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(71) Demandeur/Applicant:
CIBA SPECIALTY CHEMICALS HOLDING INC., CH

(72) Inventeurs/Inventors:
STOLL, KLAUS, DE;
TINKL, MICHAEL, DE;
ANDREWS, STEPHEN MARK, US;
VOLDRICH, JAN, CH;
STAMP, MELISSA B., US;
REINICKER, ROGER, US;

...

(74) Agent: FETHERSTONHAUGH & CO.

(54) Titre : COMPOSITIONS DE POLYESTER ET DE POLYAMIDE A FAIBLE CONTENU EN ALDEHYDE RESIDUEL

(54) Title: POLYESTER AND POLYAMIDE COMPOSITIONS OF LOW RESIDUAL ALDEHYDE CONTENT

(57) **Abrégé/Abstract:**

A mixture of a polyester or a polyamide, such as poly(ethylene terephthalate) PET, and a suitable stabilizer selected from the group consisting of certain Mannich base compounds, when extrusion compounded exhibits a lower residual acetaldehyde content than does PET or polyamide alone when similarly treated. The invention pertains to any polyester or polyamide used in the manufacture of molded articles, fibers or films, for instance bottles or containers which are used to store consumer materials, for example food, beverages and water.



(72) **Inventeurs(suite)/Inventors(continued)**: ODORISIO, PAUL ANGELO, US; FISCHER, WALTER, CH; MUELLER, DANIEL, CH; BERTHELON, NATACHA, FR; SIMON, DIRK, DE

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Kückengasse 9, CH-4051 Basel (CH). **BERTHELON, Natacha** [FR/FR]; 77, rue de l'Espérance, F-68120 Pfaffstätt (FR). **SIMON, Dirk** [DE/DE]; Birkenstrasse 13, 67112 Mutterstadt (DE).

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(74) Common Representative: **CIBA SPECIALTY CHEMICALS HOLDING INC.**; Patentabteilung, Klybeckstrasse 141, CH-4057 Basel (CH).

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

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(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **STOLL, Klaus** [DE/DE]; Am Sonnenrain 18, D-79589 Binzen (DE). **TINKL, Michael** [DE/DE]; Schlossweg 3c, 79639 Grenzach-Wyhlen (DE). **ANDREWS, Stephen, Mark** [US/US]; 5B East Lake Road, New Fairfield, CT 06812 (US). **VOLDRICH, Jan** [CH/CH]; St. Johannis-Ring 92, CH-4056 Basel (CH). **STAMP, Melissa, B.** [US/US]; 791 West Denney's Road, Dover, DE 19904 (US). **REINICKER, Roger** [US/US]; 202 David Drive, Hockessin, DE 19707 (US). **ODORISIO, Paul, Angelo** [US/US]; 319 Moore Avenue, Leonia, NJ 07605 (US). **FISCHER, Walter** [CH/CH]; Vogesenstrasse 77, CH-4153 Reinach (CH). **MÜLLER, Daniel** [CH/CH];

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(54) Title: POLYESTER AND POLYAMIDE COMPOSITIONS OF LOW RESIDUAL ALDEHYDE CONTENT

(57) Abstract: A mixture of a polyester or a polyamide, such as poly(ethylene terephthalate) PET, and a suitable stabilizer selected from the group consisting of certain Mannich base compounds, when extrusion compounded exhibits a lower residual acetaldehyde content than does PET or polyamide alone when similarly treated. The invention pertains to any polyester or polyamide used in the manufacture of molded articles, fibers or films, for instance bottles or containers which are used to store consumer materials, for example food, beverages and water.



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Polyester and polyamide compositions of low residual aldehyde content

A mixture of a polyester, such as poly(ethylene terephthalate) PET, or a polyamide, and a suitable compound selected from the group consisting of the Mannich bases, when melt processed exhibits a lower residual aldehyde content than does polyester or polyamide alone when similarly treated. The invention pertains to any polyester or polyamide used in the manufacture of fibers, films or molded articles, for instance bottles or containers which are used to store consumer materials, for example food, beverages and water.

Acetaldehyde is known as a decomposition product of polyesters such as PET. The acetaldehyde imparts an undesirable taste or flavor to bottled water stored in PET bottles. It has been a long sought objective of the industry to reduce the level of acetaldehyde which migrates out of the PET bottle walls into the water or other beverage stored therein. A number of engineering or design changes to extruders, injection molding machines for preforms and bottle making machinery have been made to minimize formation of acetaldehyde when poly(ethylene terephthalate) PET is processed. Modification to the PET composition itself have been made to lower its melting point or its melt viscosity in order to allow less severe thermal or mechanical damage when PET is processed into preforms or bottles.

Aldehydes may be formed in polyamides, for instance polyamide 6 and polyamide 6,6, under conditions of thermal stress. These aldehydes initiate a chain of events that lead to unwanted yellowing and a reduction in mechanical properties.

U.S. 4,361,681 teaches that polyester containing anhydride end-cap agents have a reduced acetaldehyde generation rate.

U.S. 5,459,224 discloses polyesters having 4-oxybenzylidene end-cap agents to impart improved weatherability and photostability, but no mention is made as to evolution of acetaldehyde. However, it is indicated that such polyesters are suitable for food and beverage packaging.

Polyesters can be synthesized by a number of routes known in the art using a variety of catalyst systems. EP-A-0 826 713 teaches that lower levels of acetaldehyde occur during copoly-

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merization of PET when a phosphite such as bis(2,4-di-tert-butylphenyl)pentaerythritol phosphite is present during the polymerization.

U.S. 4,837,115; U.S. 5,258,233; U.S. 5,266,413; U.S. 5,340,884; U.S. 5,648,032 U.S. 5,650,469; WO-A-93/20147; WO-A-93/23474; WO-A-98/07786 and WO-A-98/39388 teach the use of polyamides as a means of reducing the concentration of acetaldehyde, presumably via a Schiff-base reaction with the aldehyde, which is reversible in the presence of water.

EP-A-0 191 701 describes biaxially oriented containers having excellent barrier properties said container comprising a blend of a poly(ethylene terephthalate) resin and an ethylene-vinyl alcohol copolymer resin. This reference is focused on improved gas barrier properties and is silent as to any reduction of acetaldehyde content.

JP Sho 62-257959 describes biaxially stretched vessels built of synthetic resin consisting of poly(ethylene terephthalate) blended with a copolymer of a polyamide, or blended with ethylene-vinyl alcohol at a weight fraction of 0.1 to 15 percent. The examples are limited to a single EVOH polymer (EVEL G110, Kuraray Co.). It is taught that a lower level of acetaldehyde occurs when the EVOH polymer is present.

EP-A-0 714 832 teaches a method of manufacturing a container comprising poly(ethylene terephthalate), polycarbonate or PEN polyester with an additive in the bottle wall which binds acetaldehyde. The additives is generally described as a polyamide.

U.S. 5,656,221 describes a process of producing polyester with reduced acetaldehyde concentration using certain catalysts or inert gas conditions or by adding an amide compound. These include commercial polyamides or long chain aliphatic amide compounds.

U.S. 5,856,385 teaches the use of polyamide or amide-wax to reduce the level of acetaldehyde which occurs when sorbitol-based clarifying agent is heated in polyolefins.

U.S. 4,873,279 discloses a composition comprising a copolyester-carbonate resin, a polyester resin, and a minor amount of a mixture of a polyol and at least one epoxide.

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U.S. 4,394,470 discloses a polyethylene terephthalate molding composition with a caramel colorant. The caramel colorant may have been formed in situ from a mono- or disaccharide.

U.S. 5,681,879 discloses a flame-retardant polyester composition comprising a polyester resin, a polyhydric alcohol having not less than 3 hydroxyl groups, an inorganic flame retardant and a halogen-based flame retardant.

WO-A-00/66659 discloses molding compositions comprising PET and polyhydric alcohol additives for the reduction of acetaldehyde formation.

WO-A-01/00724 discloses the use of polyols towards reducing acetaldehyde formation in extruded products of PET.

WO-A01/30899 discloses the use of fumed silicon dioxide towards a marginal reduction in the formation of acetaldehyde in molded performs of PET.

U.S. 6,274,212 teach the use of various organic compounds towards reducing acetaldehyde formation.

Despite the efforts towards a solution for reducing aldehydic contaminants in PET water bottles, there still remains a need for more effective solutions.

The instant invention is useful for any polyester or polyamide where aldehydic compounds, for instance acetaldehyde, are formed or evolved during thermal processing of said polyester or polyamide. Thermal processing of polyester or polyamide includes the synthesis thereof, thermal exposure during solid state polymerization (SSP), any injection molding, injection-blow molding or stretch-blow molding used in the manufacture of preforms, parissons, or bottles and containers, or extrusion of film, or melt-spinning of fiber, or during any melt processing of polyester or polyamide above its glass transition temperature and below its decomposition temperature.

The instant invention provides for a lower amount of contaminants (i.e. aldehydes) in PET water bottles thus providing for improved taste or flavor in bottled water or other bottled beve-

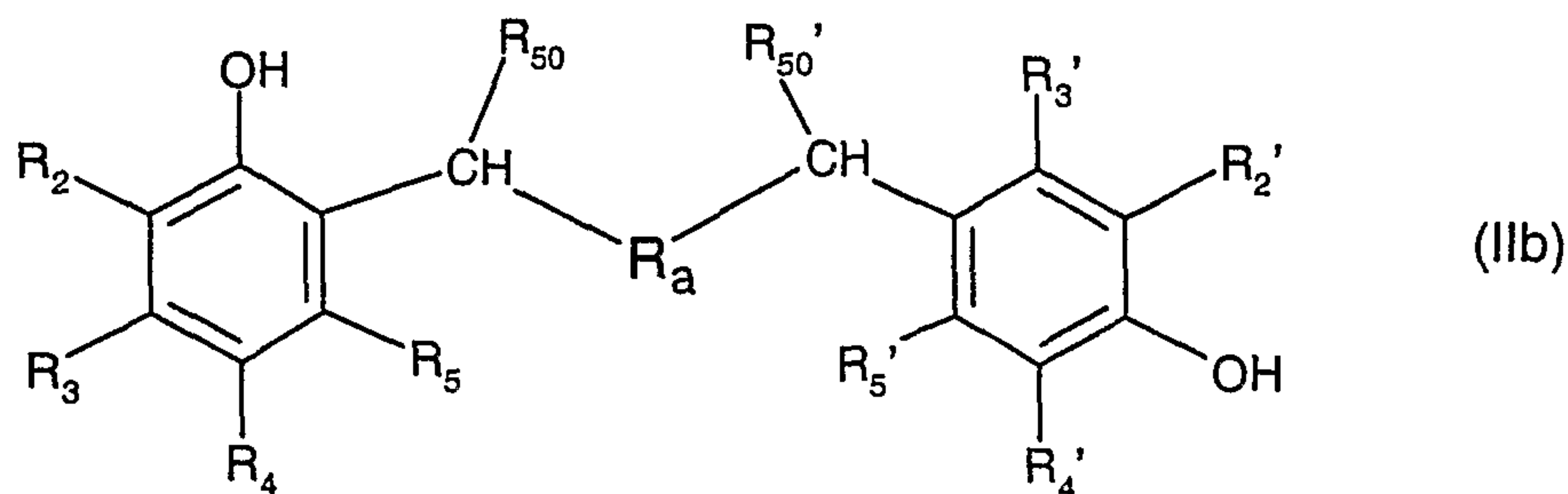
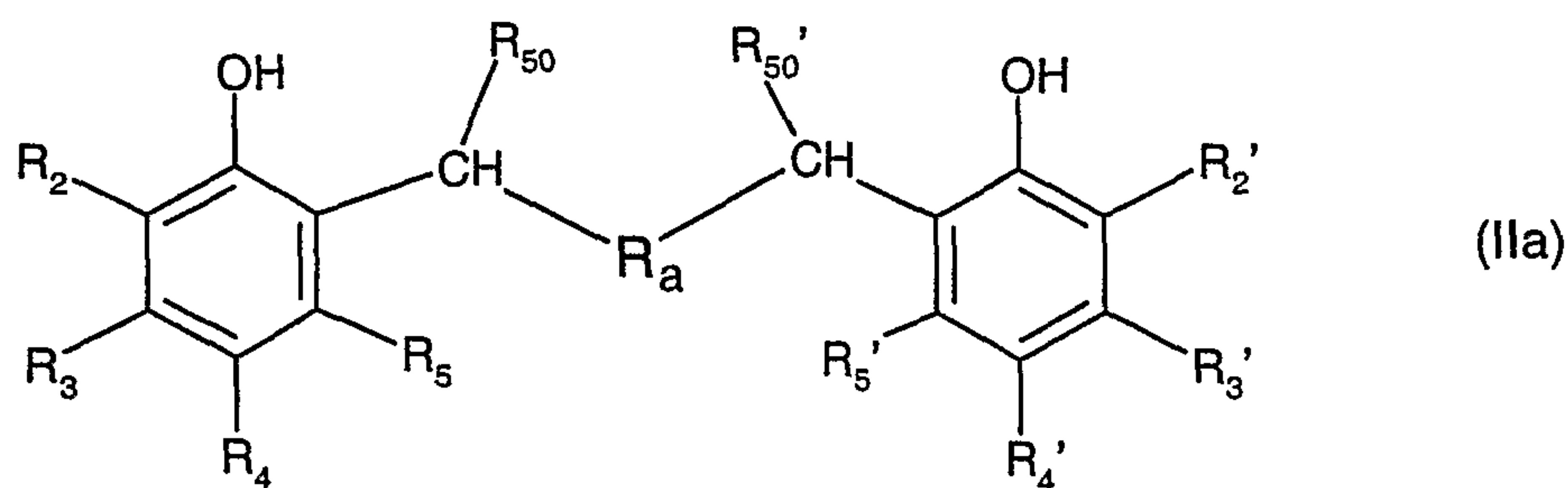
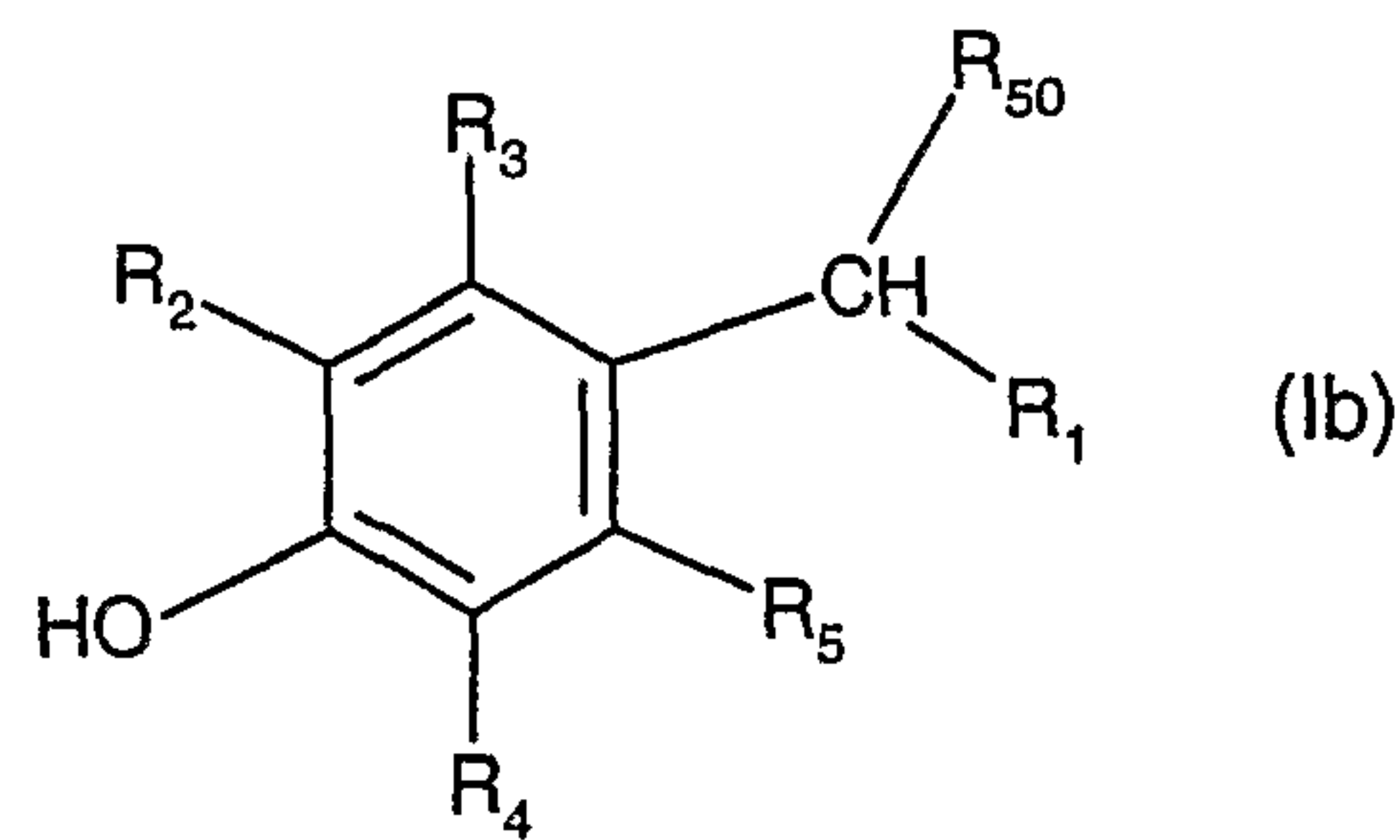
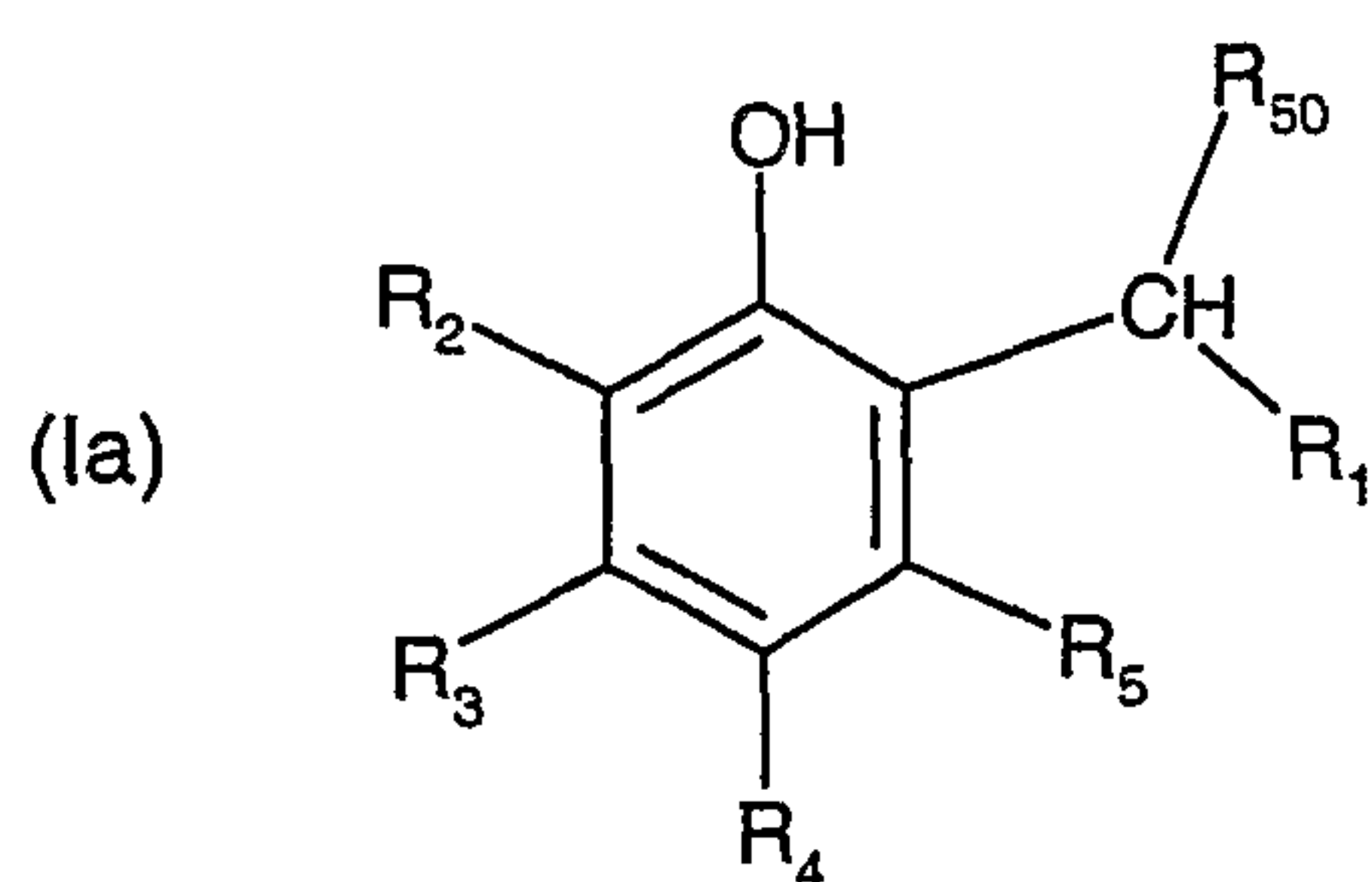
- 4 -

rages in said PET containers. The reduction in the amount of acetaldehyde is highly beneficial in this respect.

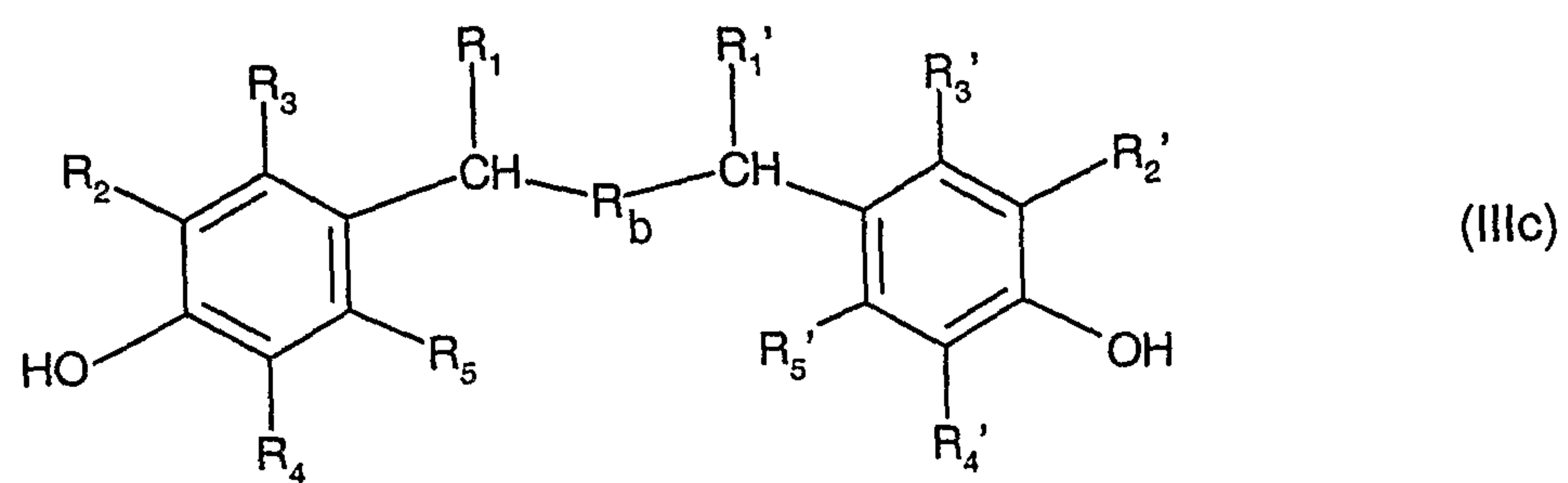
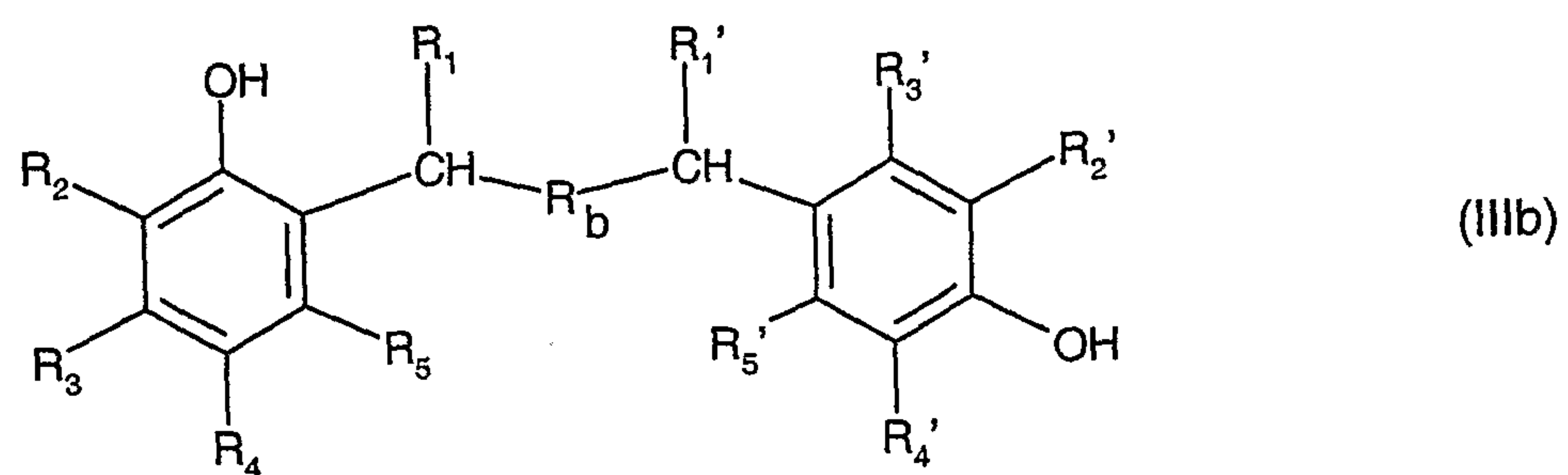
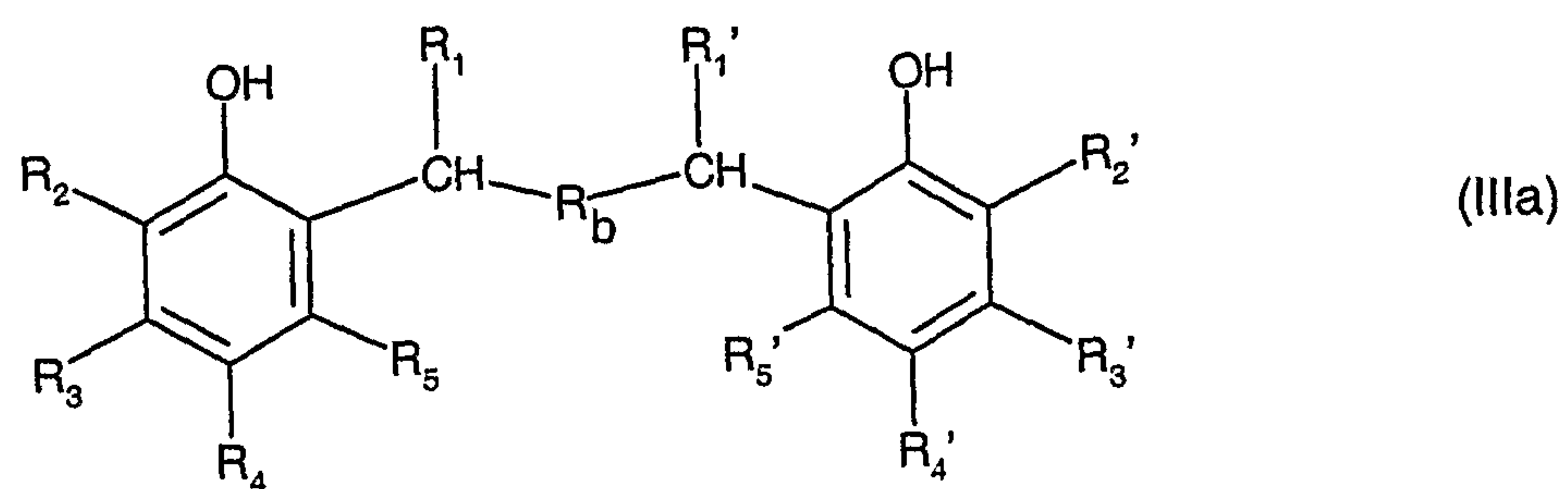
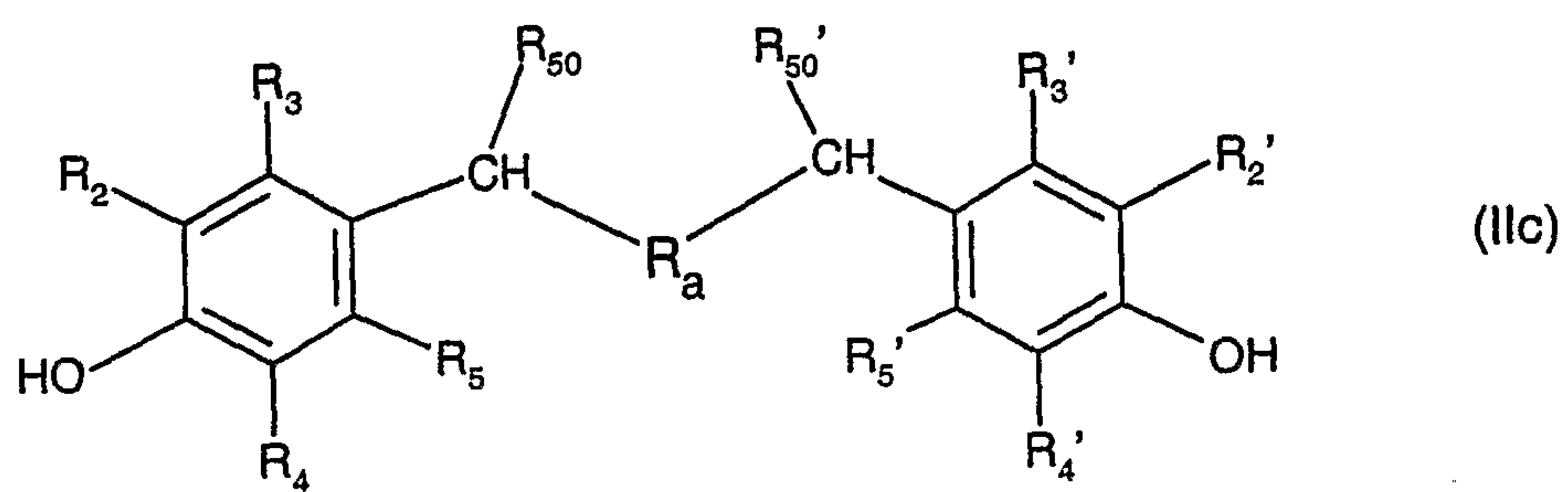
Further, the compositions of the present invention impart no unacceptable color or haze to PET bottles. "Haze" is an undesirable, perceptible graying effect.

