

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property

Organization

International Bureau

(43) International Publication Date

29 June 2023 (29.06.2023)



(10) International Publication Number

WO 2023/115290 A1

(51) International Patent Classification:

C07C 209/60 (2006.01) C07C 209/24 (2006.01)

C07C 209/00 (2006.01) C07C 211/08 (2006.01)

TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

(21) International Application Number:

PCT/CN2021/139861

Published:

— with international search report (Art. 21(3))

(22) International Filing Date:

21 December 2021 (21.12.2021)

(25) Filing Language:

English

(26) Publication Language:

English

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, IT, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,

(54) Title: PROCESS FOR PREPARING SECONDARY AMINES

(57) Abstract: The present invention relates to a simple and environmentally friendly process for preparing secondary amines by the aminomethylation of alkenes. This process features relatively mild reaction conditions, i.e. at a temperature lower than 115 °C.

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PROCESS FOR PREPARING SECONDARY AMINES

TECHNICAL FIELD

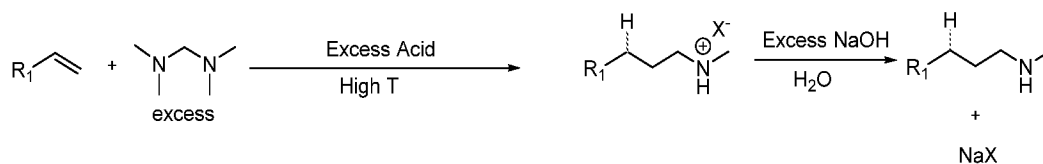
The present invention relates to a process for preparing secondary amines.

BACKGROUND

5 The following discussion of the prior art is provided to place the invention in an appropriate technical context and enable the advantages of it to be more fully understood. It should be appreciated, however, that any discussion of the prior art throughout the specification should not be considered as an express or implied admission that such prior art is widely known or forms part of common
10 general knowledge in the field.

Amines are of significant importance for the chemical industry, but also for numerous biological processes. For instance, amino acids and nucleotides constitute essential biological building blocks and numerous bioactive compounds such as vitamins, hormones, alkaloids, neurotransmitters, or natural
15 toxics contain amino groups. It is, therefore, not surprising, that numerous amines and their derivatives find application as agrochemicals, pharmaceuticals, or food additives. Several million tons of amines are produced annually. They are widely used in both the bulk and fine chemical industries as fundamental materials, additives, dyes, and agrochemicals.

20 As disclosed by Acta Chemica Scandinavica, Series B: Organic Chemistry and Biochemistry (1986), B40(3), 190-195, secondary amines can be obtained by the aminomethylation of alkenes, which is a reaction involving an imino-ene step and/or 1,5-hydride transfer. The reaction requires excess aminational, which is preformed by condensation of formaldehyde and dimethylamine (DMA), and a
25 strong acid in acid medium as solvent. As a result, excess sodium hydroxide has to be added into the reaction mixture at the end of the reaction to separate the amine salt, leading to excess waste (eg. NaAc/NaCF₃COOH). Therefore, this method needs aminomethylation of olefin with aminational to form secondary amine salt and then hydrolysis of salt to form secondary amine. Moreover, a high
30 temperature is compulsory.



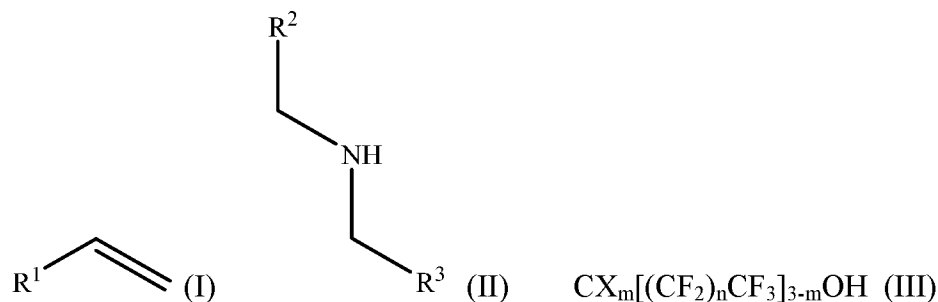
As such, there remains a need for an improved process for preparing secondary amines.

