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(71) Applicant *(for all designated States except IT, US)*: **CIBA HOLDING INC.** [CH/CH]; Klybeckstrasse 141, CH-4057 Basel (CH).

(71) Applicant *(for IT only)*: **CIBA S.P.A.** [IT/IT]; Via Pila, 6/3 Fraz. Pontecchio Marconi, I-40037 Sasso Marconi (bo) (IT).

(72) Inventor; and

(75) Inventor/Applicant *(for US only)*: **SALA, Massimiliano** [IT/IT]; Via della Repubblica, 20, I-41051 Castelnuovo Rangone (mo) (IT).

(74) Common Representative: **CIBA HOLDING INC.**; Patent Department;, Klybeckstrasse 141, CH-4057 Basel (CH).

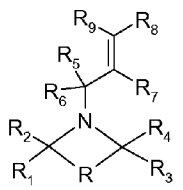
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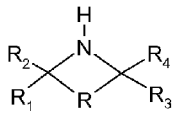
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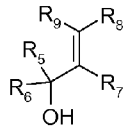
(54) **Title:** PROCESS FOR THE PREPARATION OF TERTIARY N-ALLYL STERICALLY HINDERED AMINES



(I)



(II)



(III)

(57) **Abstract:** The instant invention discloses a process for the preparation of compounds of the formula (I), wherein the general symbols are as defined in claim 1, which process comprises reacting a sterically hindered amine of the formula (II), wherein the general symbols are as defined in claim 1, with a compound of the formula (III) wherein the general symbols are as defined in claim 1, in the presence of a catalyst. The compounds of the formula (I) are useful as stabilizers for protecting organic materials, in particular synthetic polymers, reprographic materials or coating materials against oxidative, thermal or light-induced degradation.

Process for the preparation of tertiary N-allyl sterically hindered amines

The present invention relates to an improved process for the preparation of tertiary N-allyl sterically hindered amines which are suitable for stabilizing organic materials against oxidative, thermal or light-induced degradation.

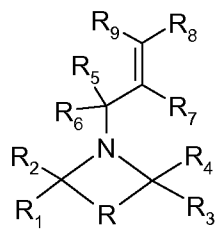
Sterically hindered amine light stabilizers which are N-allyl substituted are prepared from the corresponding sterically hindered secondary amines by alkylation with allyl halides in the presence of bases at high temperature.

The cost of allyl halides is increasing constantly and has a high impact on the production cost of these N-allyl stabilizers. A further disadvantage of using allyl halides is the fact that this synthetic route generates salts as side products which are environmentally critical and which have to be removed.

A halide free process for the preparation of tertiary N-allyl sterically hindered amines from the corresponding sterically hindered secondary amines is therefore highly desirable.

It has now been found that sterically hindered amines can be reacted with allyl alcohols in the present of a catalyst and carbon dioxide as activator to form the desired N-allyl sterically hindered amines.

The present invention therefore relates to an improved process for the preparation of compounds of the formula I

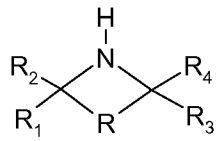


(I),

wherein the linking group R forms, together with the carbon atoms it is directly connected to and the nitrogen atom, a substituted 5-, 6- or 7-membered cyclic ring structure,

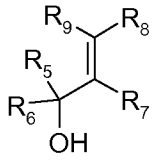
R_1, R_2, R_3 and R_4, independently of each other, are C_1-C_8alkyl or C_1-C_5hydroxyalkyl, or R_1 and R_2 together with the carbon atom they are attached to are C_5-C_{12}cycloalkyl, or R_3 and R_4 together with the carbon atom they are attached to are C_5-C_{12}cycloalkyl,
R_5, R_6, R_7, R_8 and R_9, independently of each other, are hydrogen, C_1-C_8alkyl, C_2-C_8alkenyl, unsubstituted or with C_1-C_4alkyl, C_1-C_4alkoxy or halogen substituted C_5-C_{12}aryl; C_1-C_4haloalkyl, cyano, nitro, halogen or -$COOR_{10}$; and R_7 and R_8 together may also form a chemical bond,
R_{10} is C_1-C_{12}alkyl, C_5-C_{12}cycloalkyl, C_7-C_9phenylalkyl or phenyl,

which process comprises reacting a compound of the formula II



(II),

wherein R, R_1, R_2, R_3 and R_4 are as defined above, with a compound of the formula III



(III),

wherein R_5, R_6, R_7, R_8 and R_9 are as defined above, in the presence of a catalyst.

