was charged with 2-butoxyethanol (220 mL) and *N,N'*-diisopropylcarbodiimide (151.4 g, 1.2 mol), and warmed to 60ºC. 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



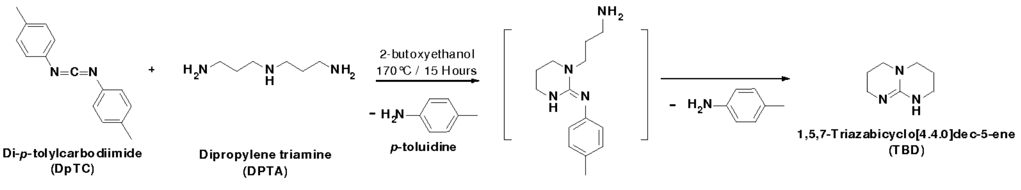
[0024] A 4-neck flask was equipped with a temperature probe, stainless steel mechanical stirrer, and an ice water condenser. Dry nitrogen was swept through the flask and out through the condenser. The flask was charged with 2-butoxyethanol (220 mL) and *N,N'*-dicyclohexylcarbodiimide (247.6 g, 1.2 mol), and warmed to 60 ºC. 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).

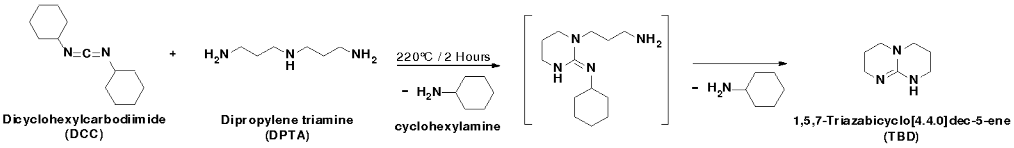
Example 4: DpTC Route in 2-butoxyethanol



[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

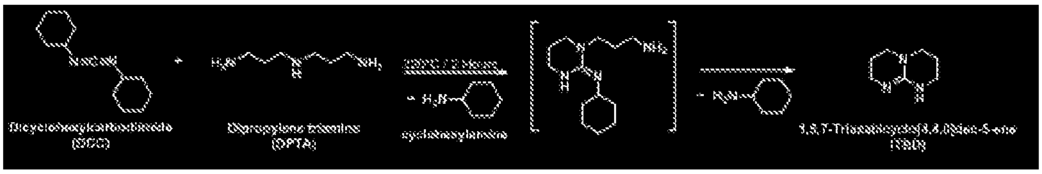
HPLC (19.9 wt%, 79.1% conversion). ^{13}C NMR and GC analyses indicated that the material consisted of 1,5,7-triazabicyclo[4.4.0]dec-5-ene and *p*-toluidine (36.8%) in 2-butoxyethanol.

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

☒ Further documents are listed in the continuation of Box C.

☒ 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 13 September 2013	Date of mailing of the international search report 23/09/2013
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Papathoma, Sofia

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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.

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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

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Information on patent family members

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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.

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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.

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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.