5 SUMMARY OF THE INVENTION

The aim of the present invention is then to provide a process preparing secondary amines, which features a simple and environmental-friendly system and relatively mild reaction conditions, i.e. at a temperature lower than 115 °C.

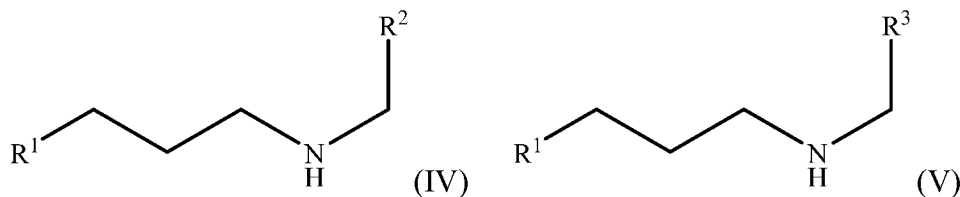
10 Upon diligent research, the inventors have discovered surprisingly that such an aim can be achieved by selecting a specific solvent in the aminomethylation reaction of alkenes.

Thus, the present invention is directed to a process for preparing at least one first secondary amine by reacting an alkene represented by general formula (I) with formaldehyde and at least one other secondary amine represented by general formula (II) in a solvent being a compound represented by general formula (III),
 15



20 wherein:

- the at least one first secondary amine is a compound represented by general formula (IV) and/or a compound represented by general formula (V);



wherein :

- R^1 , R^2 , and R^3 are same or different and each independently H or a hydrocarbon radical which is optionally interrupted by one or more heteroatoms and/or heteroatom(s) containing groups and/or which is optionally substituted with one or more functional groups;
- m is an integer being 0, 1 or 2;
- n is an integer from 0 to 20;
- X is H or F; and
- with the proviso that when m is 2, X is not H.

With the process according to the present invention, it is possible to prepare secondary amine(s) under mild reaction conditions, i.e. at a temperature lower than 115 °C.

In addition, the secondary amine can be prepared without using a basic compound and a metal catalyst. Thus, this process is more simple and environmental-friendly.

Furthermore, the starting reactants, especially the starting secondary amine can be used directly without pre-treatment, such as prior conversion into a salt.

Other subjects and characteristics, aspects and advantages of the present invention will emerge even more clearly on reading the detailed description and the examples that follow.

DEFINITIONS

Throughout the description, including the claims, the term "comprising one" should be understood as being synonymous with the term "comprising at least one", unless otherwise specified, and "between" should be understood as being inclusive of the limits.

As used herein, the terminology " $(\text{C}_n\text{--C}_m)$ " in reference to an organic group, wherein n and m are both integers, indicates that the group may contain from n carbon atoms to m carbon atoms per group.

The articles "a", "an" and "the" are used to refer to one or to more than one (i.e., to at least one) of the grammatical object of the article.

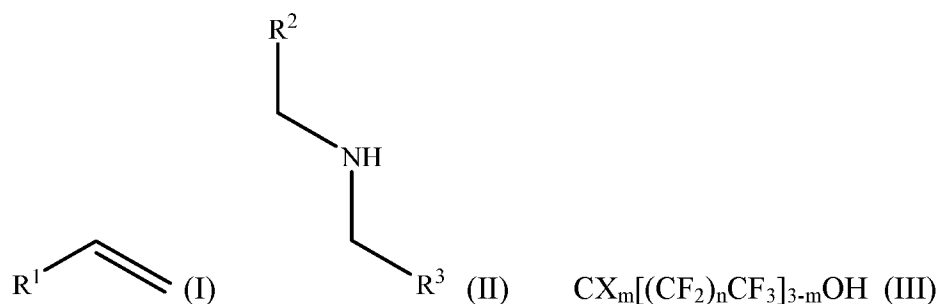
The term “and/or” includes the meanings “and”, “or” and also all the other possible combinations of the elements connected to this term.

It is specified that, in the continuation of the description, unless otherwise indicated, the values at the limits are included in the ranges of values which are given.