Alkyl having up to 12 carbon atoms is a branched or unbranched radical, for example methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, 2-ethylbutyl, n-pentyl, isopentyl, 1-methylpentyl, 1,3-dimethylbutyl, n-hexyl, 1-methylhexyl, n-heptyl, isoheptyl, 1,1,3,3-tetramethylbutyl, 1-methylheptyl, 3-methylheptyl, n-octyl, 2-ethylhexyl, 1,1,3-trimethylhexyl, 1,1,3,3-tetramethylpentyl, nonyl, decyl, undecyl, 1-methylundecyl, dodecyl or 1,1,3,3,5,5-hexamethylhexyl.

Hydroxyalkyl having up to 5 carbon atoms is a branched or unbranched radical which contains preferably 1 to 3, in particular 1 or 2, hydroxyl groups, such as, for example, 1-

hydroxymethyl, 1-hydroxyethyl, 1-hydroxypropyl, 1-hydroxybutyl, 1-hydroxybutyl, 2-hydroxyethyl, 2-hydroxypropyl, 2-hydroxybutyl, 2-hydroxybutyl, 2-hydroxypropyl or 3-hydroxybutyl.

C_5-C_{12}cycloalkyl is, for example, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl, cycloundecyl or cyclododecyl.

Alkenyl having 2 to 8 carbon atoms is a branched or unbranched radical such as, for example, vinyl, propenyl, 2-butenyl, 3-butenyl, isobutenyl, n-2,4-pentadienyl, 3-methyl-2-butenyl or n-2-octenyl.

Aryl stands for a group obeying the Debye-Hueckel rule; preferred as C_5-C_{12}aryl are phenyl and naphthyl.

Halogen is for example fluoro, chloro, bromo or iodo.

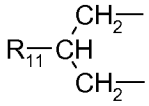
C_7-C_9Phenylalkyl is, for example, benzyl, α-methylbenzyl, α,α-dimethylbenzyl or 2-phenyl-ethyl. Preference is given to benzyl and α,α-dimethylbenzyl.

Alkoxy having up to 4 carbon atoms is a branched or unbranched radical, for example methoxy, ethoxy, propoxy, isopropoxy, n-butoxy or isobutoxy.

Of interest is a process for the preparation of compounds of the formula I wherein R_1, R_2, R_3 and R_4 are methyl.

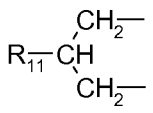
Also of interest is a process for the preparation of compounds of the formula I wherein R_5, R_6, R_7, R_8 and R_9 are hydrogen.

Of very special interest is a process for the preparation of compounds of the formula I,

wherein R is  , and

R_{11} is nitrogen which is attached to triazine ring.

Preferred is a process for the preparation of compounds of the formula I, wherein

R is  ,

R_1, R_2, R_3 and R_4 are methyl,

R_5, R_6, R_7, R_8 and R_9 are hydrogen, and

R_{11} is nitrogen which is attached to triazine ring.

Also preferred is a process for the preparation of compounds of the formula I, wherein the compounds of the formula I are part of monomeric, oligomeric or polymeric sterically hindered amine light stabilizers.

Preferably, the compound of the formula III is used in equimolar to 100 fold excess, for example 1 to 50 fold excess, preferably, 1 to 20 fold excess, typically 1 to 4 fold excess, with respect to each unit of secondary sterically hindered amine of the formula II.

Preferably the catalyst is a metal catalyst. Of interest are metal catalysts selected from the group consisting of palladium, rhodium, ruthenium, osmium, copper, nickel, manganese, iron and cobalt catalysts.

Preferably, the catalyst is used in the process for the preparation of the compounds of the formula I in an amount of from 0.01 to 30 mol%, preferably 0.01 to 20 mol%, typically 0.1 to 10 mol%, with respect to each unit of secondary sterically hindered amine of the formula II.

Of interest is also a process for the preparation of the compounds of the formula I wherein the catalyst is a metal catalyst containing phosphine ligands.

Examples for phosphines are compounds of the formula IV

$$P(Q)_3 \qquad (IV)$$

wherein Q is the same or different and is for example alkyl having 1 to 10 carbons, cycloalkyl having 4 to 10 carbons and/or aryl having 6 to 10 carbons, examples of which are

methyl, butyl, cyclohexyl, phenyl, tolyl. Preferably at least one is aryl and most preferably, the ligand is triaryl.