The instant invention pertains to a composition, stabilized against the formation of aldehydic contaminants during melt processing of said composition, which comprises

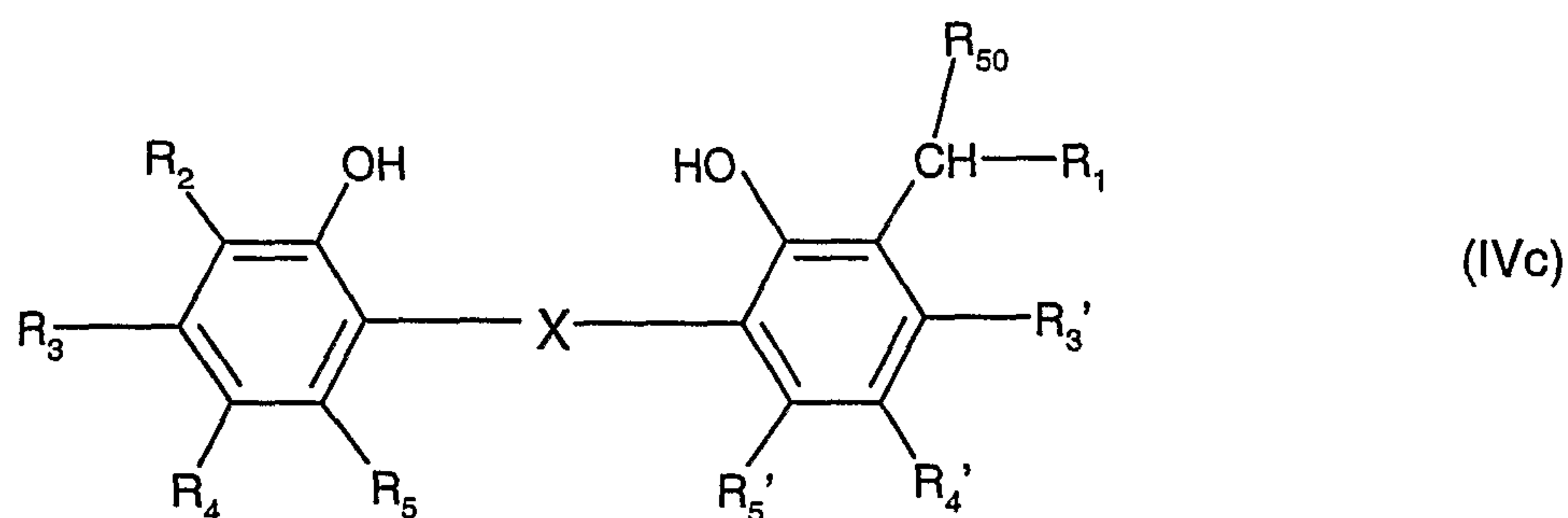
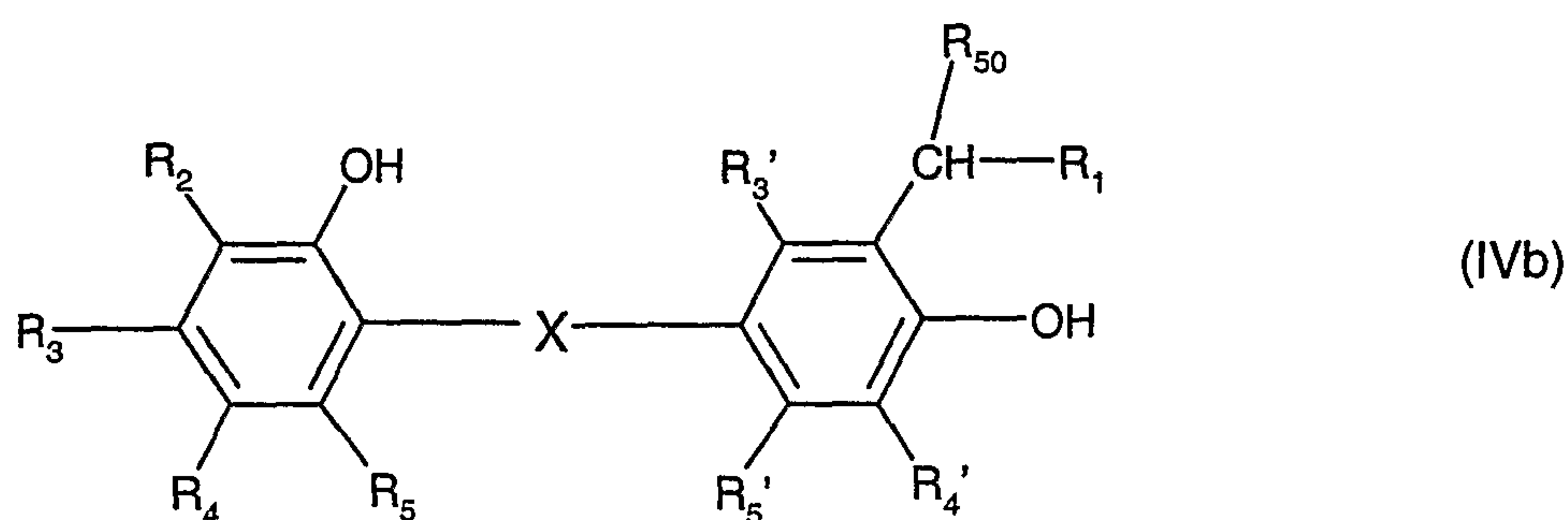
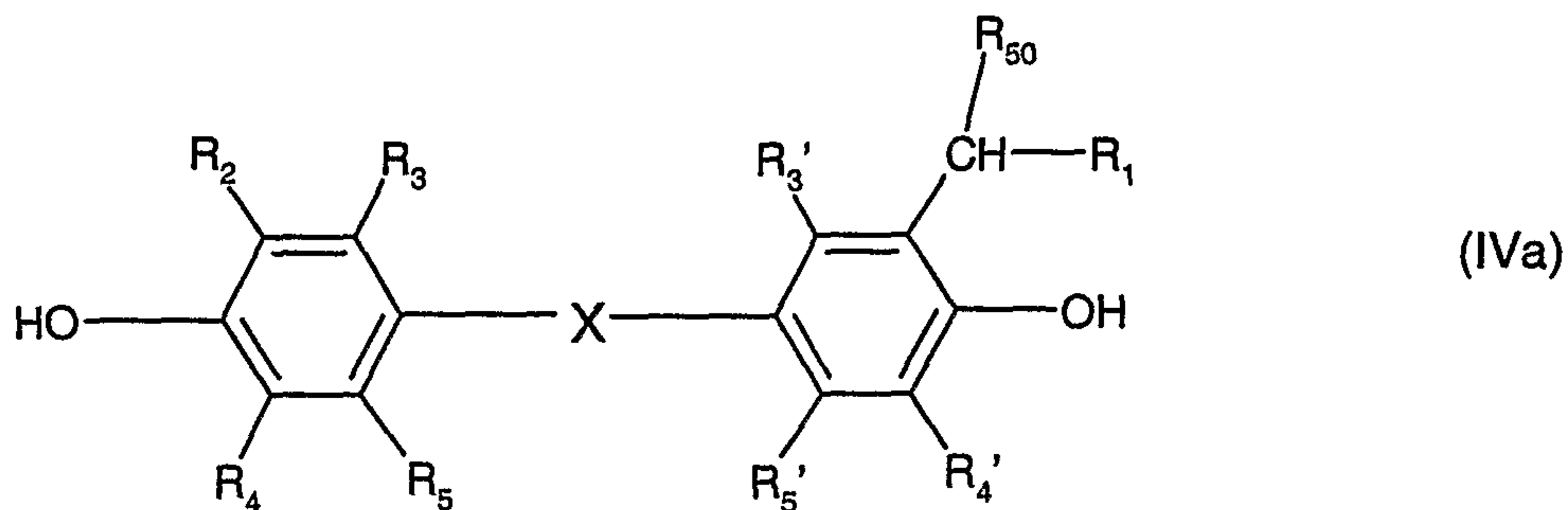
- (a) a polyester or polyamide, and
- (b) an effective stabilizing amount of at least one effective stabilizing amount of at least one compound selected from the group consisting of the Mannich base compounds of formulae (Ia), (Ib), (IIa), (IIb), (IIc), (IIIa), (IIIb), (IIIc) (IVa), (IVb) and (IVc)



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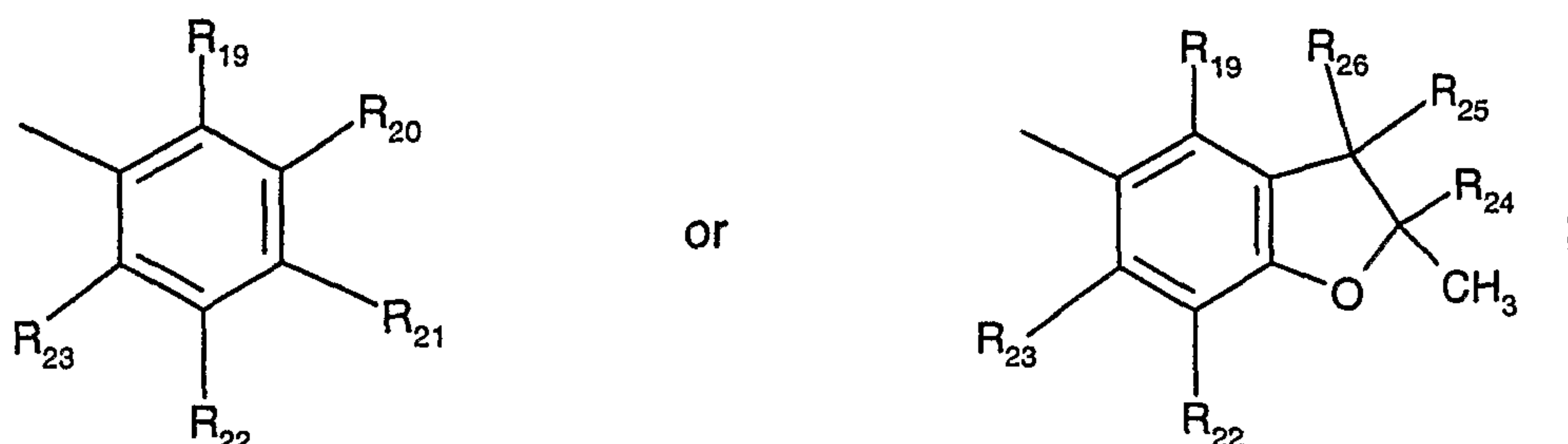


wherein

R₁ is hydrogen, hydroxy, C₁-C₂₅alkyl, C₇-C₉phenylalkyl, unsubstituted or C₁-C₄alkyl-substituted C₅-C₈cycloalkyl; naphthyl, phenanthryl, anthryl, 5,6,7,8-tetrahydro-2-naphthyl, thienyl, benzo[b]thienyl, naphtho[2,3-b]thienyl, thianthrenyl, furyl, benzofuryl, isobenzofuryl, dibenzofuryl, xanthenyl, phenoxathiinyl, pyrrolyl, imidazolyl, pyrazolyl, pyridinyl, pyrazinyl, pyrimidinyl, pyridazinyl, indoliziny, isoindolyl, indolyl, indazolyl, purinyl, quinoliziny, isoquinolyl, quinolyl, phthalazinyl, naphthyridinyl, quinoxalinyl, quinazolinyl, cinnolinyl, pteridinyl, carbazolyl, β-carbolinyl, phenanthridinyl, acridinyl, perimidinyl, phenanthrolinyl, phenazinyl, isothiazolyl, phenothiazinyl, isoxazolyl, furazanyl, biphenyl, terphenyl, fluorenyl or phenoxazinyl, each of

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which is unsubstituted or substituted by fluorine, hydroxy, C₁-C₁₈alkyl, C₁-C₁₈alkoxy, C₁-C₁₈alkylthio, di(C₁-C₄alkyl)amino, phenyl, benzyl, benzoyl or by benzoyloxy or R₁ is a radical of formula



R₂, R₃, R₄ and R₅ are each independently hydrogen, fluorine, hydroxy, C₁-C₂₅alkyl, C₁-C₂₅alkenyl, C₇-C₉phenylalkyl, C₇-C₉phenylalkenyl, unsubstituted or C₁-C₄alkyl- or alkenyl- substituted phenyl, unsubstituted or C₁-C₄alkyl-substituted C₅-C₈cycloalkyl, C₁-C₁₈alkoxy, C₁-C₁₈alkylthio, C₁-C₄alkylamino, di(C₁-C₄alkyl)amino, C₁-C₂₅alkanoyloxy, C₁-C₂₅alkanoylamino, C₃-C₂₅alkanoyloxy interrupted by oxygen, sulfur or by >NR₈; -(CH₂)_p-C(O)OR₈, C₆-C₉cycloalkylcarbonyloxy, benzoyloxy or C₁-C₁₂alkyl-substituted benzoyloxy, or adjacent radicals R₂ and R₃ or R₃ and R₄ or R₄ and R₅, together with the carbon atoms to which they are bonded, form a benzo ring, or R₂ and R₄ may each be -(CH₂)_p-COR₉ or -(CH₂)_qOH, or

R₂ and R₄ may each be -CH(R₁)R₅₀;

R₁' , R₂' , R₃' , R₄' and R₅' are independently defined as for R₁, R₂, R₃, R₄ and R₅ respectively;

R_a is C₁-C₁₈alkylene; C₂-C₁₈alkylene interrupted by oxygen, sulfur or by >NR₁₄; or R_a is C₂-C₂₀alkylidene, C₇-C₂₀phenylalkylidene, C₅-C₈cycloalkylene, C₇-C₈bicycloalkylene, phenylene or naphthylene each unsubstituted or substituted by C₁-C₄alkyl or by fluorine; or is -R₆-Y-R₇;

R_b is -NR₅₃, C₁-C₂₅alkylenediimino, C₁-C₂₅alkylenetriimino, C₁-C₂₅alkylenetetraimino, or C₅-C₈cycloalkylenediimino;

X is defined as for R_a or is a direct bond, -CR₁R₂-, -O-, -NR₁₀- or -S-, or X is phenylene substituted by R₂, R₃, R₄ and R₅, or X is alkylene substituted by -CF₃, C₁-C₁₂alkyl or phenyl, or X is a C₅-C₈cycloalkylene ring unsubstituted or substituted by 1 to 3 C₁-C₄alkyl groups;

Y is a direct bond, oxygen, sulfur or -NR₁₀;

R₆ and R₇ are each independently of the other phenylene or naphthylene each unsubstituted or substituted by C₁-C₄alkyl;

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R₈ is C₁-C₂₅alkyl;

R₉ is hydroxy, $\left[-\text{O}^- \frac{1}{r} \text{M}^{r+} \right]$, C₁-C₁₈alkoxy or $-\text{N} \begin{matrix} \text{R}_{12} \\ \text{R}_{13} \end{matrix}$;

R₁₀ is hydrogen, hydroxy, C₁-C₂₅alkyl or said alkyl unsubstituted or substituted by -OH, -OR₈, -NH(R₈) or -N(R₈)₂; C₂-C₂₅alkyl interrupted by oxygen or by sulfur, C₇-C₉phenylalkyl, unsubstituted or C₁-C₄alkyl-substituted C₅-C₈cycloalkyl, or a dendrimeric, oligomeric or polymeric C₄-C₁₀₀hydrocarbon radical;

R₁₂ and R₁₃ are each independently of the other hydrogen or C₁-C₁₈alkyl;

R₁₄ is hydrogen or C₁-C₁₈alkyl;

R₁₉, R₂₀, R₂₁, R₂₂ and R₂₃ are each independently hydrogen, cyano, perfluoroalkyl of 1 to 12 carbon atoms, fluoro, chloro, hydroxy, C₁-C₂₅alkyl; C₂-C₂₅alkyl interrupted by oxygen, sulfur or by >NR₈; C₁-C₂₅alkoxy; C₂-C₂₅alkoxy interrupted by oxygen, sulfur or by >NR₈; C₁-C₄alkylamino, di(C₁-C₄alkyl)amino, C₁-C₂₅alkanoyl, C₁-C₂₅alkanoyloxy, C₁-C₂₅alkanoylamino; C₁-C₂₅alkylthio, C₇-C₉phenylalkyl, C₇-C₉phenylalkoxy, unsubstituted or C₁-C₄alkyl-substituted phenyl; unsubstituted or C₁-C₄alkyl-substituted phenoxy; unsubstituted or C₁-C₄alkyl-substituted C₅-C₈cycloalkyl; unsubstituted or C₁-C₄alkyl-substituted C₅-C₈cycloalkoxy; C₃-C₂₅alkanoyl interrupted by oxygen, sulfur or by >NR₈; C₁-C₂₅alkanoylcarbonyl; C₃-C₂₅alkanoylcarbonyl interrupted by oxygen, sulfur or by >NR₈; C₁-C₂₅alkylaminocarbonyl; C₃-C₂₅alkylaminocarbonyl interrupted by oxygen, sulfur or by >NR₈; di-C₁-C₂₅alkylaminocarbonyl; di-C₃-C₂₅alkylaminocarbonyl interrupted by oxygen, sulfur or by >NR₈; C₁-C₂₅alkanoyloxy; C₃-C₂₅alkanoyloxy interrupted by oxygen, sulfur or by >NR₈; C₁-C₂₅alkanoylamino, C₆-C₉cycloalkylcarbonyl, C₆-C₉cycloalkylcarbonyloxy, benzoyl or C₁-C₁₂alkyl-substituted benzoyl; benzoyloxy or

C₁-C₁₂alkyl-substituted benzoyloxy; $-\text{O}-\begin{matrix} \text{R}_{27} & \text{O} \\ | & || \\ \text{C} & - & \text{C} & - & \text{R}_9 \\ | \\ \text{R}_{28} \end{matrix}$ or $-\text{O}-\begin{matrix} \text{R}_{29} & \text{R}_{30} \\ | & | \\ \text{C} & - & \text{C} & - & \text{O} & - & \text{R}_{32} \\ | & | \\ \text{H} & \text{R}_{31} \end{matrix}$;

R₂₄ is hydrogen, C₁-C₄alkyl, or unsubstituted or C₁-C₄alkyl-substituted phenyl;

R₂₅ and R₂₆ are hydrogen, C₁-C₄alkyl or phenyl, with the proviso that at least one of the radicals R₂₅ and R₂₆ is hydrogen;

R₂₇ and R₂₈ are each independently of the other hydrogen, C₁-C₄alkyl or phenyl;

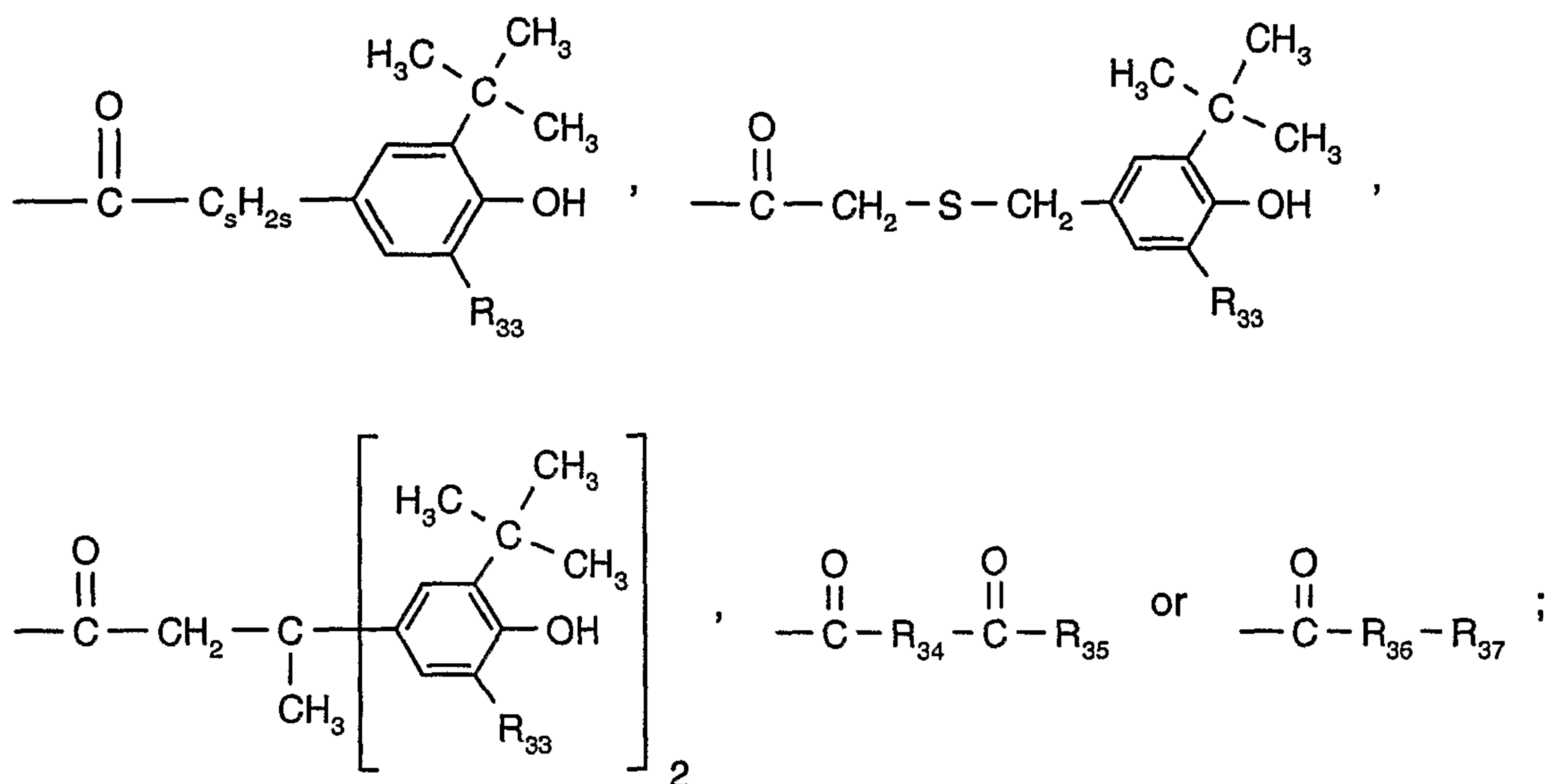
R₂₉ is hydrogen or C₁-C₄alkyl;