Ratios, concentrations, amounts, and other numerical data may be presented herein in a range format. It is to be understood that such a range format is used merely for convenience and brevity and should be interpreted flexibly to include not only the numerical values explicitly recited as the limits of the range, but also all the individual numerical values or sub-ranges encompassed within that range as if each numerical value or sub-range is explicitly recited.

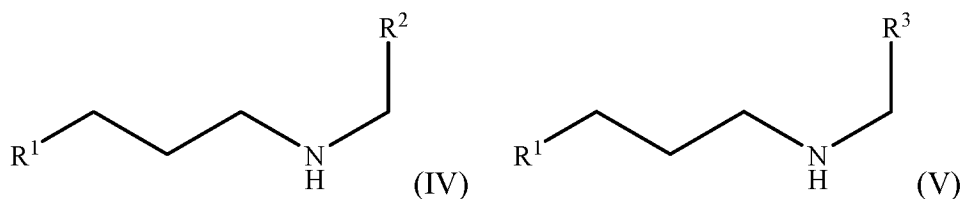
DETAILS OF THE INVENTION

The present invention provides a process for preparing at least one first secondary amine by reacting an alkene represented by general formula (I) with formaldehyde and at least one other secondary amine represented by general formula (II) in a solvent being a compound represented by general formula (III),



wherein:

- the at least one first secondary amine is a compound represented by general formula (IV) and/or a compound represented by general formula (V);



wherein:

- R^1 , R^2 , and R^3 are same or different and each independently H or a hydrocarbon radical which is optionally interrupted by one or more heteroatoms and/or heteroatom(s) containing groups and/or which is optionally substituted with one or more functional groups;

- 5 - m is an integer being 0, 1 or 2;
 - n is an integer from 0 to 20;
 - X is H or F; and
 - with the proviso that when m is 2, X is not H.

In some embodiments, R^1 is an aryl or a heteroaryl.

10 As used herein, the term "aryl" means a monocyclic or bicyclic aromatic hydrocarbon radical of 6 to 10 ring atoms which is optionally substituted independently with one to four substituents, preferably one, two, or three substituents selected from alkyl, alkenyl, alkynyl, aryl, halo, nitro, cyano, hydroxy, alkoxy, amino, mono-alkylamino, di-alkylamino and heteroalkyl.

15 As used herein, the term "heteroaryl" means a monocyclic or bicyclic radical of 5 to 12 ring atoms having at least one aromatic ring containing one, two, or three ring heteroatoms selected from N, O, or S, the remaining ring atoms being C, with the understanding that the attachment point of the heteroaryl radical will be on an aromatic ring. The heteroaryl ring is optionally substituted
20 independently with one to four substituents, preferably one or two substituents, selected from alkyl, aryl, halo, nitro, cyano, hydroxy, alkoxy, amino, acylamino, mono-alkylamino, di-alkylamino, heteroalkyl. More specifically the term heteroaryl includes, but is not limited to, pyridyl, furanyl, thienyl, thiazolyl, isothiazolyl, triazolyl, imidazolyl, isoxazolyl, pyrrolyl, pyrazolyl, pyridazinyl,
25 pyrimidinyl, benzofuranyl, tetrahydrobenzofuranyl, isobenzofuranyl, benzothiazolyl.

In a preferred embodiment, the alkene represented by general formula (I) can be styrene or styrene substituted with alkyl, phenyl, halo or alkoxy. Said alkyl can be a C_1 - C_6 straight or branched chain alkyl. Preferably, C_1 - C_6 straight
30 chain alkyl can be selected from the group consisting of methyl, ethyl, 1-propyl, n-butyl and n-pentyl. Preferably, C_1 - C_6 branched chain alkyl can be isopropyl or isobutyl. Said alkoxy preferably can be a C_1 - C_6 alkoxy and more preferably methoxy or ethoxy. Said halo can be F, Cl, Br or I.

As previously expressed, R^2 and R^3 are same or different and each
35 independently H or a hydrocarbon radical which is optionally interrupted by one

or more heteroatoms and/or heteroatom(s) containing groups and/or which is optionally substituted with one or more functional groups.