Examples of suitable ligands having the aforementioned structure are the following: trimethylphosphine, tricyclohexylphosphine, tris(*m*-sulfonatophenyl)phosphine (TPPTS), triphenylphosphine, 2,2'-bis(diphenylphosphino)-1,1'-binaphthalene (BINAP). Preferred ligand is triphenylphosphine.

Preferably, the quantity of the ligand is from 1 to 10 moles per atom of the metal. An especially preferred ligand/atom metal ratio is from 2 to 6.

Of special interest is a process for the preparation of compounds of the formula I wherein the catalyst is palladium(tetrakistriphenylphosphine).

The process for the preparation of compounds of the formula I may comprise additionally a solvent and/or a base.

Useful solvents for the instant process are for example saturated and aromatic hydrocarbons, ketones, esters, water or alcohols or mixtures thereof. Preferably, the solvent may be the compound of the formula III (allyl alcohol). Examples of especially preferred organic solvents are toluene, xylene, acetone, methanol or ethyl acetate.

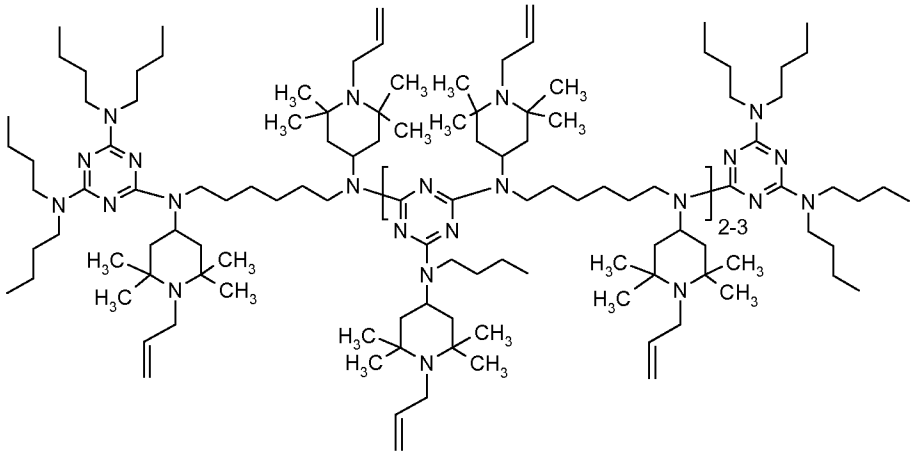
The bases are inorganic or organic in nature. Bases of special interest are for example sodium carbonate, potassium carbonate, sodium hydroxide, triethylamine or pyridine.

The reaction temperature in the instant process for the preparation of the compounds of the formula I is for example between 10 and 180°C, preferably between 20 and 140°C, and pressures of 1 to 30 atmospheres absolute, preferably of 1 to 15 atmospheres absolute.

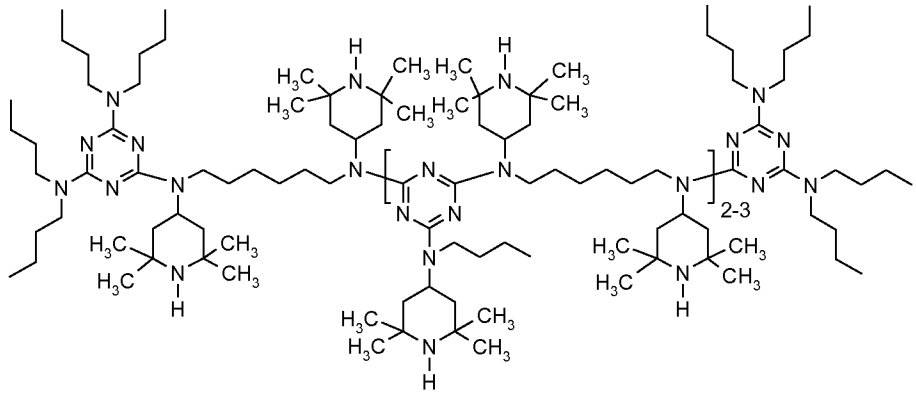
Of very special interest is also a process for the preparation of compounds of the formula I wherein additionally carbon dioxide or another inert gas or a mixture thereof is present. Examples of inert gases are for example nitrogen or argon. Preferably, mixtures of inert gases are used comprising carbon dioxide and nitrogen.

The following Examples illustrate the invention further. Parts or percentages relate to weight.