R₃₀ is hydrogen, unsubstituted or C₁-C₄alkyl-substituted phenyl; C₁-C₂₅alkyl; C₂-C₂₅alkyl interrupted by oxygen, sulfur or by >NR₈; C₇-C₉phenylalkyl unsubstituted or substituted on

the phenyl radical by from 1 to 3 C₁-C₄alkyl groups; or C₇-C₂₅phenylalkyl interrupted by oxygen, sulfur or by >NR₈ and unsubstituted or substituted on the phenyl radical by from 1 to 3 C₁-C₄alkyl groups;

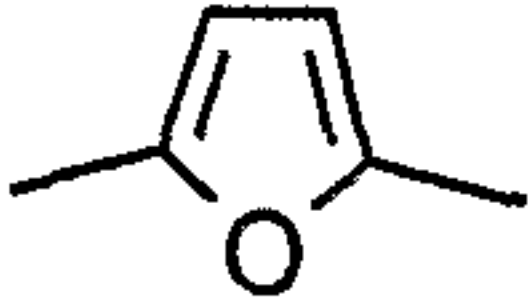
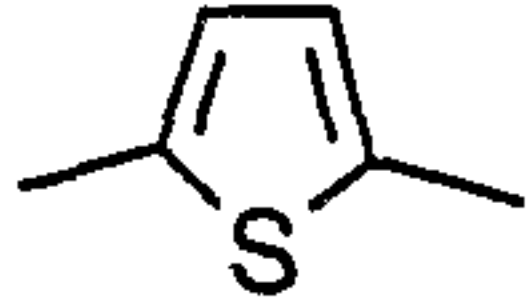
R₃₁ is hydrogen or C₁-C₄alkyl;

R₃₂ is hydrogen, C₁-C₂₅alkanoyl; C₃-C₂₅alkanoyl interrupted by oxygen, sulfur or by >NR₈; C₂-C₂₅alkanoyl substituted by a di(C₁-C₆alkyl) phosphonate group; C₆-C₉cycloalkylcarbonyl, thenoyl, furoyl, benzoyl or C₁-C₁₂alkyl-substituted benzoyl,



R₃₃ is hydrogen or C₁-C₈alkyl;

R₃₄ is a direct bond, C₁-C₁₈alkylene; C₂-C₁₈alkylene interrupted by oxygen, sulfur or by >NR₈; C₂-C₂₀alkylidene; C₇-C₂₀phenylalkylidene, C₅-C₈cycloalkylene, C₇-C₈bicycloalkylene,

unsubstituted or C₁-C₄alkyl-substituted phenylene,  or  ;

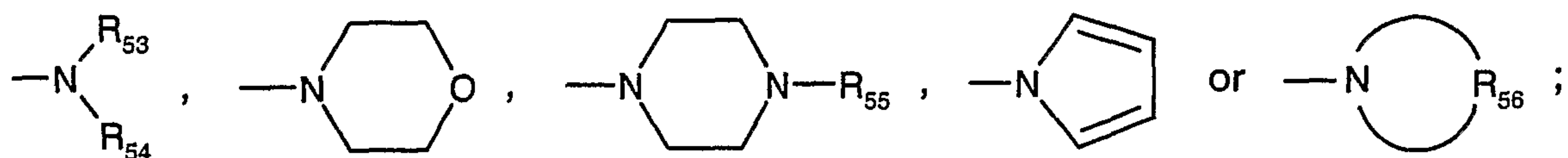
R₃₅ is hydroxy, $\left[\text{---O}^- \frac{1}{r} \text{M}^{r+} \right]$, C₁-C₁₈alkoxy or $\text{---N} \begin{array}{l} \text{R}_{12} \\ \text{R}_{13} \end{array}$;

R₃₆ is oxygen, -NH- or $\begin{array}{c} \text{O} \\ \parallel \\ \text{N} \end{array} \text{---C---NH---R}_{37}$;

R₃₇ is C₁-C₁₈alkyl or phenyl;

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R₅₀ is -OR₅₁, -O-C(O)-R₅₁, -SR₅₂, -S(O)R₅₂, -S(O)₂R₅₂, -N(H)R₅₃, pyrrolino, pyrrolidino,



R₅₀' is independently defined as for **R₅₀**;

R₅₁ is C₁-C₂₅alkyl, unsubstituted or substituted by -OH, -OR₈, -NH(R₈) or -N(R₈)₂; C₂-C₂₅alkyl interrupted by oxygen or by sulfur; C₇-C₉phenylalkyl, unsubstituted or C₁-C₄alkyl-substituted C₅-C₈cycloalkyl; unsubstituted or C₁-C₄alkyl-substituted phenyl;

R₅₂ is C₁-C₂₅alkyl, unsubstituted or substituted by -OH, -OR₈, -NH(R₈) or -N(R₈)₂; C₂-C₂₅alkyl interrupted by oxygen or by sulfur; C₇-C₉phenylalkyl, unsubstituted or C₁-C₄alkyl-substituted C₅-C₈cycloalkyl; unsubstituted or C₁-C₄alkyl-substituted phenyl;

R₅₃ and **R₅₄** are each independently of the other hydrogen, hydroxy; C₁-C₂₅alkyl, unsubstituted or substituted by -OH, -OR₈, -NH(R₈) or -N(R₈)₂; C₂-C₂₅alkyl interrupted by oxygen or by sulfur; C₇-C₉phenylalkyl, unsubstituted or C₁-C₄alkyl-substituted C₅-C₈cycloalkyl; or a dendrimeric, oligomeric or polymeric C₄-C₁₀₀hydrocarbon radical;

R₅₅ is C₁-C₂₅alkyl; C₂-C₂₅alkyl interrupted by oxygen or by sulfur; C₇-C₉phenylalkyl, unsubstituted or C₁-C₄alkyl-substituted C₅-C₈cycloalkyl; unsubstituted or C₁-C₄alkyl-substituted phenyl;

R₅₆ is unsubstituted or C₁-C₄alkyl-substituted C₂-C₁₂alkylene;

M is an r-valent metal cation;

p is 0, 1 or 2;

q is 1, 2, 3, 4, 5 or 6;

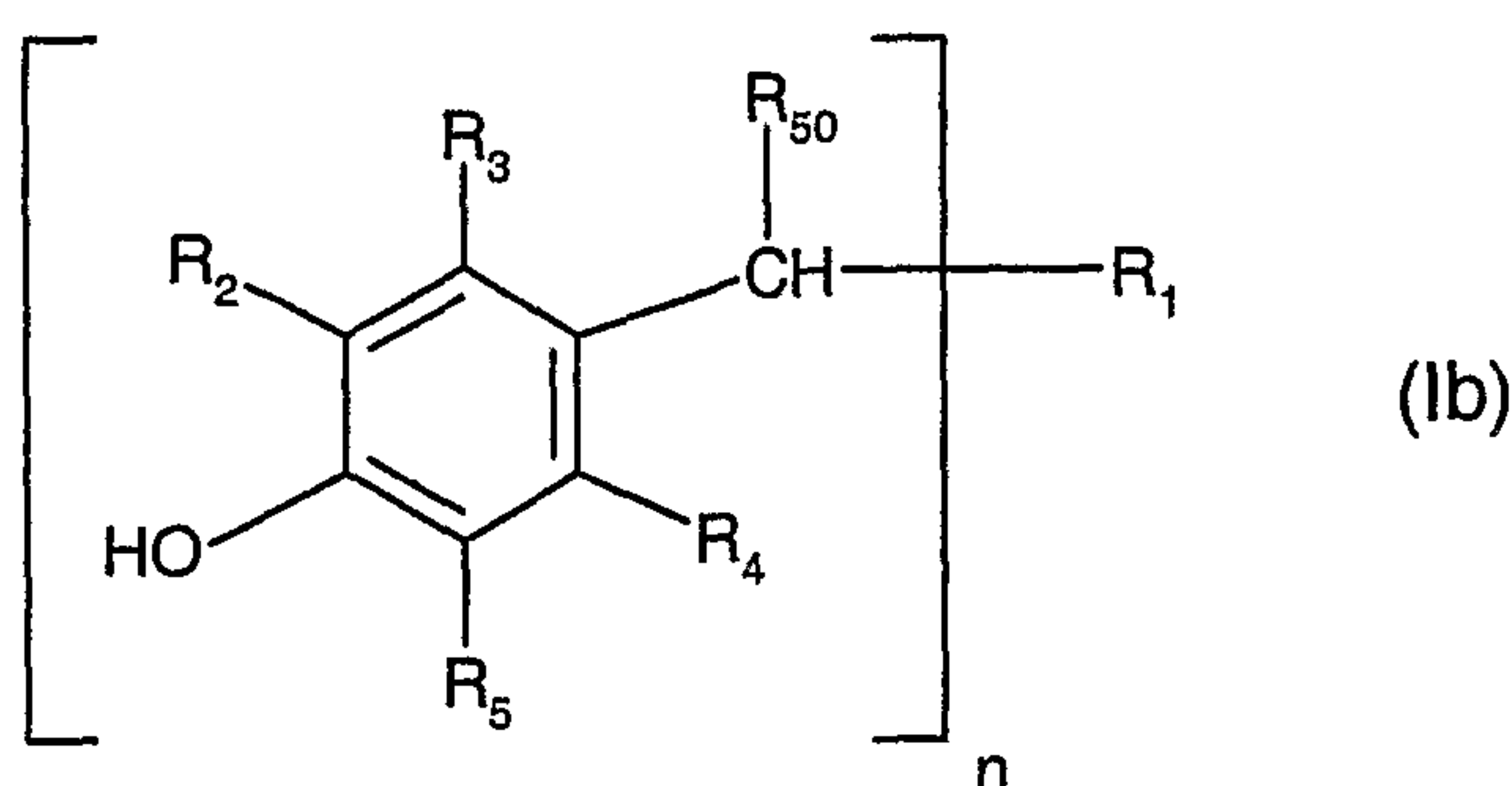
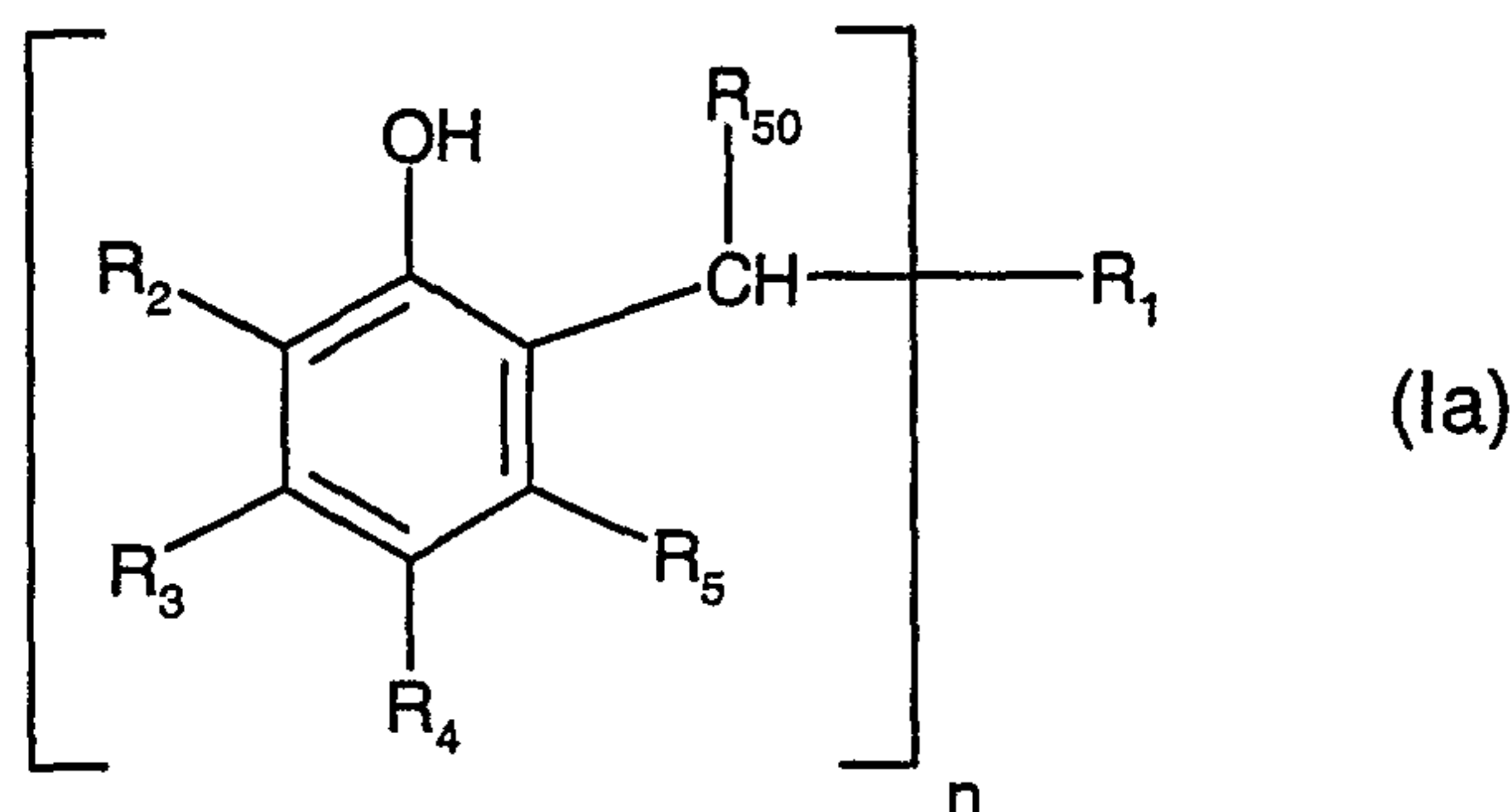
r is 1, 2 or 3; and

s is 0, 1 or 2.

Of interest is a composition wherein component (b) is a compound selected from the group consisting of the Mannich base compounds of formulae (Ia), (Ib), (IIa), (IIb) and (IIc).

Also of interest is a composition wherein component (a) is a polyester or a polyamide, and component (b) is an effective stabilizing amount of at least one compound selected from the group consisting of the Mannich base compounds of formula (Ia) and formula (Ib)

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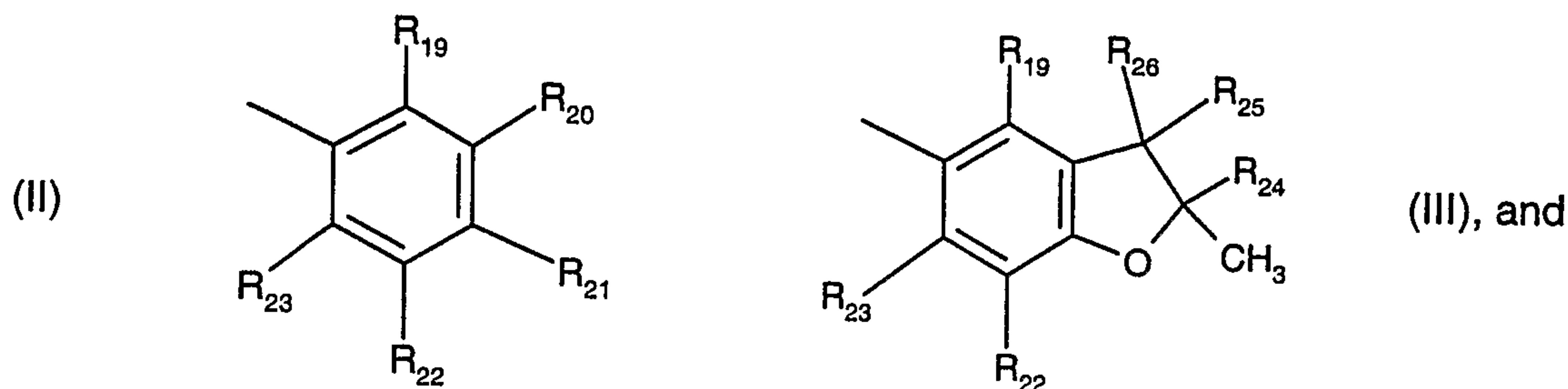
wherein

n is 1 or 2, and

when n is 1,

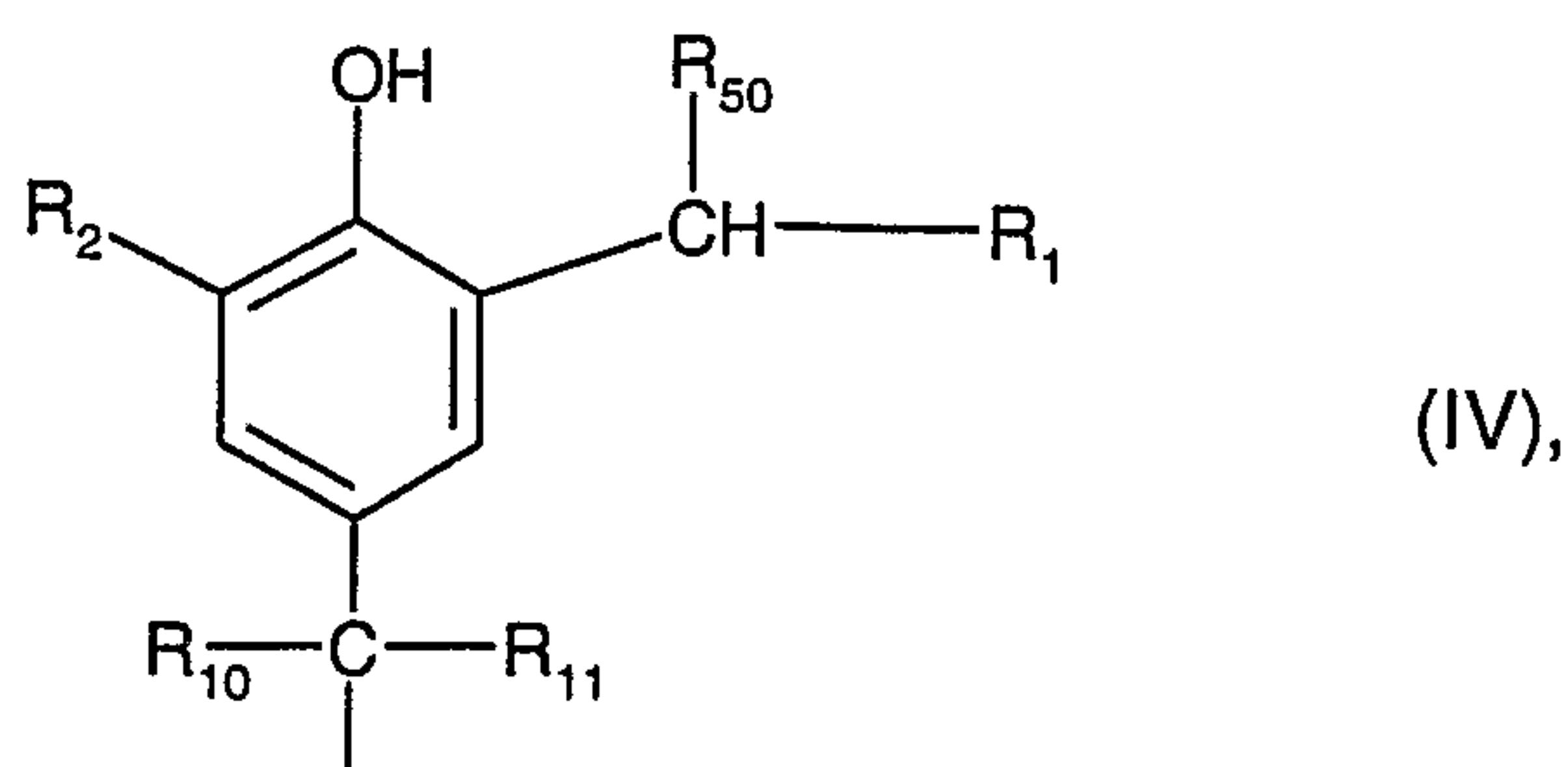
R_1 is hydrogen, C_1 - C_{25} alkyl, C_7 - C_9 phenylalkyl, unsubstituted or C_1 - C_4 alkyl-substituted C_5 - C_8 -cycloalkyl; naphthyl, phenanthryl, anthryl, 5,6,7,8-tetrahydro-2-naphthyl, thienyl, benzo[b]thienyl, naphtho[2,3-b]thienyl, thianthrenyl, furyl, benzofuryl, isobenzofuryl, dibenzofuryl, xanthenyl, phenoxathiinyl, pyrrolyl, imidazolyl, pyrazolyl, pyrazinyl, pyrimidinyl, pyridazinyl, indolizynyl, isoindolyl, indolyl, indazolyl, purinyl, quinolizynyl, isoquinolyl, quinolyl, phthalazinyl, naphthyridinyl, quinoxalinyl, quinazolinyl, cinnolinyl, pteridinyl, carbazolyl, β -carbolinyl, phenanthridinyl, acridinyl, perimidinyl, phenanthrolinyl, phenazinyl, isothiazolyl, phenothiazinyl, isoxazolyl, furazanyl, biphenyl, terphenyl, fluorenyl or phenoxazinyl, each of which is unsubstituted or substituted by fluorine, hydroxy, C_1 - C_{18} alkyl, C_1 - C_{18} alkoxy, C_1 - C_{18} alkylthio, di(C_1 - C_4 alkyl)-amino, phenyl, benzyl, benzoyl or by benzoyloxy or R_1 is a radical of formula (II) or (III)

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when n is 2,

R₁ is C₁-C₁₈alkylene; C₂-C₁₈alkylene interrupted by oxygen, sulfur or by >NR₁₄; C₂-C₂₀alkylidene, C₇-C₂₀phenylalkylidene, C₅-C₈cycloalkylene, C₇-C₈bicycloalkylene, phenylene or naphthylene each unsubstituted or substituted by C₁-C₄alkyl or by fluorine; or is -R₆-X-R₇-, **R₂, R₃, R₄ and R₅** are each independently hydrogen, fluorine, hydroxy, C₁-C₂₅alkyl, C₇-C₉phenylalkyl, unsubstituted or C₁-C₄alkyl-substituted phenyl, unsubstituted or C₁-C₄alkyl-substituted C₅-C₈cycloalkyl; C₁-C₁₈alkoxy, C₁-C₁₈alkylthio, C₁-C₄alkylamino, di(C₁-C₄alkyl)amino, C₁-C₂₅alkanoyloxy, C₁-C₂₅alkanoylamino; C₃-C₂₅alkanoyloxy interrupted by oxygen, sulfur or by >NR₈; C₆-C₉cycloalkylcarbonyloxy, benzoyloxy or C₁-C₁₂alkyl-substituted benzoyloxy, or the radicals R₂ and R₃ or the radicals R₄ and R₅, together with the carbon atoms to which they are bonded, form a benzo ring, or in the compounds of formula (Ia) the radicals R₃ and R₄, together with the carbon atoms to which they are bonded, form a benzo ring; or in the compounds of formula (Ia), R₄ is additionally -(CH₂)_p-COR₉ or -(CH₂)_qOH or also in the compounds of formula (Ia), when R₃ and R₅ are hydrogen, R₄ is may additionally be a radical of formula (IV)



wherein R₁ is as defined for the where n = 1,

R₆ and R₇ are each independently of the other phenylene or naphthylene each unsubstituted or substituted by C₁-C₄alkyl,

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R₈ is C₁-C₈alkyl,

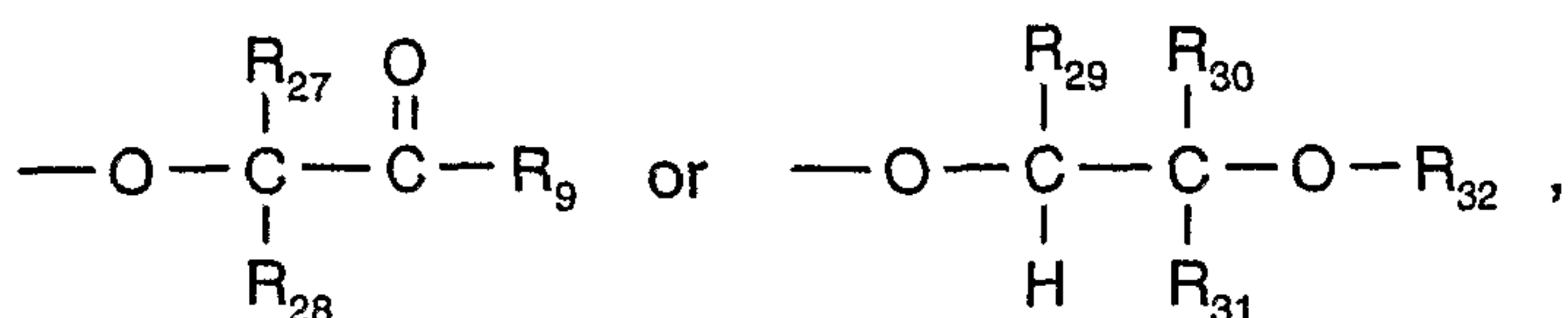
R₉ is hydroxy, $\left[-\text{O}^- \frac{1}{r} \text{M}^{r+} \right]$, C₁-C₁₈alkoxy or $-\text{N} \begin{matrix} \text{R}_{12} \\ \text{R}_{13} \end{matrix}$,

R₁₀ and **R₁₁** are each independently of the other hydrogen, CF₃, C₁-C₁₂alkyl or phenyl, or **R₁₀** and **R₁₁**, together with the carbon atom to which they are bonded, form a C₅-C₈cycloalkylidene ring unsubstituted or substituted by from 1 to 3 C₁-C₄alkyl groups;

R₁₂ and **R₁₃** are each independently of the other hydrogen or C₁-C₁₈alkyl,

R₁₄ is hydrogen or C₁-C₁₈alkyl,

R₁₉, **R₂₀**, **R₂₁**, **R₂₂** and **R₂₃** are each independently hydrogen, cyano, perfluoroalkyl of 1 to 12 carbon atoms, fluoro, chloro, hydroxy, C₁-C₂₅alkyl; C₂-C₂₅alkyl interrupted by oxygen, sulfur or by >NR₈; C₁-C₂₅alkoxy; C₂-C₂₅alkoxy interrupted by oxygen, sulfur or by >NR₈; C₁-C₂₅alkylthio, C₇-C₉phenylalkyl, C₇-C₉phenylalkoxy, unsubstituted or C₁-C₄alkyl-substituted phenyl; unsubstituted or C₁-C₄alkyl-substituted phenoxy; unsubstituted or C₁-C₄alkyl-substituted C₅-C₈cycloalkyl; unsubstituted or C₁-C₄alkyl-substituted C₅-C₈cycloalkoxy; di(C₁-C₄alkyl)amino, C₁-C₂₅alkanoyl; C₃-C₂₅alkanoyl interrupted by oxygen, sulfur or by >NR₈; C₁-C₂₅alkanoyl-carbonyl; C₃-C₂₅alkanoylcarbonyl interrupted by oxygen, sulfur or by >NR₈; C₁-C₂₅alkylaminocarbonyl; C₃-C₂₅alkylaminocarbonyl interrupted by oxygen, sulfur or by >NR₈; di-C₁-C₂₅alkylaminocarbonyl; di-C₃-C₂₅alkylaminocarbonyl interrupted by oxygen, sulfur or by >NR₈; C₁-C₂₅alkanoyloxy; C₃-C₂₅alkanoyloxy interrupted by oxygen, sulfur or by >NR₈; C₁-C₂₅alkanoylamino, C₆-C₉cycloalkylcarbonyl, C₆-C₉cycloalkylcarbonyloxy, benzoyl or C₁-C₁₂alkyl-substituted benzoyl; benzoyloxy or C₁-C₁₂alkyl-substituted benzoyloxy;