Preferably, R^2 and R^3 are same or different and each independently H or a C_1 - C_4 alkyl.

5 In some embodiments, R^2 and R^3 are different. In this embodiment, the compound represented by general formula (IV) and the compound represented by general formula (V) are different chemical compounds. The at least one first secondary amine can be a compound represented by general formula (IV), a compound represented by general formula (V) or their mixture. When a mixture
10 is prepared, the molar ratio of the compound represented by general formula (IV) to the compound represented by general formula (V) depends on the relative reactivity of R^2 and R^3 .

In some embodiments, R^2 and R^3 are same. In this embodiment, the compound represented by general formula (IV) and the compound represented
15 by general formula (V) are the same chemical compounds.

In a specific embodiment, R^2 and R^3 are same and each independently H.

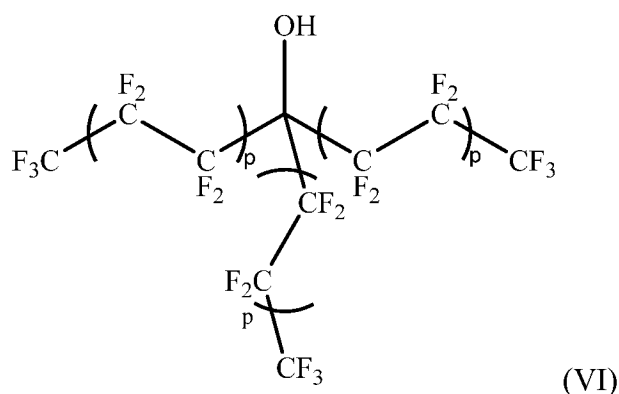
As previously expressed, the solvent is a compound represented by general formula (III).



20 wherein:

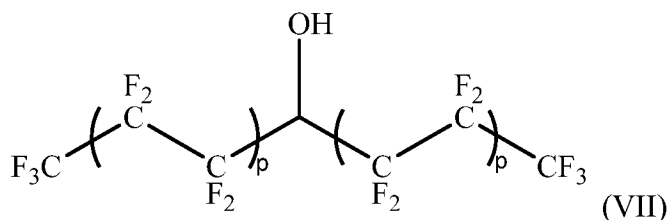
- m is an integer being 0, 1 or 2;
- n is an integer from 0 to 20 ;
- X is H or F; and
- with the proviso that when m is 2, X is not H.

25 In a preferred embodiment, m are 0. The solvent in this embodiment can be a compound having the following general formula (VI).



wherein p is an integer from 0 to 10.

In another preferred embodiment, X is H, m is 1. The solvent in this embodiment can be a compound having the following general formula (VII).



wherein p is an integer from 0 to 10.

Non limitative examples of the compound having the following general formula (VII) is hexafluoroisopropanol(HFIP).

10 According to the process of the present invention, formaldehyde can be introduced in the form of an aqueous solution. The concentration of formaldehyde in the aqueous solution can be from 35% to 55% and preferably from 35% to 40%. In a preferred embodiment, the aqueous solution of formaldehyde can be formalin.

15 When R^2 and R^3 are different, the molar ratio of the alkene represented by general formula (I) to formaldehyde can be from 1:1 to 1:10 and preferably 1:1 to 1:5.

When R^2 and R^3 are same and not hydrogen, the molar ratio of the alkene represented by general formula (I) to formaldehyde can be from 1:1 to 1:10 and preferably 1:1 to 1:5.

20 When R^2 and R^3 are same and each independently H, the molar ratio of the alkene represented by general formula (I) to formaldehyde can be from 1:1 to 10:1 and preferably 1:1 to 5:1.

25 According to the process of the present invention, the at least one other secondary amine represented by general formula (II) can either be introduced as a pure chemical or be introduced in the form of a solution. For example, when the secondary amine represented by general formula (II) is dimethylamine(DMA), it can be introduced in the form of an aqueous solution. The concentration of DMA in the aqueous solution can be from 30% to 45% and preferably from 35% to 40%.