Example 1: Preparation of compound 101 starting from compound A.



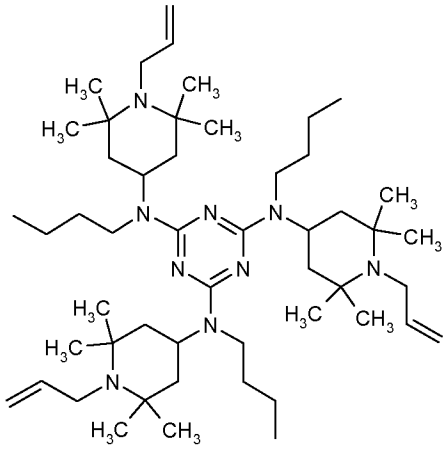
(101)



(A)

In a round-bottom flask equipped with mechanical stirrer, condenser and a rubber balloon containing CO_2, 7.0 g (Mw 3889, 23.27 mmol of piperidine units) of compound A [prepared according to Example 1 in U.S. 6,117,995], 2.7 g (46.9 mmol) of allyl alcohol, 0.46 g (0.4 mmol) of palladium(tetrakistriphenylphosphine) and 2.37 g (22.8 mmol) of triethylamine are added to 25 ml of toluene. The mixture is stirred for 22 hours at 50°C. Then, the crude reaction is analyzed by ^{1}H-NMR to reveal that 47% of N-H groups of 2,2,6,6-tetramethylpiperidinic units of compound A are converted into the corresponding N-allyl thus forming also compound 101.

Example 2: Preparation of compound 102.



(102)

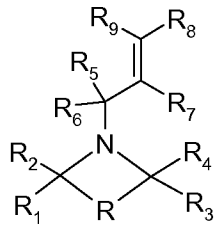
In an autoclave equipped with mechanical stirrer 7.12 g (10.0 mmol) of 2,4,6-tris(N-n-butyl-N-2,2,6,6-tetramethylpiperidin-4-yl))-1,3,5-triazine, 3.45 g (60 mmol) of allyl alcohol, 0.57 g (0.5 mmol) of palladium(tetrakistriphenylphosphine) are added to 30 ml of acetone. Then, the atmosphere is saturated with CO_2 and the reaction mixture is maintained under vigorous stirring for 60 hours at 30°C. Then, the crude reaction is analyzed by ^{1}H-NMR to reveal that 70% of N-H groups of 2,2,6,6-tetramethylpiperidinic unit of 2,4,6-tris(N-n-butyl-N-2,2,6,6-tetramethylpiperidin-4-yl)-1,3,5-triazine are converted into the corresponding N-allyl thus forming also compound 102.

Example 3: Preparation of compound 102 (see formula in Example 2).

In an autoclave equipped with mechanical stirrer 5.00 g (7.0 mmol) of 2,4,6-tris(N-n-butyl-N-2,2,6,6-tetramethylpiperidin-4-yl))-1,3,5-triazine, 4.89 g (84.2 mmol) of allyl alcohol are added to 25 ml of toluene. Then 0.16 g (0.7 mmol) of palladium acetate and 0.37 g (1.4 mmol) of triphenylphosphine are successively added to the solution maintained under nitrogen atmosphere. The reaction mixture is left to react under vigorous stirring for 16 hours at 80°C. Then, the crude reaction is analyzed by ^{1}H-NMR to reveal that 19% of N-H groups of 2,2,6,6-tetramethylpiperidinic unit of 2,4,6-tris(N-n-butyl-N-2,2,6,6-tetramethylpiperidin-4-yl)-1,3,5-triazine are converted into the corresponding N-allyl thus forming also compound 102.

What is claimed is:

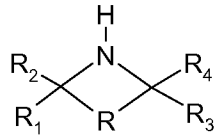
1. A process for the preparation of compounds of the formula I