R₂₄ is hydrogen, C₁-C₄alkyl, or unsubstituted or C₁-C₄alkyl-substituted phenyl,

R₂₅ and **R₂₆** are hydrogen, C₁-C₄alkyl or phenyl, with the proviso that at least one of the radicals **R₂₅** and **R₂₆** is hydrogen,

R₂₇ and **R₂₈** are each independently of the other hydrogen, C₁-C₄alkyl or phenyl,

R₂₉ is hydrogen or C₁-C₄alkyl,

R₃₀ is hydrogen, unsubstituted or C₁-C₄alkyl-substituted phenyl; C₁-C₂₅alkyl; C₂-C₂₅alkyl interrupted by oxygen, sulfur or by >NR₈; C₇-C₉phenylalkyl unsubstituted or substituted on the phenyl radical by from 1 to 3 C₁-C₄alkyl groups; or C₇-C₂₅phenylalkyl interrupted by oxy-

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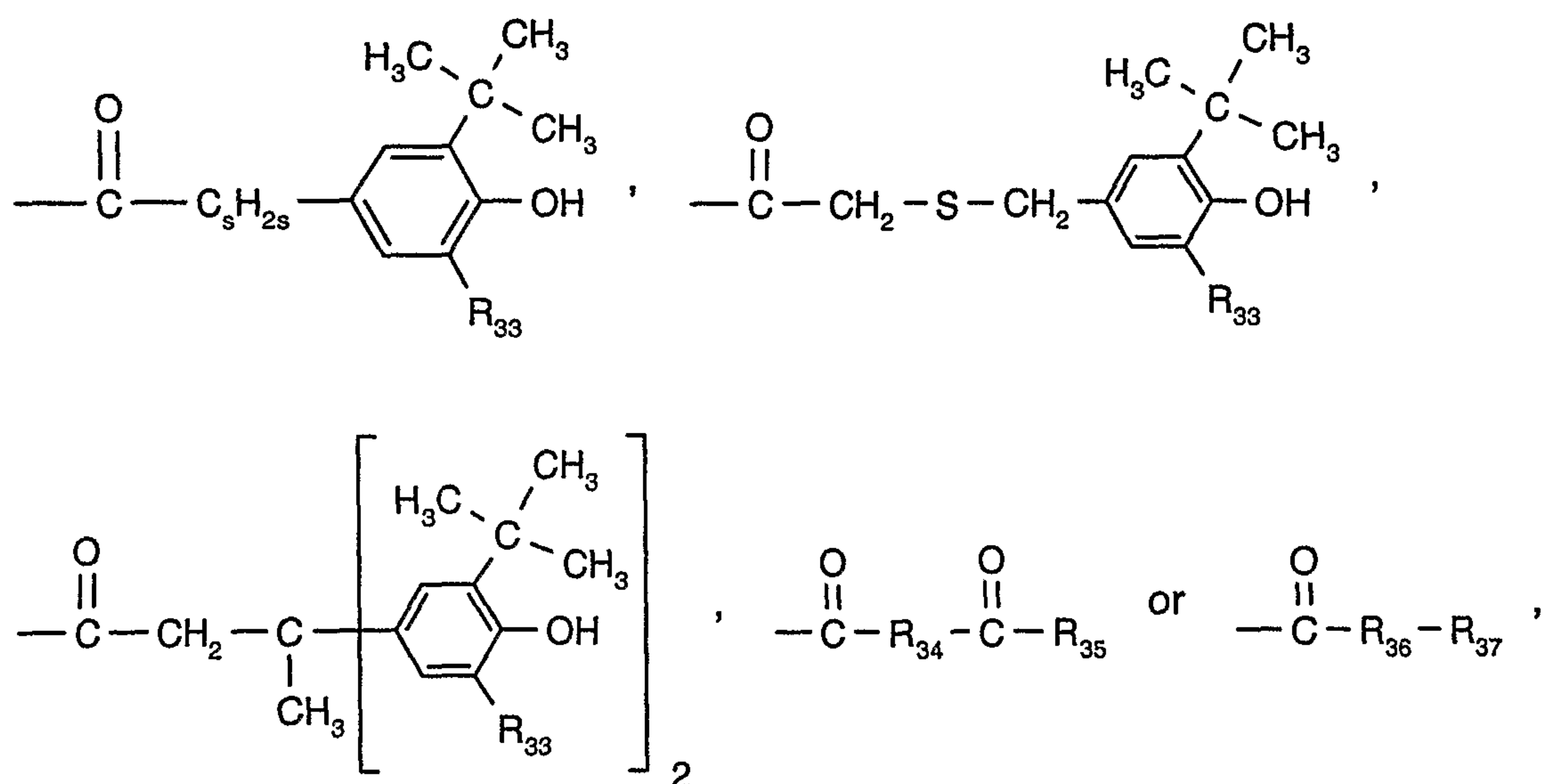
gen, sulfur or by $>NR_8$ and unsubstituted or substituted on the phenyl radical by from 1 to 3 C_1 - C_4 alkyl groups,

R_{31} is hydrogen or C_1 - C_4 alkyl,

R_{32} is hydrogen, C_1 - C_{25} alkanoyl; C_3 - C_{25} alkanoyl interrupted by oxygen, sulfur or by $>NR_8$;

C_2 - C_{25} alkanoyl substituted by a di(C_1 - C_6 alkyl) phosphonate group;

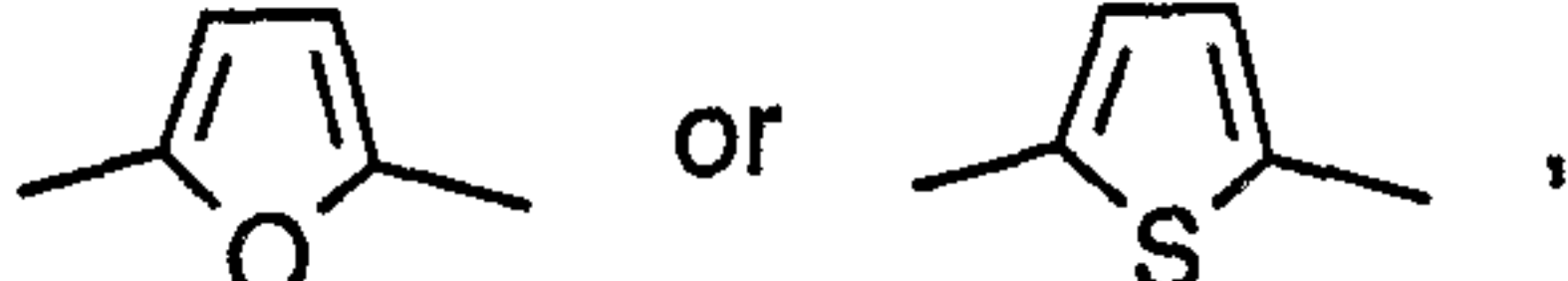
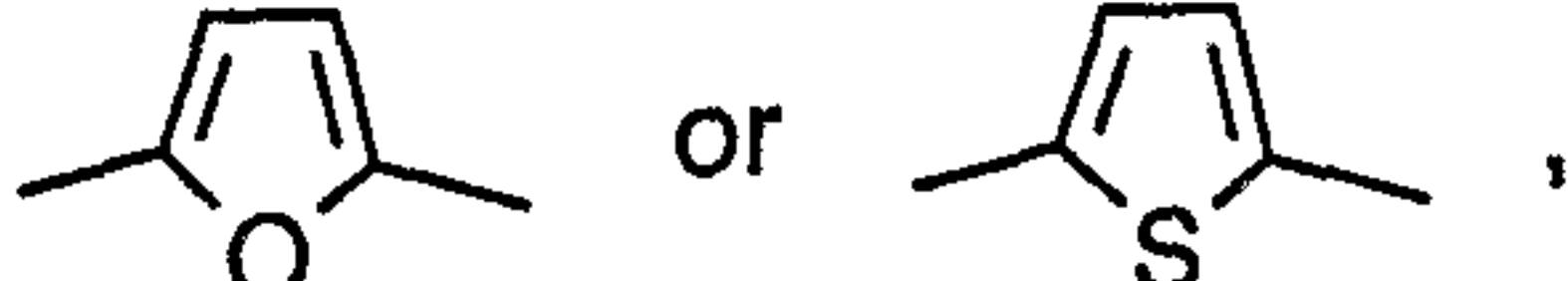
C_6 - C_9 cycloalkylcarbonyl, thenoyl, furoyl, benzoyl or C_1 - C_{12} alkyl-substituted benzoyl;



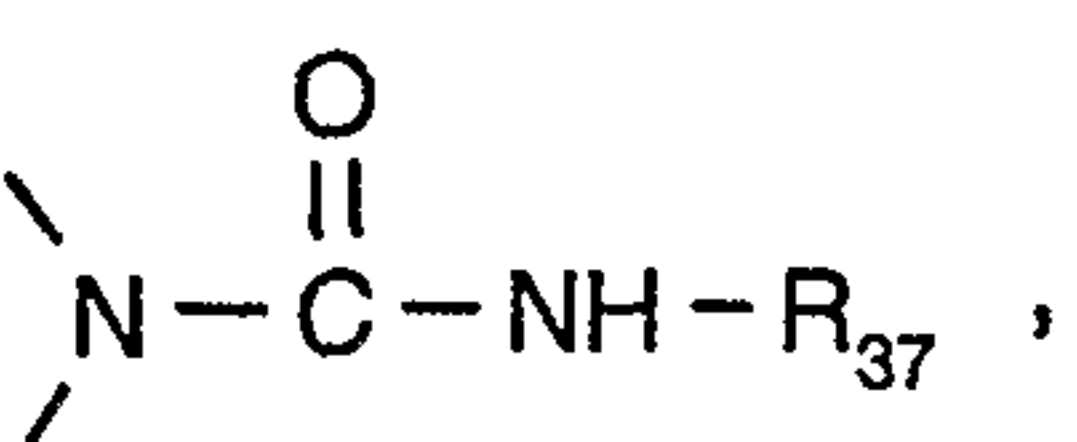
R_{33} is hydrogen or C_1 - C_8 alkyl,

R_{34} is a direct bond, C_1 - C_{18} alkylene; C_2 - C_{18} alkylene interrupted by oxygen, sulfur or by $>NR_8$;

C_2 - C_{20} alkylidene, C_7 - C_{20} phenylalkylidene, C_5 - C_8 cycloalkylene, C_7 - C_8 bicycloalkylene, unsub-

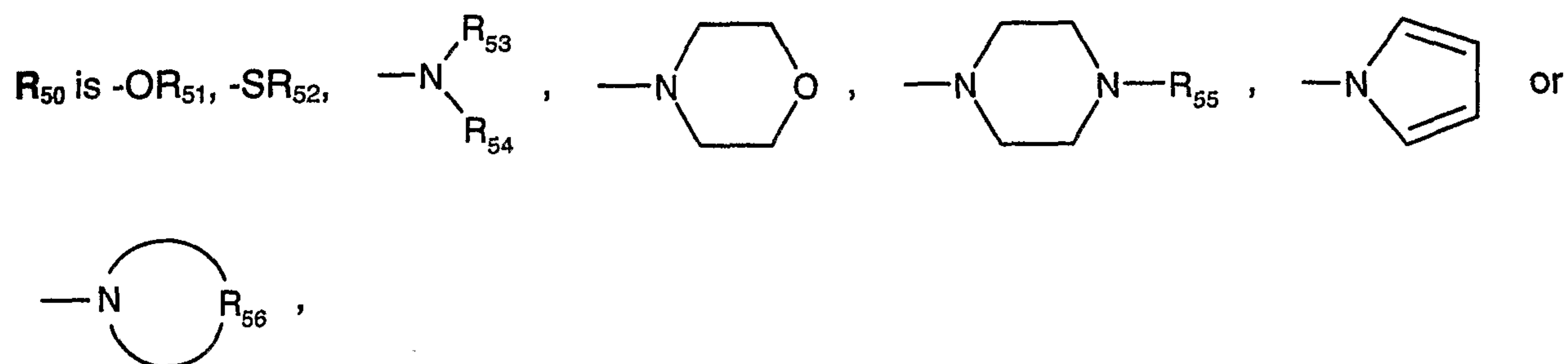
stituted or C_1 - C_4 alkyl-substituted phenylene,  or ,

R_{35} is hydroxy, $\left[-O^- \frac{1}{r} M^{r+} \right]$, C_1 - C_{18} alkoxy or $-N \begin{matrix} R_{12} \\ R_{13} \end{matrix}$,

R_{36} is oxygen, -NH- or ,

R_{37} is C_1 - C_{18} alkyl or phenyl,

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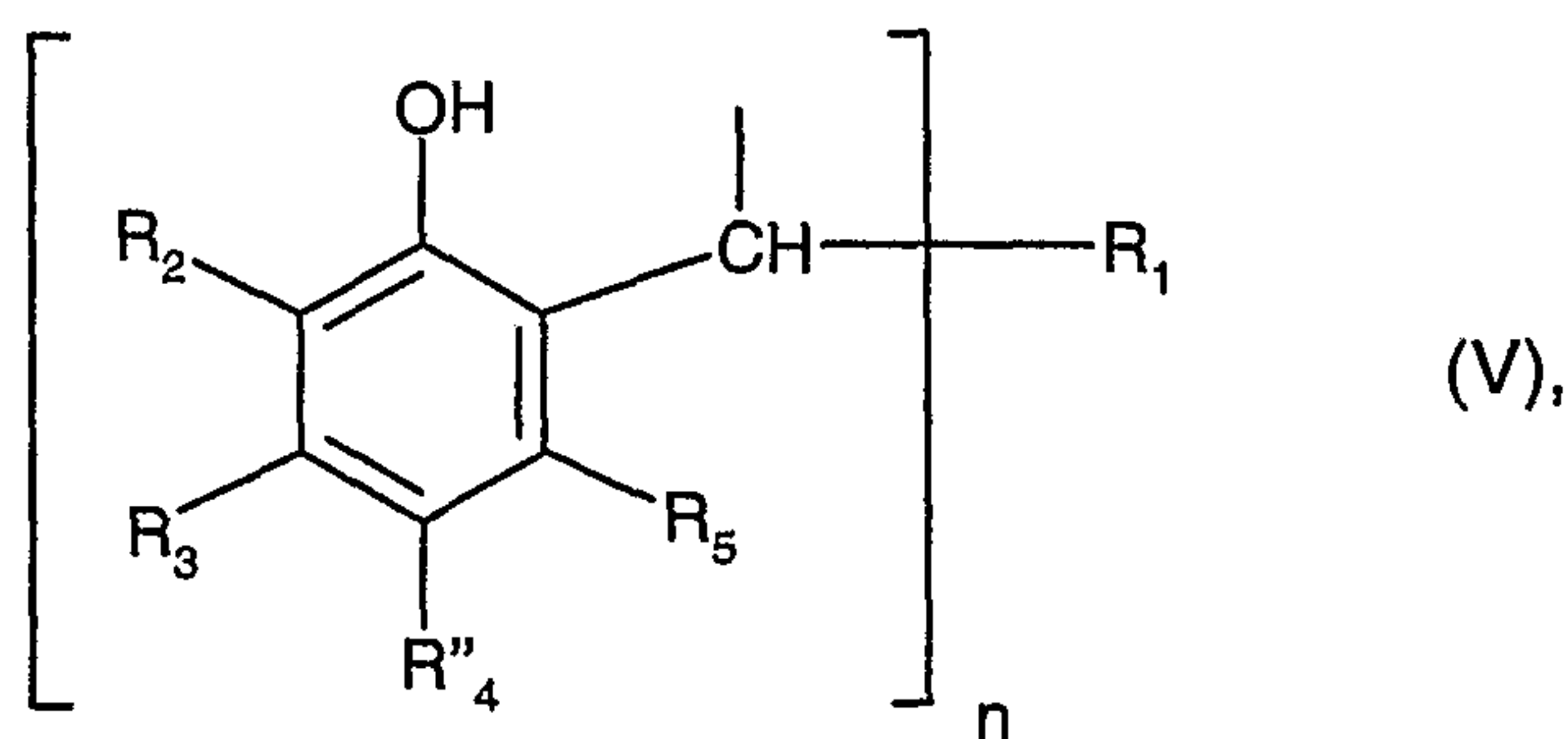


R_{51} is C_1 - C_{25} alkyl; C_2 - C_{25} alkyl interrupted by oxygen or by sulfur; C_7 - C_9 phenylalkyl, unsubstituted or C_1 - C_4 alkyl-substituted C_5 - C_8 cycloalkyl; unsubstituted or C_1 - C_4 alkyl-substituted phenyl,

R_{52} is C_1 - C_{25} alkyl; C_2 - C_{25} alkyl interrupted by oxygen or by sulfur; C_7 - C_9 phenylalkyl, unsubstituted or C_1 - C_4 alkyl-substituted C_5 - C_8 cycloalkyl; unsubstituted or C_1 - C_4 alkyl-substituted phenyl,

R_{53} and R_{54} are each independently of the other hydrogen, C_1 - C_{25} alkyl; C_2 - C_{25} alkyl interrupted by oxygen or by sulfur; C_7 - C_9 phenylalkyl, unsubstituted or C_1 - C_4 alkyl-substituted C_5 - C_8 cycloalkyl; or a dendrimeric, oligomeric or polymeric C_4 - C_{100} hydrocarbon radical,

R_{55} is C_1 - C_{25} alkyl; C_2 - C_{25} alkyl interrupted by oxygen or by sulfur; C_7 - C_9 phenylalkyl, unsubstituted or C_1 - C_4 alkyl-substituted C_5 - C_8 cycloalkyl; unsubstituted or C_1 - C_4 alkyl-substituted phenyl; or a radical of formula (V)



wherein R_1 , R_2 , R_3 , R_4 , R_5 and n are as defined previously,

R_{56} is unsubstituted or C_1 - C_4 alkyl-substituted C_2 - C_{12} alkylene,

M is an r -valent metal cation,

X is a direct bond, oxygen, sulfur or $-NR_{14}$,

p is 0, 1 or 2,

q is 1, 2, 3, 4, 5 or 6,

r is 1, 2 or 3, and

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s is 0, 1 or 2.

Of special interest is a composition in which in the compounds of formulae (Ia), (Ib), (IIa), (IIb), (IIc), (IIIa), (IIIb), (IIIc), (IVa), (IVb) and (IVc)

R_1 is hydrogen, C_1 - C_{25} alkyl or C_1 - C_{18} alkylene;

R_a is C_1 - C_{18} alkylene, phenylene or naphthylene each unsubstituted or substituted by C_1 - C_4 alkyl or by fluorine; or is $-R_6-Y-R_7-$;

R_b is $-NR_{53}$, C_1 - C_{25} alkylenedimino or C_5 - C_8 cycloalkylenediimino; and

X is C_1 - C_{18} alkylene, $-O-$, $-NR_{10}-$ or $-S-$.

For example in the present compounds of formulae (Ia)-(IVc), R_2 , R_3 , R_4 and R_5 are each independently hydrogen, fluorine, hydroxy or C_1 - C_{25} alkyl.

For example, in the present compounds of formulae (Ia)-(IVc), R_2 , R_3 , R_4 and R_5 are each hydrogen or tert-butyl.

For example, in the compositions of the present invention, the compounds of formulae (Ia)-(IVc) are selected from the group consisting of

2,4-di-tert-butyl-6-(phenyl-piperidin-1-yl-methyl)-phenol,
 2,4-di-tert-butyl-6-(dimethylamino-phenyl-methyl)-phenol,
 2,6-bis-dimethylaminomethyl-4-(1,1,3,3-tetramethyl-butyl)-phenol,
 2,4-di-tert-butyl-6-piperidin-1-ylmethyl-phenol,
 2,6-di-tert-butyl-4-(phenyl-piperidin-1-yl-methyl)-phenol,
 2,6-di-tert-butyl-4-piperidin-1-yl-methyl-phenol,
 3-[3-tert-Butyl-4-hydroxy-5-(phenyl-piperidin-1-yl-methyl)-phenyl]-propionic acid methyl ester,
 2,4-di-tert-butyl-6-dimethylaminomethyl-phenol,
 2,4-di-tert-butyl-6-N-morpholino-4-ylmethyl-phenol,
 2,4-di-tert-butyl-6-di-n-butylaminomethyl-phenol,
 2,4-di-tert-butyl-6-cyclohexylaminomethyl-phenol,
 2,6-bis-dimethylaminomethyl-4-(1,1,3,3-tetramethyl-butyl)-phenol,
 2,4,6-tris-dimethylaminomethyl-phenol,
 2,4-bis-dimethylaminomethyl-6-methyl-phenol,
 2,6,2',6'-tetrakis(dimethylaminomethyl)-4,4'-isopropylidene-diphenol,

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1-(N-morpholino-4-yl-methyl)-2-naphthol,
 n-butyl-bis-(2-hydroxy-1-naphthylmethyl)-amine,
 3,5-di-tert-butyl-2-hydroxy-benzyl-acetate,
 2,4-di-tert-butyl-6-methoxymethyl-phenol and
 2,4-bis-(n-octadecylthiomethyl)-6-methyl-phenol.

Mannich bases are well known, and are for example the reaction product of an amine, an aldehyde or aldehyde equivalent, and a nucleophilic carbon. Reviews on their syntheses disclosing useful reaction components and possibilities for their preparation are described in the literature, for example by M. Tramontini in *Synthesis* (1973), pages 703 – 775, M. Tramontini & L. Angiolini in *Tetrahedron* 46, No. 6 (1990) pages 1791 – 1837 and M. Arend, B. Westermann & N. Risch in *Angew. Chem. Int. Ed.* 37 (1998) pages 1044 – 1070, the contents of which are incorporated herewith by reference.

Mannich bases may be classified as amino-alkylation products of alkyl- and aryl-ketones, phenols, indols, nitro- and cyano-compounds and the like. Many Mannich bases are easily prepared from common raw materials in good yields, and further show good thermal and chemical stability. Specific Mannich bases may be selected according to economical and ecological criteria.

Mannich bases suitable in the present invention are taught for example in WO-A-99/67232 the relevant parts of which are incorporated herein by reference.

Alkanoyl having up to 25 carbon atoms is a branched or unbranched radical, for example formyl, acetyl, propionyl, butanoyl, pentanoyl, hexanoyl, heptanoyl, octanoyl, nonanoyl, decanoyl, undecanoyl, dodecanoyl, tridecanoyl, tetradecanoyl, pentadecanoyl, hexadecanoyl, heptadecanoyl, octadecanoyl, icosanoyl or docosanoyl. Alkanoyl has for instance from 2 to 18, for example from 2 to 12, e.g. from 2 to 6, carbon atoms. For example acetyl.

C₂-C₂₅Alkanoyl substituted by a di(C₁-C₆alkyl) phosphonate group is, for example, (CH₃CH₂O)₂POCH₂CO-, (CH₃O)₂POCH₂CO-, (CH₃CH₂CH₂CH₂O)₂POCH₂CO-, (CH₃CH₂O)₂POCH₂CH₂CO-, (CH₃O)₂POCH₂CH₂CO-, (CH₃CH₂CH₂CH₂O)₂POCH₂CH₂CO-, (CH₃CH₂O)₂PO(CH₂)₄CO-, (CH₃CH₂O)₂PO(CH₂)₈CO- or (CH₃CH₂O)₂PO(CH₂)₁₇CO-.

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Alkanoyloxy having up to 25 carbon atoms is a branched or unbranched radical, for example formyloxy, acetoxy, propionyloxy, butanoyloxy, pentanoyloxy, hexanoyloxy, heptanoyloxy, octanoyloxy, nonanoyloxy, decanoyloxy, undecanoyloxy, dodecanoyloxy, tridecanoyloxy, tetradecanoyloxy, pentadecanoyloxy, hexadecanoyloxy, heptadecanoyloxy, octadecanoyloxy, icosanoyloxy or docosanoyloxy. For example alkanoyloxy having from 2 to 18, for example from 2 to 12, e.g. from 2 to 6, carbon atoms. For example acetoxy.

C₃-C₂₅Alkenoyloxy interrupted by oxygen, sulfur or by >NR₈ is, for example, CH₃OCH₂CH₂CH=CHCOO- or CH₃OCH₂CH₂OCH=CHCOO-.

C₃-C₂₅Alkanoyl interrupted by oxygen, sulfur or by >NR₈ is, for example, CH₃-O-CH₂CO-, CH₃-S-CH₂CO-, CH₃-N(CH₃)-CH₂CO-, CH₃-O-CH₂CH₂-O-CH₂CO-, CH₃-(O-CH₂CH₂-)₂O-CH₂CO-, CH₃-(O-CH₂CH₂-)₃O-CH₂CO- or CH₃-(O-CH₂CH₂-)₄O-CH₂CO-.

C₃-C₂₅Alkanoyloxy interrupted by oxygen, sulfur or by >NR₈ is, for example, CH₃-O-CH₂COO-, CH₃-S-CH₂COO-, CH₃-N(CH₃)-CH₂COO-, CH₃-O-CH₂CH₂-O-CH₂COO-, CH₃-(O-CH₂CH₂-)₂O-CH₂COO-, CH₃-(O-CH₂CH₂-)₃O-CH₂COO- or CH₃-(O-CH₂CH₂-)₄O-CH₂COO-.

C₆-C₉Cycloalkylcarbonyl is, for example, cyclopentylcarbonyl, cyclohexylcarbonyl, cycloheptylcarbonyl or cyclooctylcarbonyl. For instance cyclohexylcarbonyl.

C₆-C₉Cycloalkylcarbonyloxy is, for example, cyclopentylcarbonyloxy, cyclohexylcarbonyloxy, cycloheptylcarbonyloxy or cyclooctylcarbonyloxy. For example cyclohexylcarbonyloxy.