Advantageously, the molar ratio of the alkene represented by general formula (I) to the at least one other secondary amine represented by general formula (II) can be from 1: 1 to 1: 10 and preferably from 1: 1 to 1: 5.

Advantageously, the weight ratio ratio of the alkene represented by general formula (II) to the solvent can be from 1: 10: o 1: 200 and preferably 1: 10: o 1: 50.

According to the process of the present invention, the reaction temperature can be lower than 110 °C, preferably lower than 100 °C, more preferably lower than 90 °C and most preferably lower than 80 °C. Advantageously, the reaction temperature can be in the range of 20°C to 60°C and preferably in the range of 30°C to 50°C.

According to the process of the present invention, the reaction time is not particularly limited. The preferred reaction time can be from 20 to 120 h.

The process of the present invention may comprise following steps:

- a) mixing formaldehyde, at least one other secondary amine represented by general formula (II) and a solvent being a compound represented by general formula (III) to obtain a mixture;
- b) adding an alkene represented by general formula (I) to the mixture obtained in step a) to obtain a reaction mixture;
- c) maintaining the reaction mixture obtained in step b) under proper reaction temperature and proper reaction time to obtain at least one first secondary amine.

The at least one first secondary amine, the alkene represented by general formula (I), the at least one other secondary amine represented by general formula (II), the compound represented by general formula (III), the reaction temperature and the reaction time are as defined above.

Advantageously, the process of the present invention can be a one-pot reaction as there is no need to hydrolyse a secondary amine salt to obtain the secondary amine.

An aspect of the present invention also provides a composition comprising:

- (i) formaldehyde,
- (ii) an alkene represented by general formula (I),
- (iii) at least one other secondary amine represented by general formula (II), and
- (iv) a compound represented by general formula (III).

The composition may optionally comprises at least one first secondary amine.

The at least one first secondary amine, the alkene represented by general formula (I), the at least one other secondary amine represented by general
5 formula (II), the compound represented by general formula (III), the reaction temperature and the reaction time are as defined above.

The following examples are included to illustrate embodiments of the invention. Needless to say, the invention is not limited to describe examples.

EXPERIMENTAL PART

Materials

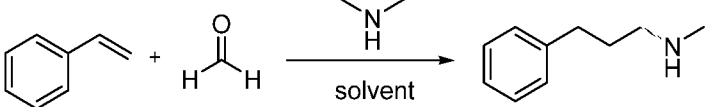
- Dimethylamine (DMA) aqueous (38wt% aqueous, reagent grade), cas:100-42-5, Merck
- 5 - Formalin (37 wt% aqueous, reagent grade), cas: 124-40-3, Merck
- Styrene (reagent grade), cas: 100-42-5, Aladin
- Hexafluoroisopropanol(HFIP) (reagent grade), cas: 920-66-1, Aladin
- AcOH (reagent grade), cas: 64-19-7, Aladin
- Toluene (reagent grade), cas: 108-88-3, Aladin
- 10 - MeOH (reagent grade), cas: 67-56-1, Aladin
- MeNO₂ (reagent grade), cas: 75-52-5, Aladin
- CF₃CH₂OH (reagent grade), cas: 75-89-8, Aladin
- 1-Fluoro-4-vinylbenzene (reagent grade), cas:405-99-2, Aladin
- 1-Chloro-4-vinylbenzene (reagent grade), cas:1073-67-2, Aladin
- 15 - 1-Chloro-2-vinylbenzene (reagent grade), cas: 2039-87-4, Aladin
- 1-Chloro-3-vinylbenzene (reagent grade), cas: 2039-85-2, Aladin
- 1-Bromo-3-vinylbenzene (reagent grade), cas: 2039-86-3, Aladin
- 1-Methyl-2-vinylbenzene (reagent grade), cas: 611-15-4, Aladin
- 4-Vinyl-1,1'-biphenyl (reagent grade), cas: 2350-89-2, Aladin
- 20 - 1-(Tert-butyl)-4-vinylbenzene (reagent grade), cas: 1746-23-2, Aladin

Examples 1-6: Preparation of N-methyl-3-phenylpropan-1-amine in different solvents