(I),

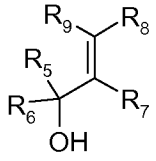
wherein the linking group R forms, together with the carbon atoms it is directly connected to and the nitrogen atom, a substituted 5-, 6- or 7-membered cyclic ring structure,
R_1, R_2, R_3 and R_4, independently of each other, are C_1-C_8alkyl or C_1-C_5hydroxyalkyl, or R_1 and R_2 together with the carbon atom they are attached to are C_5-C_{12}cycloalkyl, or R_3 and R_4 together with the carbon atom they are attached to are C_5-C_{12}cycloalkyl,
R_5, R_6, R_7, R_8 and R_9, independently of each other, are hydrogen, C_1-C_8alkyl, C_2-C_8alkenyl, unsubstituted or with C_1-C_4alkyl, C_1-C_4alkoxy or halogen substituted C_5-C_{12}aryl; C_1-C_4haloalkyl, cyano, nitro, halogen or -$COOR_{10}$; and R_7 and R_8 together may also form a chemical bond,
R_{10} is C_1-C_{12}alkyl, C_5-C_{12}cycloalkyl, C_7-C_9phenylalkyl or phenyl,

which process comprises reacting a compound of the formula II



(II),

wherein R, R_1, R_2, R_3 and R_4 are as defined above, with a compound of the formula III

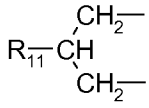


(III),

wherein R_5, R_6, R_7, R_8 and R_9 are as defined above, in the presence of a catalyst.

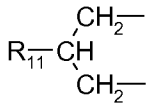
2. A process according to claim 1, wherein R_1, R_2, R_3 and R_4 are methyl.

3. A process according to claim 1, wherein R_5, R_6, R_7, R_8 and R_9 are hydrogen.

4. A process according to claim 1, wherein R is , and

R_{11} is nitrogen which is attached to triazine ring.

5. A process according to claim 1, wherein

R is ,

R_1, R_2, R_3 and R_4 are methyl,

R_5, R_6, R_7, R_8 and R_9 are hydrogen, and

R_{11} is nitrogen which is attached to triazine ring.

6. A process according to claim 1, wherein the compounds of the formula I are part of monomeric, oligomeric or polymeric sterically hindered amine light stabilizers.

7. A process according to claim 1, wherein the compound of the formula III is used in equimolar to 100 fold excess with respect to each unit of secondary sterically hindered amine of the formula II.

8. A process according to claim 1, wherein the catalyst is a metal catalyst.

9. A process according to claim 8, wherein the metal catalyst is selected from the group consisting of palladium, rhodium, ruthenium, osmium, copper, nickel, manganese, iron and cobalt catalysts.

10. A process according to claim 1, wherein the catalyst is a metal catalyst containing phosphine ligands.

11. A process according to claim 1, wherein the catalyst is palladium(tetrakistriphenylphosphine).

12. A process according to claim 1, wherein the catalyst is used in an amount of 0.01 to 30 mol% with respect to each unit of the secondary sterically hindered amine of the formula II.

13. A process according to claim 1, wherein additionally a solvent is present.

14. A process according to claim 1, wherein additionally a base is present.

15. A process according to claim 1, wherein additionally carbon dioxide or another inert gas or a mixture thereof is present.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2007/062321

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07D401/14

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 practical, search terms used)

EPO-Internal, WPI Data, BEILSTEIN Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WALCHUK B ET AL: "INITIATORS FOR NITROXIDE-MEDIATED LIVING FREE RADICAL POLYMERIZATION PREPARED BY MEISENHEIMER REARRANGEMENT OF ALLYL 2,2,6,6-TATRAMETHYL PIPERIDINE N-OXIDES" POLYMER PREPRINTS, AMERICAN CHEMICAL SOCIETY, US, vol. 39, no. 1, March 1998 (1998-03), pages 296-297, XP001128750 ISSN: 0032-3934 page 296; compounds 1A-1C page 296, column 2, paragraphs 4,5 -----	1-15
Y	MASUYAMA, Y. ET AL.: CHEMISTRY LETTERS, 1995, pages 1121-1122, XP009084454 the whole document -----	1-15

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[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

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"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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
4 February 2008	18/02/2008

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, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Marzi, Elena

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2007/062321

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	BITSI G. ET AL.: JOURNAL OF ORGANOMETALLIC CHEMISTRY, vol. 373, 1989, pages 343-352, XP002435423 page 345 - page 347	1-15
Y	US 4 014 887 A (RANDELL DONALD RICHARD ET AL) 29 March 1977 (1977-03-29) column 13, lines 21-39 column 14; example 3	1-15
Y	US 4 141 883 A (SOMA NOBUO ET AL) 27 February 1979 (1979-02-27) column 19, lines 40-60 column 31, lines 26-59	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2007/062321

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4014887 A	29-03-1977	CA 1027693 A1	07-03-1978
		CH 599273 A5	31-05-1978
		DE 2352658 A1	25-04-1974
		FR 2203849 A1	17-05-1974
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