C₁-C₁₂Alkyl-substituted benzoyl, which carries for example from 1 to 3, for instance 1 or 2, alkyl groups, is, for example, o-, m- or p-methylbenzoyl, 2,3-dimethylbenzoyl, 2,4-dimethylbenzoyl, 2,5-dimethylbenzoyl, 2,6-dimethylbenzoyl, 3,4-dimethylbenzoyl, 3,5-dimethylbenzoyl, 2-methyl-6-ethylbenzoyl, 4-tert-butylbenzoyl, 2-ethylbenzoyl, 2,4,6-trimethylbenzoyl, 2,6-dimethyl-4-tert-butylbenzoyl or 3,5-di-tert-butylbenzoyl. Examples of substituents are C₁-C₈alkyl, for instance C₁-C₄alkyl.

C₁-C₁₂Alkyl-substituted benzoyloxy, which carries for example from 1 to 3, for instance 1 or 2, alkyl groups, is, for example, o-, m- or p-methylbenzoyloxy, 2,3-dimethylbenzoyloxy, 2,4-dimethylbenzoyloxy, 2,5-dimethylbenzoyloxy, 2,6-dimethylbenzoyloxy, 3,4-dimethylbenzoyloxy, 3,5-dimethylbenzoyloxy, 2-methyl-6-ethylbenzoyloxy, 4-tert-butylbenzoyloxy, 2-ethylbenzoyloxy, 2,4,6-trimethylbenzoyloxy, 2,6-dimethyl-4-tert-butylbenzoyloxy or 3,5-di-tert-butylbenzoyloxy. Substituents are for example C₁-C₈alkyl, for instance C₁-C₄alkyl.

Alkyl having up to 25 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, 1,1,3,3,5,5-hexamethylhexyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, icosyl or docosyl. One of the definitions for R₂ and R₄ is, for example, C₁-C₁₈alkyl. For instance R₄ is C₁-C₄alkyl.

Alkenyl is an unsaturated version of alkyl, for example isopropenyl, propenyl, hexenyl, heptenyl, and the like.

C₂-C₂₅Alkyl interrupted by oxygen, sulfur or by >NR₈ is, for example, CH₃-O-CH₂-, CH₃-S-CH₂-, CH₃-N(CH₃)-CH₂-, CH₃-O-CH₂CH₂-O-CH₂-, CH₃-(O-CH₂CH₂)₂O-CH₂-, CH₃-(O-CH₂CH₂)₃O-CH₂- or CH₃-(O-CH₂CH₂)₄O-CH₂-.

C₇-C₉Phenylalkyl is, for example, benzyl, α-methylbenzyl, α,α-dimethylbenzyl or 2-phenylethyl. For example benzyl and α,α-dimethylbenzyl.

C₇-C₉Phenylalkyl unsubstituted or substituted on the phenyl radical by from 1 to 3 C₁-C₄alkyl groups is, for example, benzyl, α-methylbenzyl, α,α-dimethylbenzyl, 2-phenylethyl, 2-methylbenzyl, 3-methylbenzyl, 4-methylbenzyl, 2,4-dimethylbenzyl, 2,6-dimethylbenzyl or 4-tert-butylbenzyl. For example benzyl.

C₇-C₂₅Phenylalkyl interrupted by oxygen, sulfur or by >NR₈ and unsubstituted or substituted on the phenyl radical by from 1 to 3 C₁-C₄alkyl groups is a branched or unbranched radical, for example phenoxymethyl, 2-methyl-phenoxymethyl, 3-methyl-phenoxymethyl, 4-methyl-

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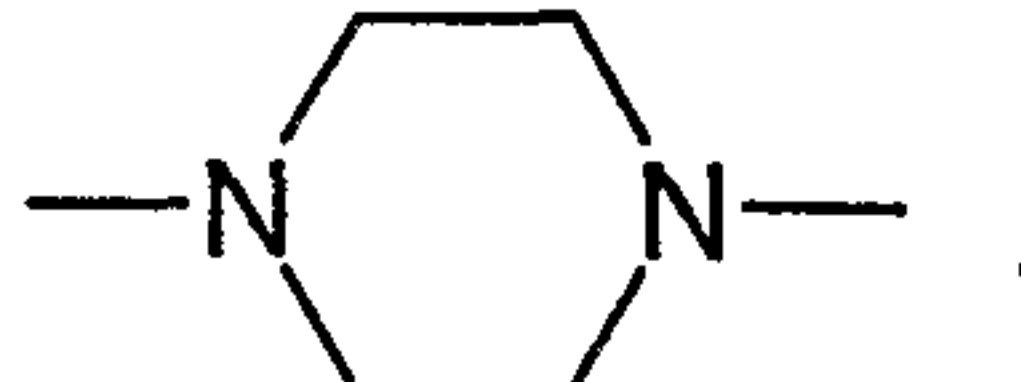
phenoxymethyl, 2,4-dimethyl-phenoxymethyl, 2,3-dimethyl-phenoxymethyl, phenylthiomethyl, N-methyl-N-phenyl-aminomethyl, N-ethyl-N-phenyl-aminomethyl, 4-tert-butyl-phenoxymethyl, 4-tert-butyl-phenoxyethoxy-methyl, 2,4-di-tert-butyl-phenoxymethyl, 2,4-di-tert-butyl-phenoxyethoxymethyl, phenoxyethoxyethoxyethoxymethyl, benzyloxymethyl, benzyloxyethoxymethyl, N-benzyl-N-ethyl-aminomethyl or N-benzyl-N-isopropyl-aminomethyl.

C₇-C₉Phenylalkoxy is, for example, benzyloxy, α -methylbenzyloxy, α,α -dimethylbenzyloxy or 2-phenylethoxy. For example benzyloxy.

C₁-C₄Alkyl-substituted phenyl, which contains for example 1 to 3, for instance 1 or 2, alkyl groups, is, for example, o-, m- or p-methylphenyl, 2,3-dimethylphenyl, 2,4-dimethylphenyl, 2,5-dimethylphenyl, 2,6-dimethylphenyl, 3,4-dimethylphenyl, 3,5-dimethylphenyl, 2-methyl-6-ethylphenyl, 4-tert-butylphenyl, 2-ethylphenyl or 2,6-diethylphenyl.

C₁-C₄Alkyl-substituted phenoxy, which contains for example from 1 to 3, for instance 1 or 2, alkyl groups, is, for example, o-, m- or p-methylphenoxy, 2,3-dimethylphenoxy, 2,4-dimethylphenoxy, 2,5-dimethylphenoxy, 2,6-dimethylphenoxy, 3,4-dimethylphenoxy, 3,5-dimethylphenoxy, 2-methyl-6-ethylphenoxy, 4-tert-butylphenoxy, 2-ethylphenoxy or 2,6-diethylphenoxy.

Unsubstituted or C₁-C₄alkyl-substituted C₅-C₈cycloalkyl is, for example, cyclopentyl, methylcyclopentyl, dimethylcyclopentyl, cyclohexyl, methylcyclohexyl, dimethylcyclohexyl, trimethylcyclohexyl, tert-butylcyclohexyl, cycloheptyl or cyclooctyl. For example cyclohexyl and tert-butylcyclohexyl.

Cycloalkylenediimino is for example piperazinyl, that is .

Alkylenediimino, triimino and tetraimino are for example hexamethylenediimino, that is -NH(CH₂)₆NH-, and the like.

Unsubstituted or C₁-C₄alkyl-substituted C₅-C₈cycloalkoxy is, for example, cyclopentyloxy, methylcyclopentyloxy, dimethylcyclopentyloxy, cyclohexyloxy, methylcyclohexyloxy, dimethyl-

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cyclohexyloxy, trimethylcyclohexyloxy, tert-butylcyclohexyloxy, cycloheptyloxy or cyclooctyloxy. For example cyclohexyloxy and tert-butylcyclohexyloxy.

Alkoxy having up to 25 carbon atoms is a branched or unbranched radical, for example methoxy, ethoxy, propoxy, isopropoxy, n-butoxy, isobutoxy, pentyloxy, isopentyloxy, hexyloxy, heptyloxy, octyloxy, decyloxy, tetradecyloxy, hexadecyloxy or octadecyloxy. For example alkoxy having from 1 to 12, for instance from 1 to 8, e.g. from 1 to 6, carbon atoms.

C₂-C₂₅Alkoxy interrupted by oxygen, sulfur or by >NR₈ is, for example,
 CH₃-O-CH₂CH₂O-, CH₃-S-CH₂CH₂O-, CH₃-N(CH₃)-CH₂CH₂O-,
 CH₃-O-CH₂CH₂-O-CH₂CH₂O-, CH₃-(O-CH₂CH₂)₂O-CH₂CH₂O-,
 CH₃-(O-CH₂CH₂)₃O-CH₂CH₂O- or CH₃-(O-CH₂CH₂)₄O-CH₂CH₂O-.

Alkylthio having up to 25 carbon atoms is a branched or unbranched radical, for example methylthio, ethylthio, propylthio, isopropylthio, n-butylthio, isobutylthio, pentylthio, isopentylthio, hexylthio, heptylthio, octylthio, decylthio, tetradecylthio, hexadecylthio or octadecylthio. For example alkylthio having from 1 to 12, for example from 1 to 8, e.g. from 1 to 6, carbon atoms.

Alkylamino having up to 4 carbon atoms is a branched or unbranched radical, for example methylamino, ethylamino, propylamino, isopropylamino, n-butylamino, isobutylamino or tert-butylamino.

Di(C₁-C₄alkyl)amino means also that the two radicals are each independently of the other branched or unbranched, for example, dimethylamino, methylethylamino, diethylamino, methyl-n-propylamino, methylisopropylamino, methyl-n-butylamino, methylisobutylamino, ethylisopropylamino, ethyl-n-butylamino, ethylisobutylamino, ethyl-tert-butylamino, diethylamino, diisopropylamino, isopropyl-n-butylamino, isopropylisobutylamino, di-n-butylamino or di-isobutylamino.

Alkanoylamino having up to 25 carbon atoms is a branched or unbranched radical, for example formylamino, acetylamino, propionylamino, butanoylamino, pentanoylamino, hexanoylamino, heptanoylamino, octanoylamino, nonanoylamino, decanoylamino, undecanoylamino, dodecanoylamino, tridecanoylamino, tetradecanoylamino, pentadecanoylamino,

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hexadecanoylamino, heptadecanoylamino, octadecanoylamino, icosanoylamino or docosanoylamino. For example alkanoylamino having from 2 to 18, for instance from 2 to 12, e.g. from 2 to 6, carbon atoms.

C₁-C₁₈Alkylene is a branched or unbranched radical, for example methylene, ethylene, propylene, trimethylene, tetramethylene, pentamethylene, hexamethylene, heptamethylene, octamethylene, decamethylene, dodecamethylene or octadecamethylene. For example C₁-C₁₂alkylene, for instance C₁-C₈alkylene. R₅₆ is for example C₂-C₈alkylene, for instance C₄-C₈alkylene, for example tetramethylene or pentamethylene.

C₂-C₁₈Alkylene interrupted by oxygen, sulfur or by >NR₈ is, for example, -CH₂-O-CH₂-, -CH₂-S-CH₂-, -CH₂-N(CH₃)-CH₂-, -CH₂-O-CH₂CH₂-O-CH₂-, -CH₂-(O-CH₂CH₂)₂O-CH₂-, -CH₂-(O-CH₂CH₂)₃O-CH₂-, -CH₂-(O-CH₂CH₂)₄O-CH₂- or -CH₂CH₂-S-CH₂CH₂-.

Alkylidene having from 2 to 20 carbon atoms is, for example, ethylidene, propylidene, butylidene, pentylidene, 4-methylpentylidene, heptylidene, nonylidene, tridecylidene, nonadecylidene, 1-methylethylidene, 1-ethylpropylidene or 1-ethylpentylidene. For example C₂-C₈alkylidene.

Phenylalkylidene having from 7 to 20 carbon atoms is, for example, benzylidene, 2-phenylethylidene or 1-phenyl-2-hexylidene. For example C₇-C₉phenylalkylidene.

C₅-C₈Cycloalkylene is a saturated hydrocarbon group having two free valences and at least one ring unit and is, for example, cyclopentylene, cyclohexylene, cycloheptylene or cyclooctylene. For example cyclohexylene.

C₇-C₈Bicycloalkylene is, for example, bicycloheptylene or bicyclooctylene.

Phenylene or naphthylene each unsubstituted or substituted by C₁-C₄alkyl is, for example, 1,2-, 1,3- or 1,4-phenylene or 1,2-, 1,3-, 1,4-, 1,6-, 1,7-, 2,6- or 2,7-naphthylene. For instance 1,4-phenylene.

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A C₅-C₈cycloalkylidene ring substituted by C₁-C₄alkyl, which contains for example from 1 to 3, for instance 1 or 2, branched or unbranched alkyl group radicals, is, for example, cyclopentylidene, methylcyclopentylidene, dimethylcyclopentylidene, cyclohexylidene, methylcyclohexylidene, dimethylcyclohexylidene, trimethylcyclohexylidene, tert-butylcyclohexylidene, cycloheptylidene or cyclooctylidene. For example cyclohexylidene and tert-butylcyclohexylidene.

A mono-, di- or tri-valent metal cation is for example an alkali metal cation, alkaline earth metal cation or aluminium cation, for example Na⁺, K⁺, Mg⁺⁺, Ca⁺⁺ or Al⁺⁺⁺.

Dendrimeric, oligomeric or polymeric C₄-C₁₀₀hydrocarbon radicals are, for example, those such as are disclosed by R. Mülhaupt et al. in Angew. Chem., Int. Ed. 32 (9), 1306 (1993).

Alkanoylcarbonyl groups are ester groups, for example -COOalkyl. Alkylaminocarbonyl and di-alkylaminocarbonyl groups are amide groups, for example -CONHalkyl and -CON(di-alkyl), respectively. Perfluoroalkyl of 1 to 12 carbon atoms is for example -CF₃.

The polyester or polyamide of component (a) is for example 95 to 99.99 % by weight and the stabilizer or stabilizers of component (b), in total, are 5 to 0.01 % by weight, based on the total weight of (a) and (b).

Component (a) is preferably 98 to 99.99 % by weight and component (b) is preferably 2 to 0.01 % by weight of the total of (a) and (b); for example component (a) is 99 to 99.97 % by weight and component (b) is 1 to 0.01 % by weight, based on the total weight of (a) and (b).

For example, component (b) is from 0.75 to 0.01 %, from 0.50 to 0.01 %, from 0.25 to 0.01 % or from 0.125 to 0.01 % by weight, based on the total weight of (a) and (b).

The additives of component (b) may be added to the polyester or polyamide of component (a) by known techniques. For example, the additives of component (b) may be added neat or as a solution or dispersion in a suitable solid or liquid carrier, with or without subsequent evaporation of the solvent. Component (b) may also be added to the polyester or polyamide to be stabilized in the form of a masterbatch or concentrate which contains component (b) in

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a concentration of, for example, 2.5 % to 95 % by weight. The masterbatch may contain further additives such as stabilizers, property modifiers, pigments, dyestuffs and the like.

It is contemplated that one or more than one (a combination of) Mannich base compounds of the present invention may be employed in the compositions.

The polyester of component (a) has dicarboxylic acid repeat units selected from the group consisting of aromatic dicarboxylic acids having 8 to 14 carbon atoms, aliphatic dicarboxylic acids having 4 to 12 carbon atoms, cycloaliphatic dicarboxylic acids having 8 to 12 carbon atoms, and mixtures thereof.

For example such diacids are terephthalic acid, isophthalic acid, o-phthalic acid, naphthalene dicarboxylic acid, cyclohexane dicarboxylic acid, cyclohexanediadic acid, diphenyl-4,4'-dicarboxylic acid, succinic acid, glutaric acid, adipic acid, sebacic acid and mixtures thereof.

Specific examples are terephthalic acid and 2,6-naphthalene dicarboxylic acid.

The diol or glycol portion of the polyester of component (a) are derived from the generic formula HO-R-OH where R is an aliphatic, cycloaliphatic or aromatic moiety of 2 to 18 carbon atoms.

Preferably such diols or glycols are ethylene glycol, diethylene glycol, triethylene glycol, propane-1,3-diol, propane-1,2-diol, butane-1,4-diol, pentane-1,5-diol, hexane-1,6-diol, 1,4-cyclohexanedimethanol, 3-methylpentane-2,4-diol, 2-methylpentane-1,4-diol, 2,2-diethylpropane-1,3-diol, 1,4-di-(hydroxyethoxy)benzene, 2,2-bis(4-hydroxycyclohexyl)-propane, 2,4-dihydroxy-1,1,3,3-tetramethylcyclobutane, 2,2-bis-(3-hydroxyethoxyphenyl)propane, 2,2-bis-(4-hydroxypropoxyphenyl)ethane and mixtures thereof.

Most preferably, the diol is ethylene glycol and 1,4-cyclohexanedimethanol.

The polyester of component (a) is preferably poly(ethylene terephthalate) PET or poly(ethylene 2,6-naphthalene-2,6-dicarboxylate); most preferably poly(ethylene terephthalate).

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It is also contemplated that the polyester of component (a) can also be a blend of polyesters or copolyesters including components mentioned above.

The polyamides of the present invention are for instance those prepared by the polymerization of a monoamino-monocarboxylic acid or a lactam thereof having at least 2 carbon atoms between the amino and carboxylic acid group, of substantially equimolar proportions of a diamine which contains at least 2 carbon atoms between the amino groups and a dicarboxylic acid, or of a monoaminocarboxylic acid or a lactam thereof as defined above together with substantially equimolar proportions of a diamine and a dicarboxylic acid. The term "substantially equimolar" proportions includes both strictly equimolar proportions and slight departures therefrom which are involved in conventional techniques for stabilizing the viscosity of the resultant polyamides. The dicarboxylic acid may be used in the form of a functional derivative thereof, for example, an ester or acid chloride.

Examples of the aforementioned monoamino-monocarboxylic acids or lactams thereof which are useful in preparing the polyamides include those compounds containing from 2 to 16 carbon atoms between the amino and carboxylic acid groups, said carbon atoms forming a ring containing the -CO-NH- group in the case of a lactam. As particular examples of aminocarboxylic acids and lactams there may be mentioned ϵ -aminocaproic acid, butyrolactam, pivalolactam, ϵ -caprolactam, capryllactam, enantholactam, undecanolactam, dodecanolactam and 3- and 4-aminobenzoic acids.

Diamines suitable for use in the preparation of the polyamides include the straight chain and branched chain alkyl, aryl and alkaryl diamines. Illustrative diamines are trimethylenediamine, tetramethylenediamine, pentamethylenediamine, octamethylenediamine, hexamethylenediamine, trimethylhexamethylenediamine, m-phenylenediamine and m-xylylenediamine.

The dicarboxylic acids may be represented by the formula



wherein B is a divalent aliphatic or aromatic group containing at least 2 carbon atoms. Examples of aliphatic acids are sebacic acid, octadecanedioic acid, suberic acid, glutaric acid, pimelic acid and adipic acid.

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Both crystalline and amorphous polyamides may be employed, with the crystalline species known for their solvent resistance. Typical examples of the polyamides or nylons, as these are often called, include, for example, polyamide-6 (polycaprolactam), 6,6 (polyhexamethylene adipamide), 11, 12, 4,6, 6,10 and 6,12 as well as polyamides from terephthalic acid and/or isophthalic acid and trimethylhexamethylenediamine; from adipic acid and m-xylylenediamines; from adipic acid, azelaic acid and 2,2-bis(p-aminophenyl)propane or 2,2-bis-(p-aminocyclohexyl)propane and from terephthalic acid and 4,4'-diaminodicyclohexylmethane. Mixtures and/or copolymers of two or more of the foregoing polyamides or prepolymers thereof, respectively, are also within the scope of the present invention. Polyamides of the present invention are for instance polyamide-6; 4; 6; 6,6; 6,4; 6,9; 6,10; 6,12; 11 and 12. For example, the polyamide of the present invention is polyamide-4, polyamide-6, polyamide-6,6, polyamide-12 or polyamide-6,4.

The polyamides of the present invention may also include known polyamide stabilizers, for example Irgafos[®] 168, Irganox[®] 1098, Nylostab[®] S-EED (Clariant, CAS# 42774-15-2) and Polyad[®] 201 (CuI/KI/Zn stearate; 10%/80%/10% ratio w/w). Irganox[®] 1098 (Ciba) is N,N'-bis-(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexamethylenediamide. The polyamide stabilizers are employed at their known levels, for example from 0.01 to 1% by weight, based on polyamide.

The polyamide compositions of the present invention exhibit improved resistance to yellowing and improved mechanical properties.

It is contemplated that the polymer of component (a) can be virgin polymer or alternatively polymer recycle. Additionally, it is possible to add the stabilizer or stabilizers described for component (b) as part of a concentrate with a polyester or a polyamide carrier resin.

The novel compositions provided by this invention are useful in the manufacture of containers or packages for comestibles such as beverages and food. Articles molded from these polyesters or polyamides exhibit good thin-wall rigidity, excellent clarity and good barrier properties with respect to moisture and atmospheric gases, particularly carbon dioxide and oxygen.

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The plastic containers and films of the present invention are rigid or flexible mono- and/or multi-layered constructions. Typical multi-layer constructions have two or more layer laminates, manufactured either by thermoforming, or extrusion of multi-layer flexible films, or extrusion of bottle "preforms" or "parissons" followed by subsequent blow molding of the preforms into bottles. In a multi-layer system, layers of any suitable plastic may be employed.

Multi-layered containers and films of this invention may for example, be formed from layers of polyesters, polyamides, polyolefins, polyolefin copolymers such as ethylene-vinyl acetate, polystyrene, poly(vinyl chloride), poly(vinylidene chloride), polyamides, cellulose, polycarbonates, ethylene-vinyl alcohol, poly(vinyl alcohol), styrene-acrylonitrile and ionomers, with the proviso that at least one layer comprises a polyester or polyamide composition of the present invention.

For both films and rigid packaging (bottles), typically the exterior layer, and innermost layer contacting the contents, are composed, for example, of polyesters such as PET or PEN [poly(ethylene naphthalate)], polypropylene, or polyethylene such as HDPE. The middle layers, often called 'barrier' or 'adhesive' or 'tie' layers, are composed of one or more combinations of either PET, PEN, carboxylated polyethylene ionomer such as Surlyn[®], vinyl alcohol homopolymers or copolymers such as poly(vinyl alcohol), partially hydrolyzed poly(vinyl acetate), poly(ethylene-co-vinyl alcohol) such as EVOH or EVAL, nylons or polyamides such as Sellar[®] (DuPont) or polyamides based on metaxylenediamine (sometimes called nylon MXD-6), or polyvinylidene chloride (PVDC), or polyurethanes.

Accordingly, the present invention also pertains to a mono- or multi-layered plastic container or film, stabilized against the formation of aldehydic contaminants during melt processing of said container or film, comprising at least one layer which comprises (a) a polyester or polyamide, and (b) an effective stabilizing amount of at least one compound selected from the group consisting of the Mannich base compounds of formulae (Ia), (Ib), (IIa), (IIb), (IIc), (IIIa), (IIIb), (IIIc), (IVa), (IVb) and (IVc).

Rigid containers may be manufactured by known mechanical processes:

- a) Single-stage blow molding such as performed on Nissei, Aoki, or Uniloy machines,

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- b) Two-stage, injection molding of pre-forms such as on Netstal or Husky machines, and pre-forms converted to bottles by blow molding (e.g., on Sidel, Corpoplast and Krones machines),
- c) Integrated blow molding of pre-forms to bottles, such as processes conducted on Sipa, Krupp Kautex, or Husky ISB machines, and
- d) Stretch blow molding (SBM) of pre-forms to bottles.

Preferably, the plastic container is a rigid bottle.

The pre-forms may be mono-layer or multi-layer in construction. The bottles may optionally be post-treated to alter the inner wall properties. Bottles may optionally be surface treated on the exterior such as by application of surface coatings. UV absorbers and other known stabilizers may be present in such added surface coatings.

By the use of known heat-setting techniques, certain of the polyesters are, in terms of color, I.V. and heat distortion, stable at temperatures up to about 100°C. Such stability characteristics are referred to herein as "hot-fill" stability. The linear polyesters employed in articles having "hot-fill" stability comprise poly(ethylene terephthalate), poly(ethylene terephthalate) wherein up to 5 mole percent of the ethylene glycol residues have been replaced with residues derived from 1,4-cyclohexanedimethanol and poly(ethylene 2,6-naphthalenedicarboxylate), wherein the polyesters have been sufficiently heat set and oriented by methods well known in the art to give a desired degree of crystallinity.

The polyester or polyamide fibers of the present invention are prepared by known techniques. They may be woven or nonwoven. They are prepared by melt extrusion processes to form fibers or filaments. In accordance with known technology such as continuous filament spinning for yarn or staple fiber, and nonwoven processes such as spunbond production and meltblown production, the fibers or filaments are formed by extrusion of the molten polymer through small orifices. In general, the fibers or filaments thus formed are then drawn or elongated. In nonwoven processes such as spunbonding and meltblowing, the fibers or filaments are directly deposited onto a foraminous surface, such as a moving flat conveyor and are at least partially consolidated by any of a variety of means including, but not limited to, thermal, mechanical or chemical methods of bonding. It is known to those skilled in the art to combine processes or the fabrics from different processes to produce composite fabrics

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which possess certain desirable characteristics. Examples of this are combining spunbond and meltblown to produce a laminate fabric that is best known as SMS, meant to represent two outer layers of spunbond fabric and an inner layer of meltblown fabric. Additionally either or both of these processes may be combined in any arrangement with a staple fiber carding process or bonded fabrics resulting from a nonwoven staple fiber carding process. In such described laminate fabrics, the layers are generally at least partially consolidated by one of the means listed above.

In laminate fabrics of the present invention, at least one layer comprises a composition of the present invention.

Fibers of the present invention are for example described in U.S. 5,650,509; U.S. 5,911,902; U.S. 6,294,254; U.S. 5,049,447; U.S. 5,512,340; U.S. 6,010,789; U.S. 5,589,530 and U.S. 6,020,421, the relevant disclosures of which are hereby incorporated by reference.

Fibers of the present invention may be employed for example in upholstery, clothing, garments, ropes, nets, tire cords, kites, parachutes and the like.

Molded polyamide articles are for example employed in automotive applications (under the hood), and the like.