General procedure of Examples 1-6

- A round-bottom flask was charged with HCHO (2.0 mmol, 37 wt%,
25 formalin), dimethylamine (DMA) solution (8 mmol, 38 wt% aqueous) and solvent (0.1M with respect to styrene). Then, styrene (208 mg, 2.0 mmol, 1 equiv.) was added at 30 °C and the reaction mixture was stirred under atmospheric pressure(1 bar) at 30 °C for 20h. After completion of the reaction, the mixture was filtrated and analyzed using an Agilent 7890 GC equipped with
30 an HP-5 capillary column bearing 5 wt% phenyl groups (length 30 m; inner diameter 0.25 mm). Analytical methods were adjusted for the different mixtures depending on the boiling point and polarity of the reagents and products. In all the methods, the injector temperature was set at 250 °C, the detector temperature was 300 °C and the sample injection volume was 1 uL. The calibration of the gas
35 chromatography was performed using dodecanol as an internal standard.

Table 1

			
EX	Solvent	Conversion /%	Selectivity /%
1	AcOH	<5	0
2	Toluene	<5	0
3	MeOH	<5	0
4	MeNO ₂	<5	0
5	CF ₃ CH ₂ OH	<5	0
6	HFIP	97	57

It can be seen that at room temperature (such as 30°C), the reactivity of styrene in HFIP is higher than other solvents. At the same time, high conversion and selectivity of secondary amine(N-methyl-3-phenylpropan-1-amine) can be achieved under the mild condition.

Examples 7-14: Preparation of secondary amines from different alkenes in HFIP.

General procedure of Examples 7-14 is same as Example 6. The results are summarized in Table 2.

Table 2

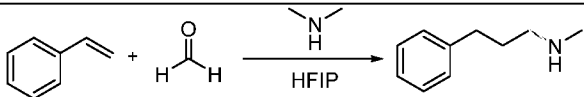
E X	Reactant (alkene)	Product (secondary amine)	Yield (%)
7	1-fluoro-4-vinylbenzene	3-(4-fluorophenyl)-N-methylpropan-1-amine	86%
8	1-chloro-4-vinylbenzene	3-(4-chlorophenyl)-N-methylpropan-1-amine	58%
9	1-chloro-2-vinylbenzene	3-(2-chlorophenyl)-N-methylpropan-1-amine	75%
10	1-chloro-3-vinylbenzene	3-(3-chlorophenyl)-N-methylpropan-1-amine	27%
11	1-bromo-3-vinylbenzene	3-(3-bromophenyl)-N-methylpropan-1-amine	23%
12	1-methyl-2-vinylbenzene	3-(2-methylphenyl)-N-methylpropan-1-amine	84%
13	4-vinyl-1,1'-biphenyl	3-([1,1'-biphenyl]-4-yl)-N-methylpropan-1-amine	57%
14	1-(tert-butyl)-4-vinylbenzene	3-(4-(tert-butyl)phenyl)-N-methylpropan-1-amine	76%

Examples 15-16: Preparation of secondary amine with different Styrene : HCHO : DMA ratios.

General procedure of Examples 15-16 is same as Example 6. The results are summarized in Table 3.

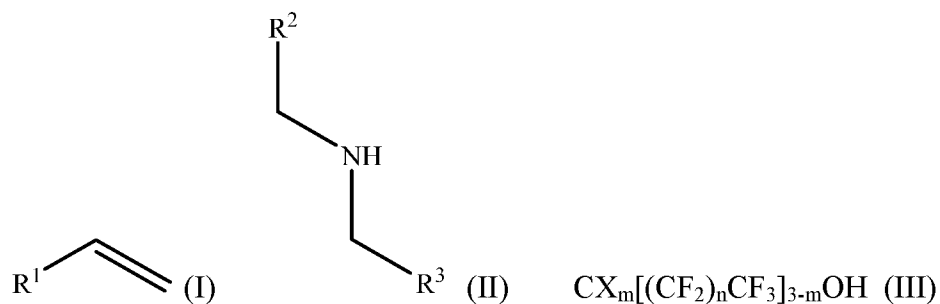
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Table 3