Polyester films are well known in the art. PET films are employed for packaging for example for medical, food, industrial and decorative products. They are used as business graphics films in labels, printing base, office graphics and signs. They are used as industrial films for example in liners, as carrier, tape backing, protective overlay, membrane switch and for laminating. They are used for example as imaging films in medial and proofing applications and as solar control and security window films. They are used for example in white coated film, white voided film, dimensionally stable film, extrusion coated film, tear resistant film, polarizing film, reflective film, dispensable film, coated film, co-extruded film, insulation film, weather resistant film, laminating film and mirror film.

PEN films are used for example in labels, flexible printed circuitry and electrical insulation.

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The polyester films of this invention may be used for example, in combination with other films such as polyolefin films.

Polyamide films, for example PA 6 and PA 6,6 films, are used for example in co-extruded films for packaging. For example, polyamide films are employed in microwaveable food packaging.

The instant invention also pertains to a process for preventing the formation of aldehydic contaminants during melt processing of a polyester or polyamide which comprises incorporating into said polyester or polyamide an effective stabilizing amount of at least one compound selected from the group consisting of the Mannich base compounds of formulae (Ia), (Ib), (IIa), (IIb), (IIc), (IIIa), (IIIb), (IIIc), (IVa), (IVb) and (IVc).

The instant invention also pertains to a process for forming a bottle preform or a bottle or container suitable for storing water (mineral, natural, ozonated) or other foodstuffs, which allows the desirable taste of the water or foodstuff after packaging to remain unaltered after being placed in said bottle or container prepared from the polyester or polyamide composition of the instant invention.

The instant plastic container or film stabilized by a compound or compounds of component (b) may also optionally have incorporated therein or applied thereto from 0.01 to 10 % by weight; for example from 0.025 to 5 % by weight, for instance from 0.05 to 2 % by weight, based on the total weight of the composition, of additional coadditives such as antioxidants, other UV absorbers, hindered amines, phosphites or phosphonites, benzofuran-2-ones, thio-synergists, polyamide stabilizers, metal stearates, nucleating agents, oxygen scavengers, fillers, reinforcing agents, lubricants, emulsifiers, dyes, pigments, optical brighteners, flame retardants, antistatic agents, blowing agents and the like, such as the materials listed below, or mixtures thereof.

1. Antioxidants

1.1. Alkylated monophenols, for example 2,6-di-tert-butyl-4-methylphenol, 2-tert-butyl-4,6-dimethylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,6-di-tert-butyl-4-n-butylphenol, 2,6-di-tert-butyl-4-isobutylphenol, 2,6-dicyclopentyl-4-methylphenol, 2-(α -methylcyclohexyl)-4,6-dimethyl-

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phenol, 2,6-dioctadecyl-4-methylphenol, 2,4,6-tricyclohexylphenol, 2,6-di-tert-butyl-4-methoxymethylphenol, nonylphenols which are linear or branched in the side chains, for example 2,6-di-nonyl-4-methylphenol, 2,4-dimethyl-6-(1'-methylundec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methylheptadec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methyltridec-1'-yl)phenol and mixtures thereof.

1.2. Alkylthiomethylphenols, for example 2,4-dioctylthiomethyl-6-tert-butylphenol, 2,4-dioctylthiomethyl-6-methylphenol, 2,4-dioctylthiomethyl-6-ethylphenol, 2,6-di-dodecylthiomethyl-4-nonylphenol.

1.3. Hydroquinones and alkylated hydroquinones, for example 2,6-di-tert-butyl-4-methoxyphenol, 2,5-di-tert-butylhydroquinone, 2,5-di-tert-amylhydroquinone, 2,6-diphenyl-4-octadecyloxyphenol, 2,6-di-tert-butylhydroquinone, 2,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyphenyl stearate, bis(3,5-di-tert-butyl-4-hydroxyphenyl) adipate.

1.4. Tocopherols, for example α -tocopherol, β -tocopherol, γ -tocopherol, δ -tocopherol and mixtures thereof (vitamin E).

1.5. Hydroxylated thiodiphenyl ethers, for example 2,2'-thiobis(6-tert-butyl-4-methylphenol), 2,2'-thiobis(4-octylphenol), 4,4'-thiobis(6-tert-butyl-3-methylphenol), 4,4'-thiobis(6-tert-butyl-2-methylphenol), 4,4'-thiobis(3,6-di-sec-amylphenol), 4,4'-bis(2,6-dimethyl-4-hydroxyphenyl)-disulfide.

1.6. Alkylidenebisphenols, for example 2,2'-methylenebis(6-tert-butyl-4-methylphenol), 2,2'-methylenebis(6-tert-butyl-4-ethylphenol), 2,2'-methylenebis[4-methyl-6-(α -methylcyclohexyl)phenol], 2,2'-methylenebis(4-methyl-6-cyclohexylphenol), 2,2'-methylenebis(6-nonyl-4-methylphenol), 2,2'-methylenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(6-tert-butyl-4-isobutylphenol), 2,2'-methylenebis[6-(α -methylbenzyl)-4-nonylphenol], 2,2'-methylenebis[6-(α,α -dimethylbenzyl)-4-nonylphenol], 4,4'-methylenebis(2,6-di-tert-butylphenol), 4,4'-methylenebis(6-tert-butyl-2-methylphenol), 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 2,6-bis(3-tert-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol, 1,1,3-tris(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-3-n-dodecylmercaptobutane, ethylene glycol bis[3,3-

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bis(3'-tert-butyl-4'-hydroxyphenyl)butyrate], bis(3-tert-butyl-4-hydroxy-5-methyl-phenyl)di-cyclopentadiene, bis[2-(3'-tert-butyl-2'-hydroxy-5'-methylbenzyl)-6-tert-butyl-4-methylphe-nyl]terephthalate, 1,1-bis-(3,5-dimethyl-2-hydroxyphenyl)butane, 2,2-bis(3,5-di-tert-butyl-4-hydroxyphenyl)propane, 2,2-bis-(5-tert-butyl-4-hydroxy-2-methylphenyl)-4-n-dodecylmercap-tobutane, 1,1,5,5-tetra(5-tert-butyl-4-hydroxy-2-methylphenyl)pentane.

1.7. O-, N- and S-benzyl compounds, for example 3,5,3',5'-tetra-tert-butyl-4,4'-dihydroxydi-benzyl ether, octadecyl-4-hydroxy-3,5-dimethylbenzylmercaptoacetate, tridecyl-4-hydroxy-3,5-di-tert-butylbenzylmercaptoacetate, tris(3,5-di-tert-butyl-4-hydroxybenzyl)amine, bis(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)dithioterephthalate, bis(3,5-di-tert-butyl-4-hydroxy-benzyl)sulfide, isooctyl-3,5-di-tert-butyl-4-hydroxybenzylmercaptoacetate.

1.8. Hydroxybenzylated malonates, for example dioctadecyl-2,2-bis(3,5-di-tert-butyl-2-hydr-oxybenzyl)malonate, di-octadecyl-2-(3-tert-butyl-4-hydroxy-5-methylbenzyl)malonate, di-do-decylmercaptoethyl-2,2-bis(3,5-di-tert-butyl-4-hydroxybenzyl)malonate, bis[4-(1,1,3,3-tetra-methylbutyl)phenyl]-2,2-bis(3,5-di-tert-butyl-4-hydroxybenzyl)malonate.

1.9. Aromatic hydroxybenzyl compounds, for example 1,3,5-tris(3,5-di-tert-butyl-4-hydroxy-benzyl)-2,4,6-trimethylbenzene, 1,4-bis(3,5-di-tert-butyl-4-hydroxybenzyl)-2,3,5,6-tetrame-thylbenzene, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)phenol.

1.10. Triazine compounds, for example 2,4-bis(octylmercapto)-6-(3,5-di-tert-butyl-4-hydroxy-anilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-tri-azine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,3,5-triazine, 2,4,6-tris-(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,2,3-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxyben-zyl)isocyanurate, 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)isocyanurate, 2,4,6-tris-(3,5-di-tert-butyl-4-hydroxyphenylethyl)-1,3,5-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxy-phenylpropionyl)-hexahydro-1,3,5-triazine, 1,3,5-tris(3,5-dicyclohexyl-4-hydroxybenzyl)iso-cyanurate.

1.11. Benzylphosphonates, for example dimethyl-2,5-di-tert-butyl-4-hydroxybenzylphospho-nate, diethyl-3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl-3,5-di-tert-butyl-4-hy-droxybenzylphosphonate, dioctadecyl-5-tert-butyl-4-hydroxy-3-methylbenzylphosphonate, the calcium salt of the monoethyl ester of 3,5-di-tert-butyl-4-hydroxybenzylphosphonic acid.

1.12. Acylaminophenols, for example 4-hydroxylauranilide, 4-hydroxystearanilide, octyl N-(3,5-di-tert-butyl-4-hydroxyphenyl)carbamate.

1.13. Esters of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, n-octanol, i-octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

1.14. Esters of β -(5-tert-butyl-4-hydroxy-3-methylphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, n-octanol, i-octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane; 3,9-bis[2-{3-(3-tert-butyl-4-hydroxy-5-methylphenyl)propionyloxy}-1,1-dimethylethyl]-2,4,8,10-tetraoxaspiro[5.5]undecane.

1.15. Esters of β -(3,5-dicyclohexyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

1.16. Esters of 3,5-di-tert-butyl-4-hydroxyphenyl acetic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

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1.17. Amides of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid e.g. N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexamethylenediamide, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)trimethylenediamide, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hydrazide, N,N'-bis[2-(3-[3,5-di-tert-butyl-4-hydroxyphenyl]propionyloxy)ethyl]oxamide (Nau-gard®XL-1, supplied by Uniroyal).

1.18. Ascorbic acid (vitamin C)

1.19. Aminic antioxidants, for example N,N'-di-isopropyl-p-phenylenediamine, N,N'-di-sec-butyl-p-phenylenediamine, N,N'-bis(1,4-dimethylpentyl)-p-phenylenediamine, N,N'-bis(1-ethyl-3-methylpentyl)-p-phenylenediamine, N,N'-bis(1-methylheptyl)-p-phenylenediamine, N,N'-dicyclohexyl-p-phenylenediamine, N,N'-diphenyl-p-phenylenediamine, N,N'-bis(2-naphthyl)-p-phenylenediamine, N-isopropyl-N'-phenyl-p-phenylenediamine, N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine, N-(1-methylheptyl)-N'-phenyl-p-phenylenediamine, N-cyclohexyl-N'-phenyl-p-phenylenediamine, 4-(p-toluenesulfamoyl)diphenylamine, N,N'-dimethyl-N,N'-di-sec-butyl-p-phenylenediamine, diphenylamine, N-allyldiphenylamine, 4-isopropoxydiphenylamine, N-phenyl-1-naphthylamine, N-(4-tert-octylphenyl)-1-naphthylamine, N-phenyl-2-naphthylamine, octylated diphenylamine, for example p,p'-di-tert-octyldiphenylamine, 4-n-butylaminophenol, 4-butyrylaminophenol, 4-nonanoylaminophenol, 4-dodecanoylaminophenol, 4-octadecanoylaminophenol, bis(4-methoxyphenyl)amine, 2,6-di-tert-butyl-4-dimethylaminomethylphenol, 2,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane, N,N,N',N'-tetramethyl-4,4'-diaminodiphenylmethane, 1,2-bis[(2-methylphenyl)amino]ethane, 1,2-bis(phenylamino)propane, (o-tolyl)biguanide, bis[4-(1',3'-dimethylbutyl)phenyl]amine, tert-octylated N-phenyl-1-naphthylamine, a mixture of mono- and dialkylated tert-butyl/tert-octyldiphenylamines, a mixture of mono- and dialkylated nonyldiphenylamines, a mixture of mono- and dialkylated dodecyldiphenylamines, a mixture of mono- and dialkylated isopropyl/isohexyldiphenylamines, a mixture of mono- and dialkylated tert-butyldiphenylamines, 2,3-dihydro-3,3-dimethyl-4H-1,4-benzothiazine, phenothiazine, a mixture of mono- and dialkylated tert-butyl/tert-octylphenothiazines, a mixture of mono- and dialkylated tert-octylphenothiazines, N-allylphenothiazine, N,N,N',N'-tetraphenyl-1,4-diaminobut-2-ene.

2. UV absorbers and light stabilizers

2.1. 2-(2'-Hydroxyphenyl)benzotriazoles, for example 2-(2'-hydroxy-5'-methylphenyl)benzotriazole, 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(5'-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-5'-(1,1,3,3-tetramethylbutyl)phenyl)benzotriazole, 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-methylphenyl)-5-chlorobenzotriazole, 2-(3'-sec-butyl-5'-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-4'-octyloxyphenyl)benzotriazole, 2-(3',5'-di-tert-amyl-2'-hydroxyphenyl)benzotriazole, 2-(3',5'-bis(α,α -dimethylbenzyl)-2'-hydroxyphenyl)benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxycarbonylethyl)phenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)carbonylethyl]-2'-hydroxyphenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-methoxycarbonylethyl)phenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-methoxycarbonylethyl)phenyl)benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxycarbonylethyl)phenyl)benzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)carbonylethyl]-2'-hydroxyphenyl)benzotriazole, 2-(3'-dodecyl-2'-hydroxy-5'-methylphenyl)benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-isooctyloxycarbonylethyl)phenyl)benzotriazole, 2,2'-methylenebis[4-(1,1,3,3-tetramethylbutyl)-6-benzotriazole-2-ylphenol]; the transesterification product of 2-[3'-tert-butyl-5'-(2-methoxycarbonylethyl)-2'-hydroxyphenyl]-2H-benzotriazole with polyethylene glycol 300; $\left[R - CH_2CH_2 - COO - CH_2CH_2 \right]_2$, where R = 3'-tert-butyl-4'-hydroxy-5'-2H-benzotriazole-2-ylphenyl, 2-[2'-hydroxy-3'-(α,α -dimethylbenzyl)-5'-(1,1,3,3-tetramethylbutyl)phenyl]benzotriazole; 2-[2'-hydroxy-3'-(1,1,3,3-tetramethylbutyl)-5'-(α,α -dimethylbenzyl)phenyl]benzotriazole.

2.2. 2-Hydroxybenzophenones, for example the 4-hydroxy, 4-methoxy, 4-octyloxy, 4-decyloxy, 4-dodecyloxy, 4-benzyloxy, 4,2',4'-trihydroxy and 2'-hydroxy-4,4'-dimethoxy derivatives.

2.3. Esters of substituted and unsubstituted benzoic acids, for example 4-tert-butylphenyl salicylate, phenyl salicylate, octylphenyl salicylate, dibenzoyl resorcinol, bis(4-tert-butylbenzoyl)resorcinol, benzoyl resorcinol, 2,4-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate, hexadecyl 3,5-di-tert-butyl-4-hydroxybenzoate, octadecyl 3,5-di-tert-butyl-4-hydroxybenzoate, 2-methyl-4,6-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate.

2.4. Acrylates, for example ethyl α -cyano- β,β -diphenylacrylate, isooctyl α -cyano- β,β -diphenylacrylate, methyl α -carbomethoxycinnamate, methyl α -cyano- β -methyl-p-methoxycinnamate, butyl α -cyano- β -methyl-p-methoxycinnamate, methyl α -carbomethoxy-p-methoxycinnamate and N-(β -carbomethoxy- β -cyanovinyl)-2-methylindoline.

2.5. Nickel compounds, for example nickel complexes of 2,2'-thiobis[4-(1,1,3,3-tetramethylbutyl)phenol], such as the 1:1 or 1:2 complex, with or without additional ligands such as n-butylamine, triethanolamine or N-cyclohexyldiethanolamine, nickel dibutyldithiocarbamate, nickel salts of the monoalkyl esters, e.g. the methyl or ethyl ester, of 4-hydroxy-3,5-di-tert-butylbenzylphosphonic acid, nickel complexes of ketoximes, e.g. of 2-hydroxy-4-methylphenylundecylketoxime, nickel complexes of 1-phenyl-4-lauroyl-5-hydroxypyrazole, with or without additional ligands.

2.6. Sterically hindered amines, for example bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate, bis(2,2,6,6-tetramethyl-4-piperidyl)succinate, bis(1,2,2,6,6-pentamethyl-4-piperidyl)sebacate, bis(1-octyloxy-2,2,6,6-tetramethyl-4-piperidyl)sebacate, bis(1,2,2,6,6-pentamethyl-4-piperidyl)n-butyl-3,5-di-tert-butyl-4-hydroxybenzylmalonate, the condensate of 1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid, linear or cyclic condensates of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-tert-octylamino-2,6-dichloro-1,3,5-triazine, tris(2,2,6,6-tetramethyl-4-piperidyl)nitrilotriacetate, tetrakis(2,2,6,6-tetramethyl-4-piperidyl)-1,2,3,4-butanetetracarboxylate, 1,1'-(1,2-ethanediyl)-bis(3,3,5,5-tetramethylpiperazinone), 4-benzoyl-2,2,6,6-tetramethylpiperidine, 4-stearyloxy-2,2,6,6-tetramethylpiperidine, bis(1,2,2,6,6-pentamethylpiperidyl)-2-n-butyl-2-(2-hydroxy-3,5-di-tert-butylbenzyl)malonate, 3-n-octyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione, bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl)sebacate, bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl)succinate, linear or cyclic condensates of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-morpholino-2,6-dichloro-1,3,5-triazine, the condensate of 2-chloro-4,6-bis(4-n-butylamino-2,2,6,6-tetramethylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane, the condensate of 2-chloro-4,6-di-(4-n-butylamino-1,2,2,6,6-pentamethylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane, 8-acetyl-3-dodecyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione, 3-dodecyl-1-(2,2,6,6-tetramethyl-4-piperidyl)pyrrolidine-2,5-dione, 3-dodecyl-1-(1,2,2,6,6-pentamethyl-4-piperidyl)pyrrolidine-2,5-dione, a mixture of 4-hexadecyloxy- and 4-stearyloxy-2,2,6,6-tetramethylpiperidine, a condensate of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-cyclohexylamino-2,6-dichloro-1,3,5-triazine, a condensate of 1,2-bis(3-aminopropylamino)ethane and 2,4,6-trichloro-1,3,5-triazine as well as 4-butylamino-2,2,6,6-tetramethylpiperidine (CAS Reg. No. [136504-96-6]); a condensate of 1,6-hexanediamine and 2,4,6-trichloro-1,3,5-triazine as well as N,N-dibutylamine and 4-butylamino-2,2,6,6-tetramethylpiperidine (CAS Reg. No.

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[192268-64-7]); N-(2,2,6,6-tetramethyl-4-piperidyl)-n-dodecylsuccinimide, N-(1,2,2,6,6-pentamethyl-4-piperidyl)-n-dodecylsuccinimide, 2-undecyl-7,7,9,9-tetramethyl-1-oxa-3,8-diaza-4-oxo-spiro[4,5]decane, a reaction product of 7,7,9,9-tetramethyl-2-cycloundecyl-1-oxa-3,8-diaza-4-oxospiro-[4,5]decane and epichlorohydrin, 1,1-bis(1,2,2,6,6-pentamethyl-4-piperidyloxycarbonyl)-2-(4-methoxyphenyl)ethene, N,N'-bis-formyl-N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine, a diester of 4-methoxymethylenemalonic acid with 1,2,2,6,6-pentamethyl-4-hydroxypiperidine, poly[methylpropyl-3-oxy-4-(2,2,6,6-tetramethyl-4-piperidyl)]siloxane, a reaction product of maleic acid anhydride- α -olefin copolymer with 2,2,6,6-tetramethyl-4-aminopiperidine or 1,2,2,6,6-pentamethyl-4-aminopiperidine.

The sterically hindered amine may also be one of the compounds described in U.S. 5,980,783, the relevant parts of which are hereby incorporated by reference, that is compounds of component I-a), I-b), I-c), I-d), I-e), I-f), I-g), I-h), I-i), I-j), I-k) or I-l), in particular the light stabilizer 1-a-1, 1-a-2, 1-b-1, 1-c-1, 1-c-2, 1-d-1, 1-d-2, 1-d-3, 1-e-1, 1-f-1, 1-g-1, 1-g-2 or 1-k-1 listed on columns 64 – 72 of said U.S. 5,980,783.

The sterically hindered amine may also be one of the compounds described in EP-A-0 782 994, for example compounds as described in claims 10 or 38 or in Examples 1-12 or D-1 to D-5 therein.

2.7. Sterically hindered amines substituted on the N-atom by a hydroxy-substituted alkoxy group, for example compounds such as 1-(2-hydroxy-2-methylpropoxy)-4-octadecanoyloxy-2,2,6,6-tetramethylpiperidine, 1-(2-hydroxy-2-methylpropoxy)-4-hexadecanoyloxy-2,2,6,6-tetramethylpiperidine, the reaction product of 1-oxyl-4-hydroxy-2,2,6,6-tetramethylpiperidine with a carbon radical from t-amylalcohol, 1-(2-hydroxy-2-methylpropoxy)-4-hydroxy-2,2,6,6-tetramethylpiperidine, 1-(2-hydroxy-2-methylpropoxy)-4-oxo-2,2,6,6-tetramethylpiperidine, bis(1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl) sebacate, bis(1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl) adipate, bis(1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl) succinate, bis(1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl) glutarate and 2,4-bis{N-[1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl]-N-butylamino}-6-(2-hydroxyethylamino)-s-triazine.

2.8. Oxamides, for example 4,4'-dioctyloxyoxanilide, 2,2'-diethoxyoxanilide, 2,2'-dioctyloxy-5,5'-di-tert-butoxanilide, 2,2'-didodecyloxy-5,5'-di-tert-butoxanilide, 2-ethoxy-2'-ethyloxanilide,

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N,N'-bis(3-dimethylaminopropyl)oxamide, 2-ethoxy-5-tert-butyl-2'-ethoxanilide and its mixture with 2-ethoxy-2'-ethyl-5,4'-di-tert-butoxanilide, mixtures of o- and p-methoxy-disubstituted oxanilides and mixtures of o- and p-ethoxy-disubstituted oxanilides.

2.9. 2-(2-Hydroxyphenyl)-1,3,5-triazines, for example 2,4,6-tris(2-hydroxy-4-octyloxyphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2,4-dihydroxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2,4-bis(2-hydroxy-4-propyloxyphenyl)-6-(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(4-methylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-dodecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-tridecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-butyloxypropoxy)phenyl]-4,6-bis(2,4-dimethyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-octyloxypropyloxy)phenyl]-4,6-bis(2,4-dimethyl)-1,3,5-triazine, 2-[4-(dodecyloxy/tridecyloxy-2-hydroxypropoxy)-2-hydroxyphenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-dodecyloxypropoxy)phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-hexyloxy)phenyl-4,6-diphenyl-1,3,5-triazine, 2-(2-hydroxy-4-methoxyphenyl)-4,6-diphenyl-1,3,5-triazine, 2,4,6-tris[2-hydroxy-4-(3-butoxy-2-hydroxypropoxy)phenyl]-1,3,5-triazine, 2-(2-hydroxyphenyl)-4-(4-methoxyphenyl)-6-phenyl-1,3,5-triazine, 2-[2-hydroxy-4-[3-(2-ethylhexyl-1-oxy)-2-hydroxypropyloxy]phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine.

3. Metal deactivators, for example N,N'-diphenyloxamide, N-salicylal-N'-salicyloyl hydrazine, N,N'-bis(salicyloyl)hydrazine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hydrazine, 3-salicyloylamino-1,2,4-triazole, bis(benzylidene)oxalyl dihydrazide, oxanilide, isophthaloyl dihydrazide, sebacoyl bisphenylhydrazide, N,N'-diacetyl adipoyl dihydrazide, N,N'-bis(salicyloyl)oxalyl dihydrazide, N,N'-bis(salicyloyl)thiopropionyl dihydrazide.

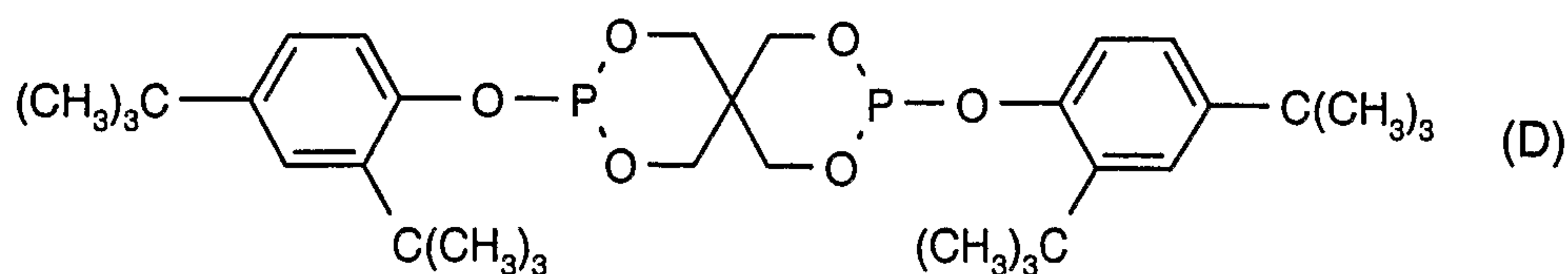
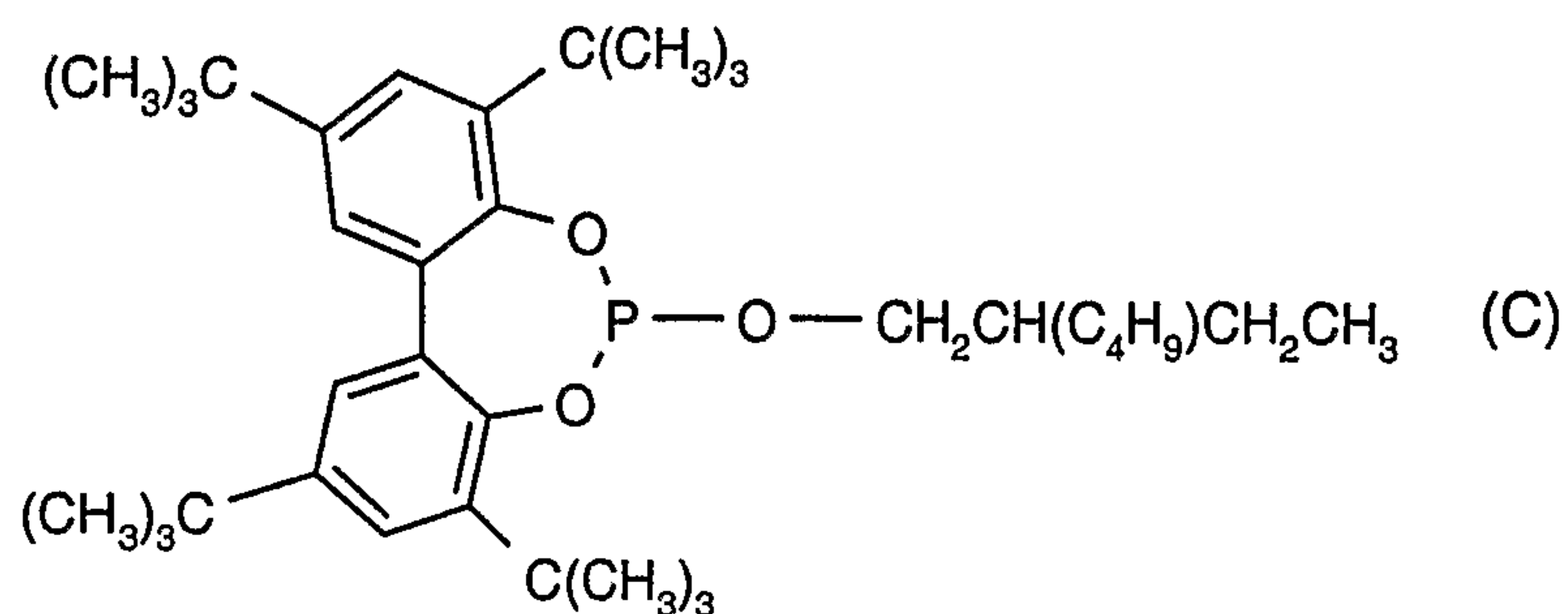
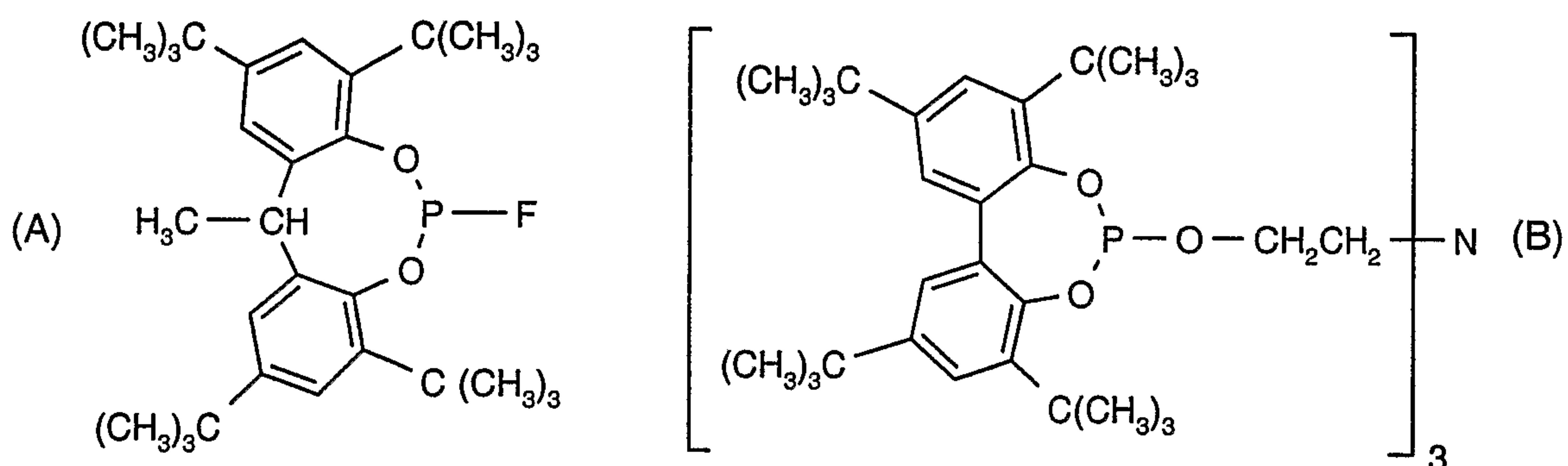
4. Phosphites and phosphonites, for example triphenyl phosphite, diphenylalkyl phosphites, phenyldialkyl phosphites, tris(nonylphenyl) phosphite, trilauryl phosphite, trioctadecyl phosphite, distearyl pentaerythritol diphosphite, tris(2,4-di-tert-butylphenyl) phosphite, diisodecyl pentaerythritol diphosphite, bis(2,4-di-tert-butylphenyl) pentaerythritol diphosphite, bis(2,4-di-cumylphenyl) pentaerythritol diphosphite, bis(2,6-di-tert-butyl-4-methylphenyl) pentaerythritol diphosphite, diisodecyloxypentaerythritol diphosphite, bis(2,4-di-tert-butyl-6-methylphenyl) pentaerythritol diphosphite, bis(2,4,6-tris(tert-butylphenyl) pentaerythritol diphosphite, tristearyl sorbitol triphosphite, tetrakis(2,4-di-tert-butylphenyl) 4,4'-biphenylene diphosphonite, 6-

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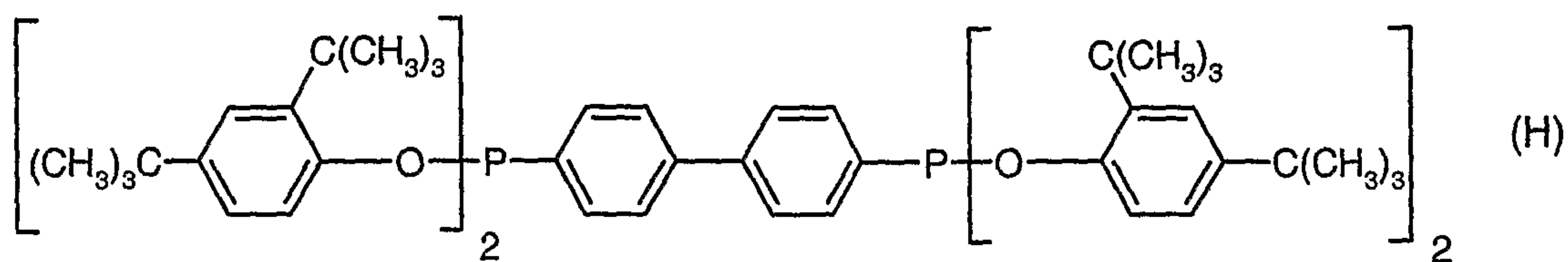
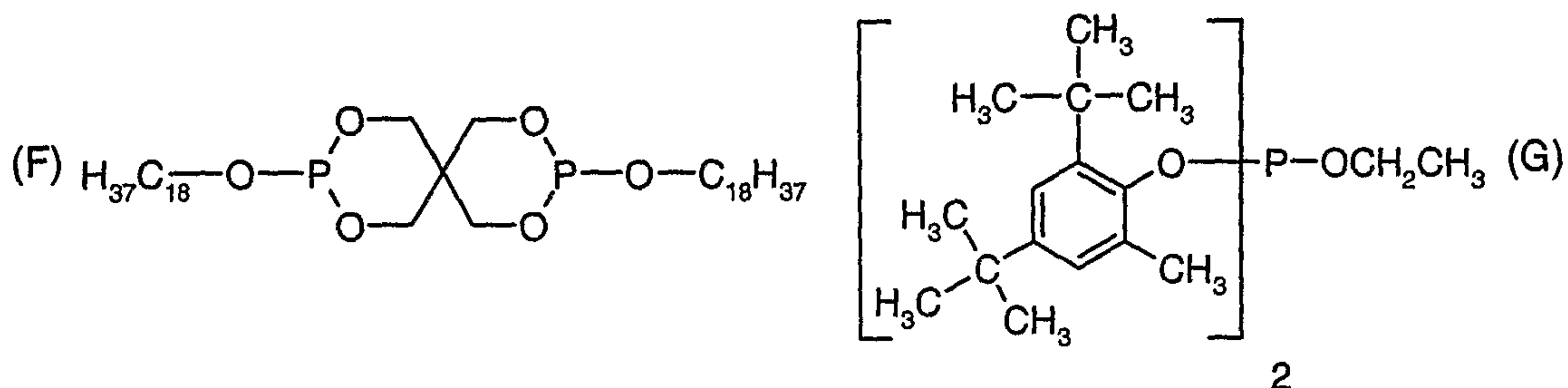
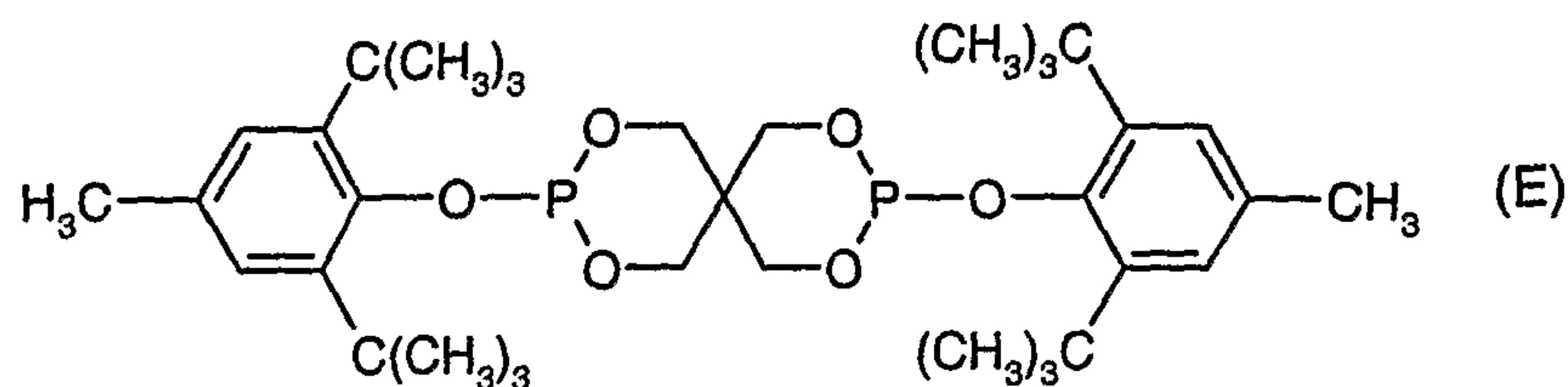
isooctyloxy-2,4,8,10-tetra-tert-butyl-12H-dibenz[d,g]-1,3,2-dioxaphosphocin, bis(2,4-di-tert-butyl-6-methylphenyl)methyl phosphite, bis(2,4-di-tert-butyl-6-methylphenyl)ethyl phosphite, 6-fluoro-2,4,8,10-tetra-tert-butyl-12-methyl-dibenz[d,g]-1,3,2-dioxaphosphocin, 2,2',2''-nitrilo-[triethyltris(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl)phosphite], 2-ethylhexyl(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl)phosphite, 5-butyl-5-ethyl-2-(2,4,6-tri-tert-butylphenoxy)-1,3,2-dioxaphosphirane.

The following phosphates and phosphonites are especially preferred:

Tris(2,4-di-tert-butylphenyl) phosphite (Irgafos®168, Ciba Specialty Chemicals Inc.), tris(nonylphenyl) phosphite,



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5. Benzofuranones and indolinones, for example those disclosed in U.S. 4,325,863; U.S. 4,338,244; U.S. 5,175,312; U.S. 5,216,052; U.S. 5,252,643; DE-A-4316611; DE-A-4316622; DE-A-4316876; EP-A-0589839 or EP-A-0591102 or 3-[4-(2-acetoxyethoxy)-phenyl]-5,7-di-tert-butylbenzofuran-2-one, 5,7-di-tert-butyl-3-[4-(2-stearoyloxyethoxy)phenyl]-benzofuran-2-one, 3,3'-bis[5,7-di-tert-butyl-3-(4-[2-hydroxyethoxy]phenyl)benzofuran-2-one], 5,7-di-tert-butyl-3-(4-ethoxyphenyl)benzofuran-2-one, 3-(4-acetoxy-3,5-dimethylphenyl)-5,7-di-tert-butylbenzofuran-2-one, 3-(3,5-dimethyl-4-pivaloyloxyphenyl)-5,7-di-tert-butylbenzofuran-2-one, 3-(3,4-dimethylphenyl)-5,7-di-tert-butylbenzofuran-2-one, 3-(2,3-dimethylphenyl)-5,7-di-tert-butylbenzofuran-2-one.

6. Thiosynergists, for example dilauryl thiodipropionate or distearyl thiodipropionate.

7. Peroxide scavengers, for example esters of β -thiodipropionic acid, for example the lauryl, stearyl, myristyl or tridecyl esters, mercaptobenzimidazole or the zinc salt of 2-mercaptobenzimidazole, zinc dibutyldithiocarbamate, dioctadecyl disulfide, pentaerythritol tetra-kis(β -dodecylmercapto)propionate.

8. Polyamide stabilizers, for example copper salts in combination with iodides and/or phosphorus compounds and salts of divalent manganese.

9. Basic co-stabilisers, for example melamine, polyvinylpyrrolidone, dicyandiamide, triallyl cyanurate, urea derivatives, hydrazine derivatives, amines, polyamides, polyurethanes, alkali metal salts and alkaline earth metal salts of higher fatty acids, for example calcium stearate, zinc stearate, magnesium behenate, magnesium stearate, sodium ricinoleate and potassium palmitate, antimony pyrocatecholate or zinc pyrocatecholate.

10. Nucleating agents, for example inorganic substances, such as talcum, metal oxides, such as titanium dioxide or magnesium oxide, phosphates, carbonates or sulfates of, preferably, alkaline earth metals; organic compounds, such as mono- or polycarboxylic acids and the salts thereof, e.g. 4-tert-butylbenzoic acid, adipic acid, diphenylacetic acid, sodium succinate or sodium benzoate; polymeric compounds, such as ionic copolymers (ionomers). Especially preferred are 1,3:2,4-bis(3',4'-dimethylbenzylidene)sorbitol, 1,3:2,4-di(paramethyl-dibenzylidene)sorbitol, and 1,3:2,4-di(benzylidene)sorbitol.

11. Fillers and reinforcing agents, for example calcium carbonate, silicates, glass fibres, glass bulbs, asbestos, talc, kaolin, mica, barium sulfate, metal oxides and hydroxides, carbon black, graphite, wood flour and flours or fibers of other natural products, synthetic fibers.

12. Dispersing agents, such as polyethylene oxide waxes or mineral oil.

13. Dyes & pigments, for example those which are of violet color, which when admixed with polyester of polyamide containing yellowness, gives an acceptable b* value coloration close to original manufactured polyester of polyamide. Such pigments and dyes include Ciba Chromophtal™ Violet B and PV-37, SV 13 to include Bayer Macrolex™ Violet B Gran., Cobalt salts such as cobalt acetate, cobalt stearate and cobalt octoate.

14. Other additives, for example plasticizers, lubricants, emulsifiers, pigments, dyes, optical brighteners, rheology additives, catalysts, flow-control agents, slip agents, crosslinking agents, crosslinking boosters, halogen scavengers, smoke inhibitors, flameproofing agents, antistatic agents, clarifiers such as substituted and unsubstituted bisbenzylidene sorbitols,

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benzoxazinone UV absorbers such as 2,2'-p-phenylene-bis(3,1-benzoxazin-4-one), anthranilamide (AAA), Cyasorb[®] 3638 (CAS# 18600-59-4), and blowing agents, and oxygen absorbers such as Cryovac's Oxbar[™] and Ciba[®] Shelfplus[™] O2.

It is also contemplated that the present polyester or polyamide compositions may be further stabilized against the formation of aldehydic contaminants during melt processing with the incorporation therein of poly(vinyl alcohol), ethylene/vinyl alcohol copolymer, polyhydric alcohols, polyacrylamide, polymethacrylamide or an acrylamide or methacrylamide copolymer with at least one ethylenically unsaturated comonomer.

It is also contemplated that the present polyester or polyamide compositions may be further stabilized against the formation of aldehydic contaminants during melt processing with the incorporation therein of a compound selected from the group consisting of hydroxylamine, substituted hydroxylamine, nitron and amine oxide stabilizers.

Accordingly, the present invention also pertains to a composition, stabilized against the formation of aldehydic contaminants during melt processing of said composition, which comprises

- (a) a polyester or polyamide, and
- (b) an effective stabilizing amount of at least one compound selected from the group consisting of the Mannich base compounds of formulae (Ia), (Ib), (IIa), (IIb), (IIc), (IIIa), (IIIb), (IIIc), (IVa), (IVb) and (IVc) according to claim 1; and optionally
- (c) an effective stabilizing amount of a polymer which is poly(vinyl alcohol) or an ethylene/vinyl alcohol copolymer; and optionally
- (d) an effective stabilizing amount of a polyhydric alcohol; and optionally
- (e) an effective stabilizing amount of a polymer which is polyacrylamide, polymethacrylamide or an acrylamide or methacrylamide copolymer with at least one ethylenically unsaturated comonomer; and optionally
- (f) an effective stabilizing amount of at least one compound selected from the group consisting of
 - i.) hydroxylamine stabilizers,
 - ii.) substituted hydroxylamine stabilizers,
 - iii.) nitron stabilizers, and
 - iv.) amine oxide stabilizers; and optionally

Polyhydric alcohols of component (d) may be for example glycerin, 1,2,3-butanetriol, 1,2,4-butanetriol, erythritol, ribitol, xylitol, dulcitol, sorbitol, 1,2,3-cyclohexatriol, inositol, glucose, galactose, mannose, galacturonic acid, xylose, glucosamine, galactosamine, 1,1,2,2-tetramethyloxy-cyclohexane, 1,1,1-trimethylolpropane, 1,1,2-trimethyloxypropane, 1,1,1-trimethylol-butane, 1,1,2-trimethylolbutane, 1,1,1-trimethylolpentane, 1,1,2-trimethylolpentane, 1,2,2-trimethylolpentane, trimethylolpentane, pentaerythritol, dipentaerythritol, 1,1,3,3-tetrahydroxypropane, 1,1,5,5-tetrahydroxypentane, 2,2,6,6-tetrakis(hydroxymethyl)cyclohexane and 2,2,6,6-tetrakis(hydroxymethyl)cyclohexanol.

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The polyhydric alcohol is for instance starch, cellulose or a sugar or a sugar alcohol.

The polyhydric alcohols include degraded starch (dextrins and cyclodextrins), maltose and its derivatives, maltitol, maltopentaose hydrate, maltoheptaose, maltotetraose, maltulose monohydrate, D,L-glucose, dextrose, sucrose and D-mannitol.

Commercial polyhydric alcohols include trimethylol propane, triethylol propane, glycerol, sorbitol and pentaerythritol.

Specific examples of compounds of component (f) are the N,N-di(alkyl)hydroxylamine produced by the direct oxidation of N,N-di(hydrogenated tallow)amine (Irgastab[®] FS-042), O-allyl-N,N-dioctadecylhydroxylamine, N-octadecyl- α -heptadecylnitrone, and Genox[™] EP, a di(C₁₆-C₁₈)alkyl methyl amine oxide, CAS# 204933-93-7.

Preferably, the alcohols of component (d) are selected from the group consisting of pentaerythritol, dipentaerythritol and trimethylolpropane and the compounds of component (f) are selected from the group consisting of the N,N-di(alkyl)hydroxylamine produced by the direct oxidation of N,N-di(hydrogenated tallow)amine, O-allyl-N,N-dioctadecylhydroxylamine, N-octadecyl- α -heptadecylnitrone and di(C₁₆-C₁₈)alkyl methyl amine oxide.

Irgastab[®] FS-042 is available from Ciba Specialty Chemicals. Genox[™] EP is available from GE Chemicals. O-allyl-N,N-dioctadecylhydroxylamine is as prepared in Example 3 of U.S. 5,045,583. N-octadecyl- α -heptadecylnitrone is as prepared in Example 3 of U.S. 4,898,901.

A hydrocarbylene moiety according to this invention is a divalent group derived from for example an aliphatic, cycloaliphatic, aromatic or a mono-, di- or poly-saccharide moiety.

The hydrocarbylene moieties for the definition of E may be interrupted by heteroatoms, for example by -O-.

The hydrocarbylene moiety E is derived for example from glycerin, 1,2,3-butanetriol, 1,2,4-butanetriol, erythritol, ribitol, xylitol, dulcitol, sorbitol, 1,2,3-cyclohexatriol, inositol, glucose, galactose, mannose, galacturonic acid, xylose, glucosamine, galactosamine, 1,1,2,2-tetramethyloxcyclohexane, 1,1,1-trimethylolpropane, 1,1,2-trimethyloxypropane, 1,1,1-trimethylol-

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butane, 1,1,2-trimethylolbutane, 1,1,1-trimethylolpentane, 1,1,2-trimethylolpentane, 1,2,2-trimethylolpentane, trimethylolpentane, pentaerythritol, dipentaerythritol, 1,1,3,3-tetrahydroxypropane, 1,1,5,5-tetrahydroxypentane, 2,2,6,6-tetrakis(hydroxymethyl)cyclohexane and 2,2,6,6-tetrakis(hydroxymethyl)cyclohexanol.

The hydrocarbylene moiety E is derived for example from starch, cellulose or a sugar or a sugar alcohol; for example degraded starch (dextrans and cyclodextrins), maltose and its derivatives, maltitol, maltopentaose hydrate, maltoheptaose, maltotetraose, maltulose monohydrate, D,L-glucose, dextrose, sucrose and D-mannitol; as well as from commercial polyhydric alcohols which include trimethylol propane, triethylol propane, glycerol, sorbitol and pentaerythritol.

The polyester or polyamide of component (a) is for example 95 to 99.99 % by weight and the polymer of component (c) is for example 5 to 0.01 % by weight, based on the total weight of (a) and (c).

For instance, the polyester or polyamide of component (a) is 99.925 to 99.995 % by weight and component (c) is 0.075 to 0.005 % by weight based on the total weight of components (a) and (c).

The polyester or polyamide of component (a) is for example 95 to 99.99 % by weight and the polyhydric alcohol of component (d) is for example 5 to 0.01 % by weight, based on the total weight of (a) and (d).

For example, component (a) is 98 to 99.99 % by weight and component (d) is 2 to 0.01 % by weight of the total weight of (a) and (d); for instance component (a) is 99 to 99.97 % by weight and component (d) is 1 to 0.03 % by weight of the total weight of (a) and (d).

The polyester or polyamide of component (a) is for example 95 to 99.99 % by weight and the polymer of component (e) is for example 5 to 0.01 % by weight, based on the total weight of (a) and (e).

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The polyester or polyamide of component (a) is for example 95 to 99.99 % by weight and the stabilizer or stabilizers of component (f), in total, are for example 5 to 0.01 % by weight, based on the total weight of (a) and (f).

For example, component (a) is 98 to 99.99 % by weight and component (f) is 2 to 0.01 % by weight of the total of (a) and (f); for instance component (a) is 99 to 99.97 % by weight and component (f) is 1 to 0.03 % by weight, based on the total weight of (a) and (f).

The polyester or polyamide of component (a) is for example 95 to 99.99 % by weight and the stabilizer or stabilizers of component (g), in total, are for example 5 to 0.01 % by weight, based on the total weight of (a) and (g).

For instance, component (a) is for example 98 to 99.99 % by weight and component (g) is for example 2 to 0.01 % by weight of the total of (a) and (g); for instance component (a) is 99 to 99.97 % by weight and component (g) is 1 to 0.03 % by weight, based on the total weight of (a) and (g).

It is well known that Mannich base compounds may be chemically converted to quinone methide compounds (and equivalents) under the action of heat and/or light. It has been found that the thermal transformation products of the present Mannich base compounds are also active as aldehyde scavengers in polyester and polyamide. The present compounds where R_{50} is selected from $-OR_{51}$, $-O-C(O)-R_{51}$, $-SR_{52}$, $-S(O)R_{52}$, $-S(O)_2R_{52}$ may also be transformed into quinone methides under the influence of heat and/or light, which compounds are also suitable to scavenge aldehydes in polyester and polyamide.

The onium salts of Mannich bases and related ethers or thioethers, i.e. when R_{50} is $-[N(H)_2 R_{52}]^+ Y^-$, $-[N(H) R_{52} R_{53}]^+ Y^-$, $-[NR_{52} R_{53} R_{54}]^+ Y^-$, $[-OR_{51} R_{52}]^+ Y^-$ or $-[S R_{51} R_{52}]^+ Y^-$, where Y^- is a mono-valent anion - are equally "capped" precursors of quinone methides and may correspondingly be used as scavengers of aldehydes formed during processing of polyester or polyamide.

Further, the activity of these thermal transformation products is increased with the addition of a co-additive amine. The amine compounds are for example the corresponding amines of the Mannich base compounds of formulae (Ia)-(IVc) according to this invention. That is, the

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amino substituents of R_{50} whose open valence is satisfied with a hydrogen atom. For example dialkylamines, piperidine, dipiperidine, morpholine, etc.

It is also contemplated that amine co-additives may be advantageously employed in addition to the present Mannich bases in polyester or polyamide compositions.

Accordingly, the present invention also pertains to a composition, stabilized against the formation of aldehydic contaminants during melt processing of said composition, which comprises

- (a) a polyester or polyamide, and
- (b) an effective stabilizing amount of at least one compound selected from the group consisting of the Mannich base compounds of formulae (Ia), (Ib), (IIa), (IIb), (IIc), (IIIa), (IIIb), (IIIc), (IVa), (IVb) and (IVc) according to claim 1, and
- (c) at least one compound selected from the group consisting of the amine compounds.

The present invention also pertains to a composition, stabilized against the formation of aldehydic contaminants during melt processing of said composition, which comprises

- (a) a polyester or polyamide, and
- (b) an effective stabilizing amount of at least one compound selected from the group consisting of the thermal products of the Mannich base compounds of formulae (Ia), (Ib), (IIa), (IIb), (IIc), (IIIa), (IIIb), (IIIc), (IVa), (IVb) and (IVc) according to claim 1, and
- (c) at least one compound selected from the group consisting of the amine compounds.

The amine compounds are for example the corresponding amines of the Mannich base compounds of formulae (Ia)-(IVc) according to this invention. That is, the amino substituents of R_{50} whose open valence is satisfied with a hydrogen atom. For example dialkylamines, piperidine, dipiperidine, morpholine, etc.

It has been discovered that certain pigments and/or dyes or other colorants, in the compositions of this invention, prevent yellowing of the stabilized polyester or polyamide compositions.

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Accordingly, the present invention also pertains to a composition, stabilized against the formation of aldehydic contaminants and against yellowing during melt processing of said composition, which comprises

- (a) a polyester or polyamide, and
- (b) an effective stabilizing amount of at least one compound selected from the group consisting of the Mannich base compounds of formulae (Ia), (Ib), (IIa), (IIb), (IIc), (IIIa), (IIIb), (IIIc), (IVa), (IVb) and (IVc) according to claim 1, and
- (c) one or more colorants selected from the group consisting of pigments and dyes.