				
EX	Styrene : HCHO : DMA /mmol	Solvent	Conversion /%	Selectivity /%
15	2:0.8:8	HFIP	87	74
16	2:0.4:2	HFIP	60	80

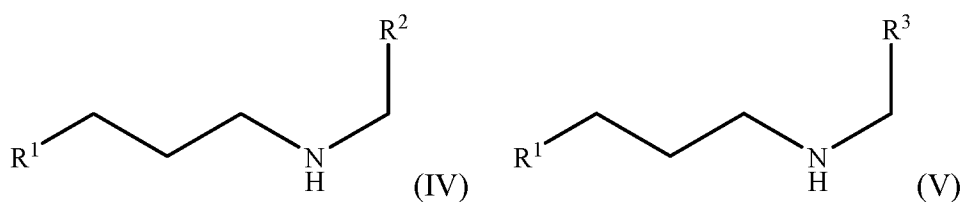
CLAIMS

1. A process for preparing at least one first secondary amine by reacting an alkene represented by general formula (I) with formaldehyde and at least one other secondary amine represented by general formula (II) in a solvent being a compound represented by general formula (III),



wherein:

- the at least one first secondary amine is a compound represented by general formula (IV) and/or a compound represented by general formula (V),

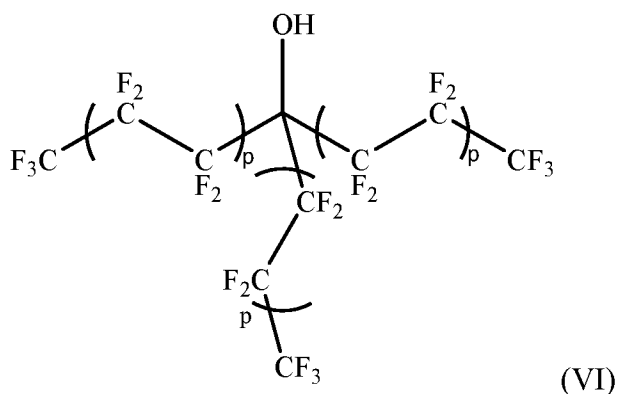


- R^1 , R^2 , and R^3 are same or different and each independently H or a hydrocarbon radical which is optionally interrupted by one or more heteroatoms and/or heteroatom(s) containing groups and/or which is optionally substituted with one or more functional groups;

- m is an integer being 0, 1 or 2;
- n is an integer from 0 to 20;
- X is H or F; and

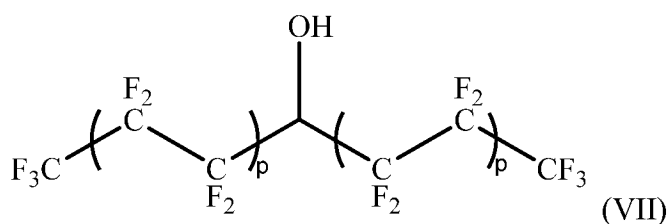
- with the proviso that when m is 2, X is not H.

2. The process according to Claim 1, wherein the solvent is a compound having the following general formula (VI),



wherein p is an integer from 0 to 10.

3. The process according to Claim 1, wherein the solvent is a compound having the following general formula (VII),



wherein p is an integer from 0 to 10.

4. The process according to any one of Claims 1 to 3, wherein R¹ is an aryl or a heteroaryl.

5. The process according to any one of Claims 1 to 4, wherein R² and R³ are same or different and each independently H or a C₁-C₄ alkyl.

6. The process according to any one of Claims 1 to 5, wherein R² and R³ are same and each independently H.

7. The process according to any one of Claims 1 to 6, wherein the molar ratio of the alkene represented by general formula (I) to formaldehyde is from 1:1 to 1:10 and preferably 1:1 to 1:5 when R^2 and R^3 are different.

5 8. The process according to any one of Claims 1 to 7, wherein the molar ratio of the alkene represented by general formula (I) to formaldehyde is from 1:1 to 1:10 and preferably 1:1 to 1:5 when R^2 and R^3 are same and not hydrogen.

9. The process according to claim any one of Claims 1 to 8, wherein the molar ratio of the alkene represented by general formula (I) to formaldehyde is from 1:1 to 10:1 and preferably 1:1 to 5:1 when R^2 and R^3 are same and each
10 independently H.

10. The process according to claim any one of Claims 1 to 9, wherein the molar ratio of the alkene represented by general formula (I) to the at least one other secondary amine represented by general formula (II) is from 1: 1 to 1: 10 and preferably from 1: 1 to 1: 5.

15 11. The process according to any one of Claims 1 to 10, wherein the reaction temperature is in the range of 20°C to 60°C and preferably in the range of 30°C to 50°C.

12. The process according to any one of Claims 1 to 11, wherein the reaction time is from 20 to 120 h.

20 13. The process according to any one of Claims 1 to 12, comprising the steps of:

a) mixing formaldehyde, at least one other secondary amine represented by general formula (II) and a solvent being a compound represented by general formula (III) to obtain a mixture;

25 b) adding an alkene represented by general formula (I) to the mixture obtained in step a) to obtain a reaction mixture;

c) maintaining the reaction mixture obtained in step b) under proper reaction temperature and proper reaction time to obtain at least one first secondary amine.

30 wherein:

- the at least one first secondary amine, the alkene represented by general formula (I), the at least one other secondary amine represented by general formula (II) and the compound represented by general formula (III) are as defined in Claim 1,
- 5 - the reaction temperature is defined in Claim 11, and
- the reaction time is defined in Claim 12.

14. A composition comprising:

- (i) formaldehyde,
- (ii) an alkene represented by general formula (I),
- 10 (iii) at least one other secondary amine represented by general formula (II),
- (iv) a compound represented by general formula (III), and
- (v) optionally at least one first secondary amine.

15 wherein the at least one first secondary amine, the alkene represented by general formula (I), the at least one other secondary amine represented by general formula (II) and the compound represented by general formula (III) are as defined in Claim 1.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2021/139861

A. CLASSIFICATION OF SUBJECT MATTER

C07C 209/60(2006.01)i; C07C 209/00(2006.01)i; C07C 209/24(2006.01)i; C07C 211/08(2006.01)i

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)

C07C209;C07C211

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)

VEN, DWPI, CNTXT, CJFD, WPABS, CAPLUS, CASREACT: amine, alkene, formaldehyde,solvent, alcohol,styrene, vinylbenzene, +fluoro+

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 3569593 A1 (UNIV WIEN) 20 November 2019 (2019-11-20) paragraphs 7-10, 100-108	1-14
A	Daniel Kaiser et al. "A General Acid-Mediated Hydroaminomethylation of Unactivated Alkenes and Alkynes" <i>Angewandte Chemie, International Edition</i> , Vol. 58, No. 41, 31 December 2019 (2019-12-31), ISSN: 1433-7851, p14639-14643	1-14
A	Kalle Manninen et al. "Hydride Transfer Reaction Products in the Aminomethylation of Styrene" <i>Acta Chemica Scandinavica, Series B: Organic Chemistry and Biochemistry</i> , Vol. B40, No. 3, 31 December 1986 (1986-12-31), ISSN: 0302-4369, p190-195	1-14
A	WO 2020064917 A1 (UNIV WIEN) 02 April 2020 (2020-04-02) the whole document	1-14
A	US 2005215825 A1 (BRIGGS JOHN R et al.) 29 September 2005 (2005-09-29) the whole document	1-14



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

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"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

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"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

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Date of the actual completion of the international search

01 September 2022

Date of mailing of the international search report

27 September 2022

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2021/139861

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4433174 A (STANDARD OIL CO INDIANA) 21 February 1984 (1984-02-21) the whole document	1-14

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2021/139861

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
EP	3569593	A1	20 November 2019	WO	2019219942	A1	21 November 2019
WO	2020064917	A1	02 April 2020	EP	3628657	A1	01 April 2020
US	2005215825	A1	29 September 2005	WO	2005077884	A2	25 August 2005
				JP	2007522212	A	09 August 2007
				EP	1713757	A2	25 October 2006
US	4433174	A	21 February 1984	None			