Suitable pigments or dyes are organic or inorganic. For example cobalt salts, ultramarine blue, polymer soluble blue dyestuffs, and copper phthalocyanine blue are suitable. Cobalt salts are for example cobalt aluminate, cobalt acetate, cobalt stearate and cobalt octoate. Suitable pigments are for example red, blue or violet organic pigments. For example, organic pigments of the Diketo pyrrolo pyrrole, quinacridone, azo condensation, anthraquinone, perinone, chrome complex, benzimidazolone, aminoanthraquinone, naphthol, indanthrone, carbazole dioxazine and perylene classes are suitable. Suitable pigments and dyes include Ciba Cromophtal™ Violet B and Violet GT (of the dioxazine class), Pigment Violet 23 and 37, Disperse Violet 57, Solvent Violet 13, Ciba Oracet™ Violet TR, Ciba Oracet™ Violet B, and Bayer Macrolex™ Violet B Gran (of the anthraquinone dye class), PV-19, Cromophtal Violet R RT-891-D, Cromophtal Red 2020, Monastral Red Y RT-759, Monastral Red B RT-790-D, PR-202, Monastral Magenta RT-235-D, and Monastral Red B RT195-D all of the quinacridone pigment class. SV-46, Filamid Violet RB (1:2 chrome complex dyes), and SB-132, Filamid Blue R (anthraquinone) are also suitable. Additional colorants include, PR-177, Cromophtal Red A3B (anthraquinone), PR-264, Irgazin DPP Rubine TR (diketo pyrrolo pyrrole), SR-135, Oracet Red G (perinone), PB 15:3, Cromophtal™ Blue 4GNP, Cromophtal Blue LGLD, PB 15:1, Irgalite Blue BSP, PB-60, Cromophtal Blue A3R (indanthrone), SB-67, and Ciba Oracet™ Blue G.

The present invention pertains also to a fiber, film or molded article stabilized against the formation of aldehydic contaminants during melt processing of said fiber, film or article, which comprises

- (a) a polyester or polyamide, and

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- (b) an effective stabilizing amount of at least one compound selected from the group consisting of the Mannich base compounds of formulae (Ia), (Ib), (IIa), (IIb), (IIc), (IIIa), (IIIb), (IIIc), (IVa), (IVb) and (IVc).

The present Mannich base additives may be advantageously added during the synthesis of a polyester or a polyamide to result in a polymer that is low in acetaldehyde formation during subsequent melt processing.

Accordingly, disclosed is a process for the preparation of a stabilized polyester or polyamide that is low in the generation of aldehydes during subsequent melt processing, which process comprises preparing the polyester or polyamide from its monomer components in the presence of an effective amount of a stabilizer selected from the group consisting of the Mannich base compounds of formulae (Ia), (Ib), (IIa), (IIb), (IIc), (IIIa), (IIIb), (IIIc), (IVa), (IVb) and (IVc).

The monomer components of the polyester and polyamide are as described herein.

Specifically, disclosed is a process for the preparation of a stabilized polyester that is low in the generation of aldehydes during subsequent melt processing, which process comprises reacting one or more diacids with one or more diols in an esterification process, and/or one or more diesters with one or more diols in a transesterification process in the presence of an effective amount of a stabilizer selected from the group consisting of the Mannich base compounds of formulae (Ia), (Ib), (IIa), (IIb), (IIc), (IIIa), (IIIb), (IIIc), (IVa), (IVb) and (IVc).

When the Mannich base additives are added during the synthesis of a polyester or polyamide, the levels of use are as before.

Another subject of the present invention is a polyester or a polyamide obtained by the process which comprises preparing the polyester or polyamide from its monomer components in the presence of an effective amount of a stabilizer selected from the group consisting of the Mannich base compounds of formulae (Ia), (Ib), (IIa), (IIb), (IIc), (IIIa), (IIIb), (IIIc), (IVa), (IVb) and (IVc).

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A preferred embodiment of the present invention is the use of component (b) for preventing the formation of aldehydic contaminants during melt processing of a polyester or a polyamide.

The following examples are for illustrative purposes only and are not to be construed to limit the scope of the instant invention in any manner whatsoever.

General - PET bottle grade pellets are subjected to extrusion compounding to simulate the heat history which PET experiences when thermally injection molded into bottle preforms and subsequently stretch-blow molded into bottles. The efficacy of an additive added to reduce the formation of acetaldehyde is determined by quantitative analysis using thermal desorption GC-MS or GC-FID after adoption of published methods. An unstabilized PET is extruded each day to provide a control polymer for measuring acetaldehyde formation.

Extrusion - PET is pre-dried in vacuo under nitrogen at an oven temperature of about 70°C to a moisture level of about 30 ppm which is verified on a Mitsubishi VA-O6 moisturemeter. A Leistritz 18 mm or 27 mm co-rotating, non-intermeshing twin screw extruder is configured as follows: set temps = throat (220-230°C), zones and die (270°C), actual extrudate melt temperature is 275-280°C, screw at 100-110 rpm, hopper feeder = 10-15 ppm.

PET Pellet Color - Yellowness Index (YI), and L*, a*, b* by ASTM D1925, D65 10degm specular included, measured on PET pellets using a DCI spectrophotometer.

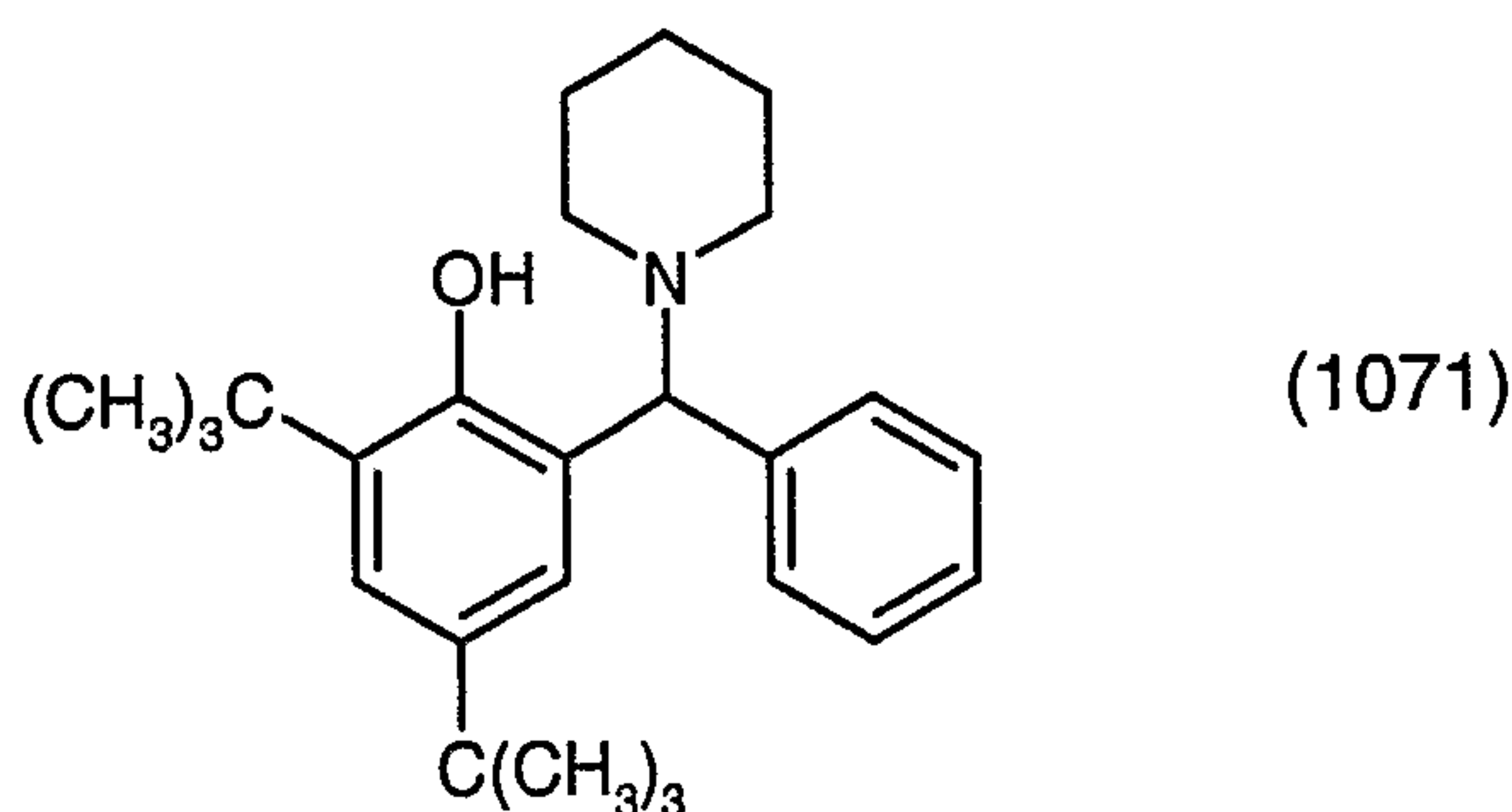
Acetaldehyde Analysis - The concentration of acetaldehyde in PET is quantitatively determined using a thermal desorption GC-FID method adapted from B. Nijassen et al., *Packaging Technology and Science*, 9, 175 (1996); S. Yong Lee, *SPE ANTEC* 1997, pp 857-861; and M. Dong et al., *J. Chromatographic Science*, 18, 242 (1980). A general example follows below:

The PET samples are analyzed, typically in triplicate, by weighing 500 mg of powdered PET pellets (obtained by cryogenically pulverizing ~ 20 grams of the PET) in a 5 ml crimp sealed headspace vial. The sample vial is heated at 120°C for one hour in a Tekmar model 7000 static headspace analyzer. The headspace gas (5 ml) is then transferred via a heated transfer line to a Varian 3600 GC-FID system for quantification of the acetaldehyde (AA). By using

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a known acetaldehyde value for PET, the ratio of peak areas for the known PET resin and for the experimental PET resin blends are compared and the amount of acetaldehyde in the experimental blend can be obtained.

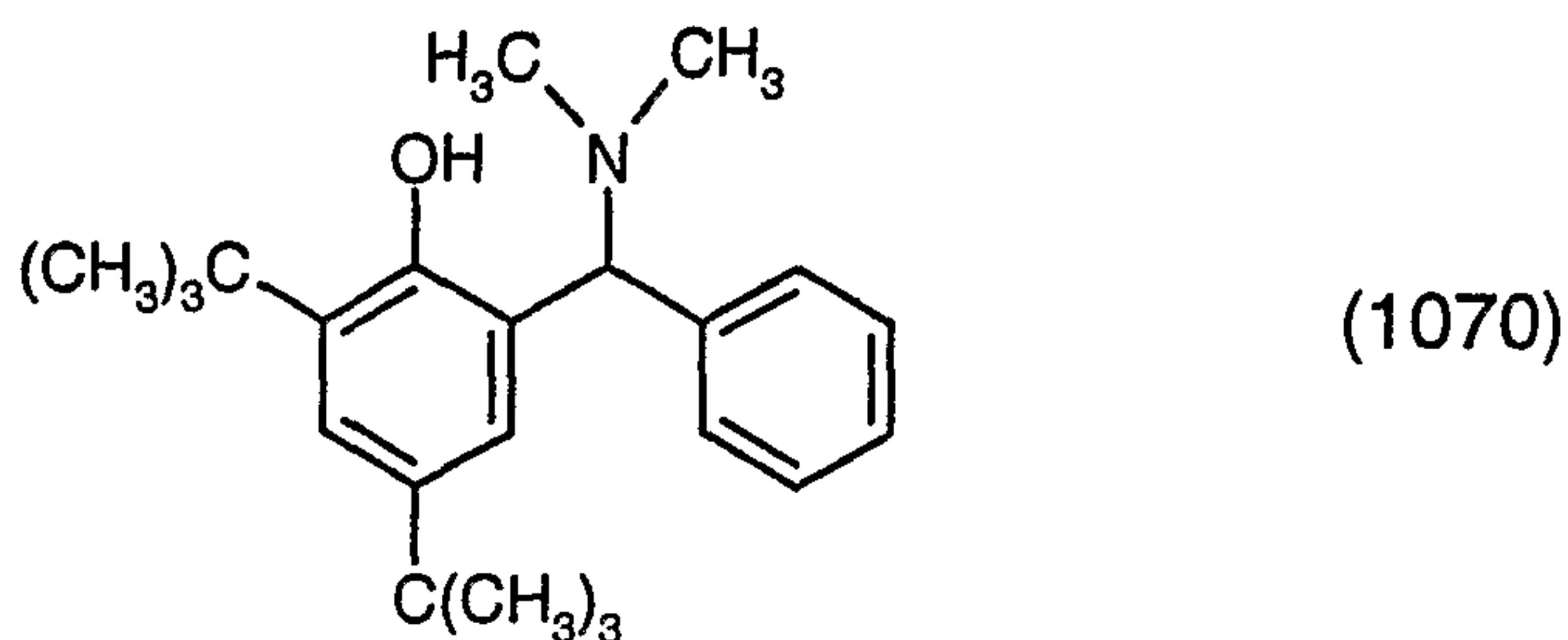
Example A: Preparation of 2,4-di-tert-butyl-6-(phenyl-piperidin-1-yl-methyl)-phenol (1071).



A solution of 255.5 g (3.00 mol) of piperidine in toluene (250 ml) is added dropwise during a time of 5 minutes, at room temperature, to a solution of 278.6 g (2.63 mol) of benzaldehyde in 500 ml of toluene. An exothermicity to 40°C is observed. The slightly yellow-colored solution is boiled under reflux for 1 hour; approximately 34 ml of water are separated using a water separator, and a solution of 515.8 g (2.50 mol) of 2,4-di-tert-butylphenol in 500 ml of toluene is then added dropwise over a period of 45 minutes. The reaction mixture is boiled at reflux for a further hour and then cooled to room temperature. Hexane is added and the mixture is cooled to 0°C whereas the product precipitates. The solid material is filtered and washed with cold hexane to yield 814 g (85 %) of the title compound as a white solid, m.p. 140-141°C. Molecular weight C₂₆H₃₇NO (379.588). Analysis, calculated: C 82.27; H 9.82; N 3.69 %. Analysis, found: C 82.06; H 9.83; N 3.77 %. ¹HNMR (300 MHz, CDCl₃, ppm): 1.24 (s, 9H); 1.50 (s, 11H); 1.66 (bs, 4H); 2.39 (bs, 4H); 4.48 (s, 1H); 6.79 (d, 1H); 7.32 (m, 6H); 12.60 (s, 1H).

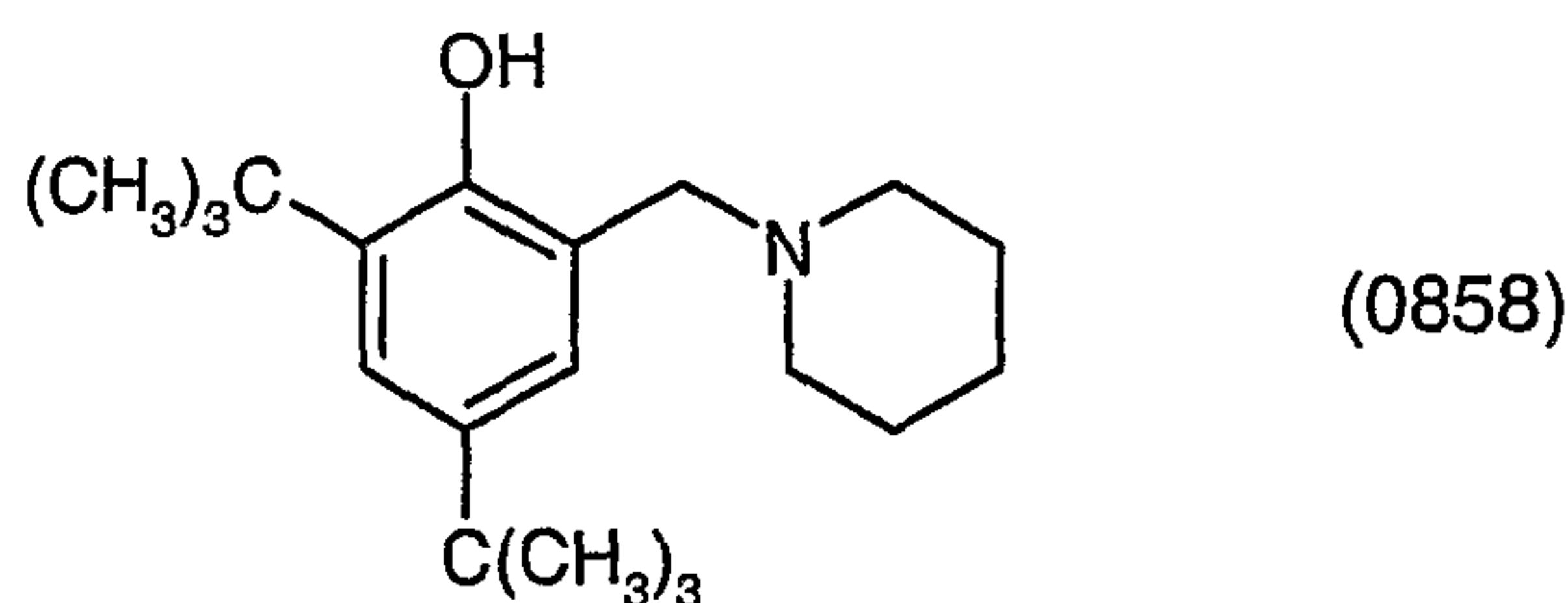
Example B: Preparation of 2,4-di-tert-butyl-6-(dimethylamino-phenyl-methyl)-phenol (1070).

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A mixture of 51.5 g (0.25 mol) of 2,4-di-tert-butylphenol, 26.5 g (0.25 mol) of benzaldehyde and 42.3 g (0.375 mol) of a 40 % aqueous solution of dimethylamine is heated in a closed vessel at 140°C (oilbath) for 10 hours, the internal pressure rising to 5 bar. After cooling to room temperature, the reaction mixture solidifies. Crystallization of the residue from isopropanol yields 65.2 g (77 %) of the title compound as a white solid, m.p. 120-123°C. Molecular weight $C_{23}H_{33}NO$ (339.52). Analysis, calculated: C 81.37; H 9.80; N 4.13 %. Analysis, found: C 81.25; H 9.86; N 4.00 %. ^1H NMR (300 MHz, $CDCl_3$, ppm): 1.19 (s, 9H); 1.44 (s, 9H); 2.26 (s, 6H); 4.34 (s, 1H); 6.75 (d, 1H); 7.29 (m, 6H); 12.43 (s, 1H).

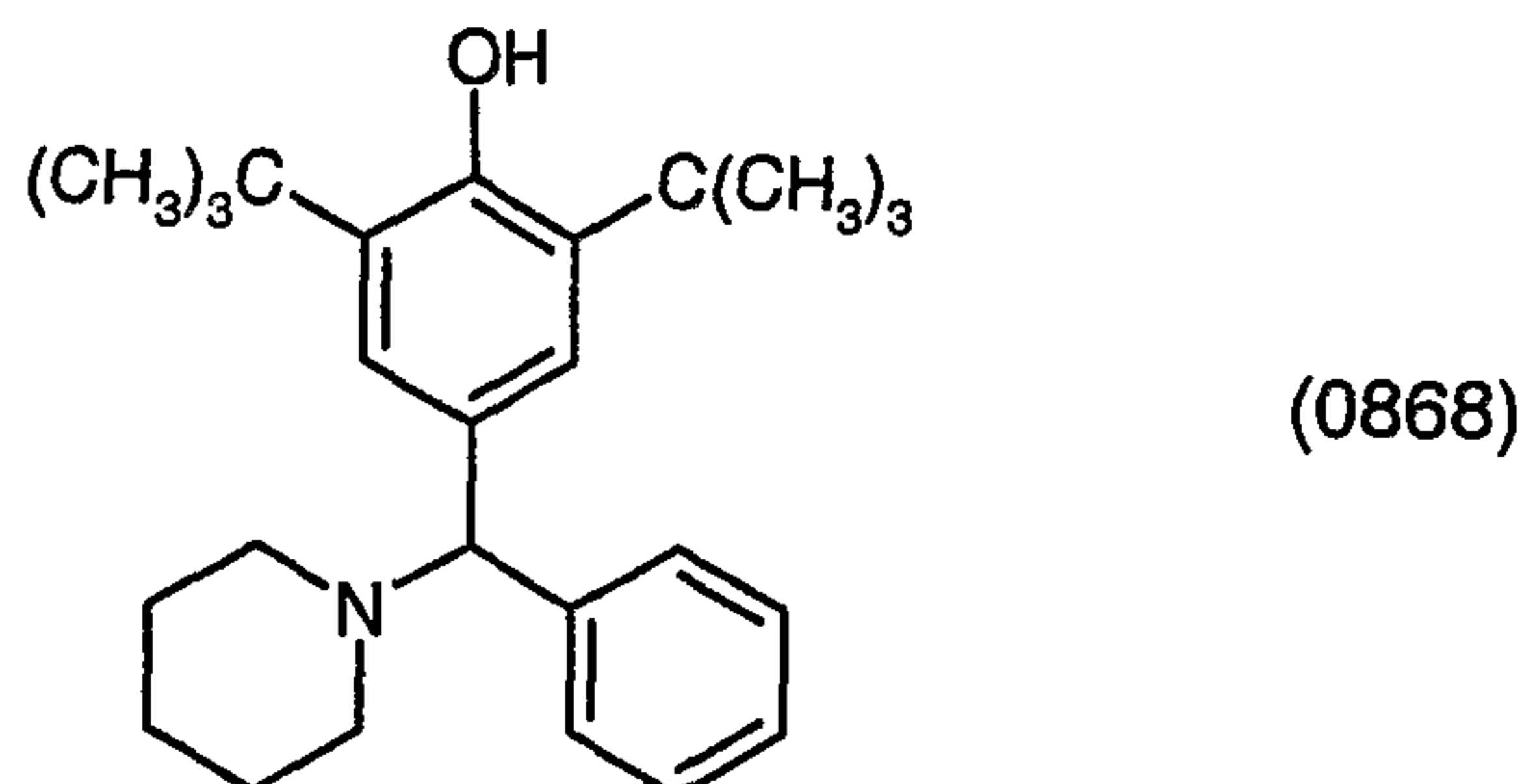
Example C: Preparation of 2,4-di-tert-butyl-6-piperidin-1-ylmethyl-phenol (0858).



2,4-Di-tert.-butylphenol (70 g, 0.34 mol), piperidine (70 ml, 0.714 mol), a formaldehyde solution (35% in water) (27 ml, 0.34 mol) and ethanol (1 liter) are added to a flask. The resulting yellow solution is stirred under reflux for 6 h. The solvent is evaporated *in vacuo* whereas a red crystalline solid is formed. Hexane is added to the residue and the resulting white crystals are filtered. The mother liquor is concentrated and the residue treated with 2-propanol to afford a total yield 56 g (54 %) of the title compound as a white solid. Molecular weight $C_{20}H_{33}NO$ (303.49). ^1H NMR (400 MHz, $CDCl_3$, ppm): 1.2 (s, 9H); 1.32 (s, 9H); 1.55 (s, 5H); 2.1-2.7 (m, 5H); 3.55 (s, 2H); 6.71 (1H); 7.1 (s, 1H); >7.2 (s, 1H).

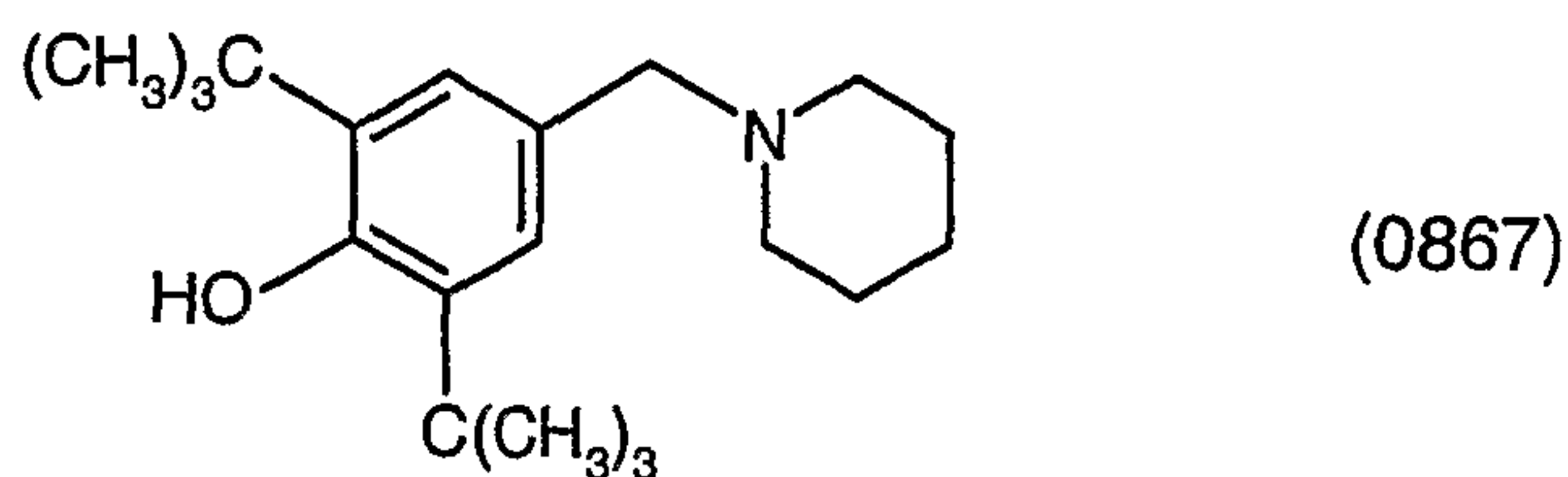
Example D: Preparation of 2,6-di-tert-butyl-4-(phenyl-piperidin-1-yl-methyl)-phenol (0868).

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2,6-Di-tert-butylphenol (70 g, 0.34 mol), piperidine (70 ml, 0.714 mol), benzaldehyde (38 ml, 0.374 mol) and ethanol (1 liter) are added to a flask. The pale yellow solution is stirred under reflux for 14 h. The mixture is cooled to room temperature, whereas white crystals precipitate that are collected. The mother liquor is concentrated, whereas further crystals are formed. The solid materials are combined and washed with cold ethanol to yield 86 g (67 %) of the title compound as a pale yellow solid. Molecular weight $C_{26}H_{37}NO$ (379,59). ^1H NMR (400 MHz, $CDCl_3$, ppm): 1.3 (s, 18H); 1.4-1.55 (m, 5H); 2.2 (s, 5H); 4.08 (s, 1H); 4.92 (s, 1H); 7.0 -7.3 (m, 7H).

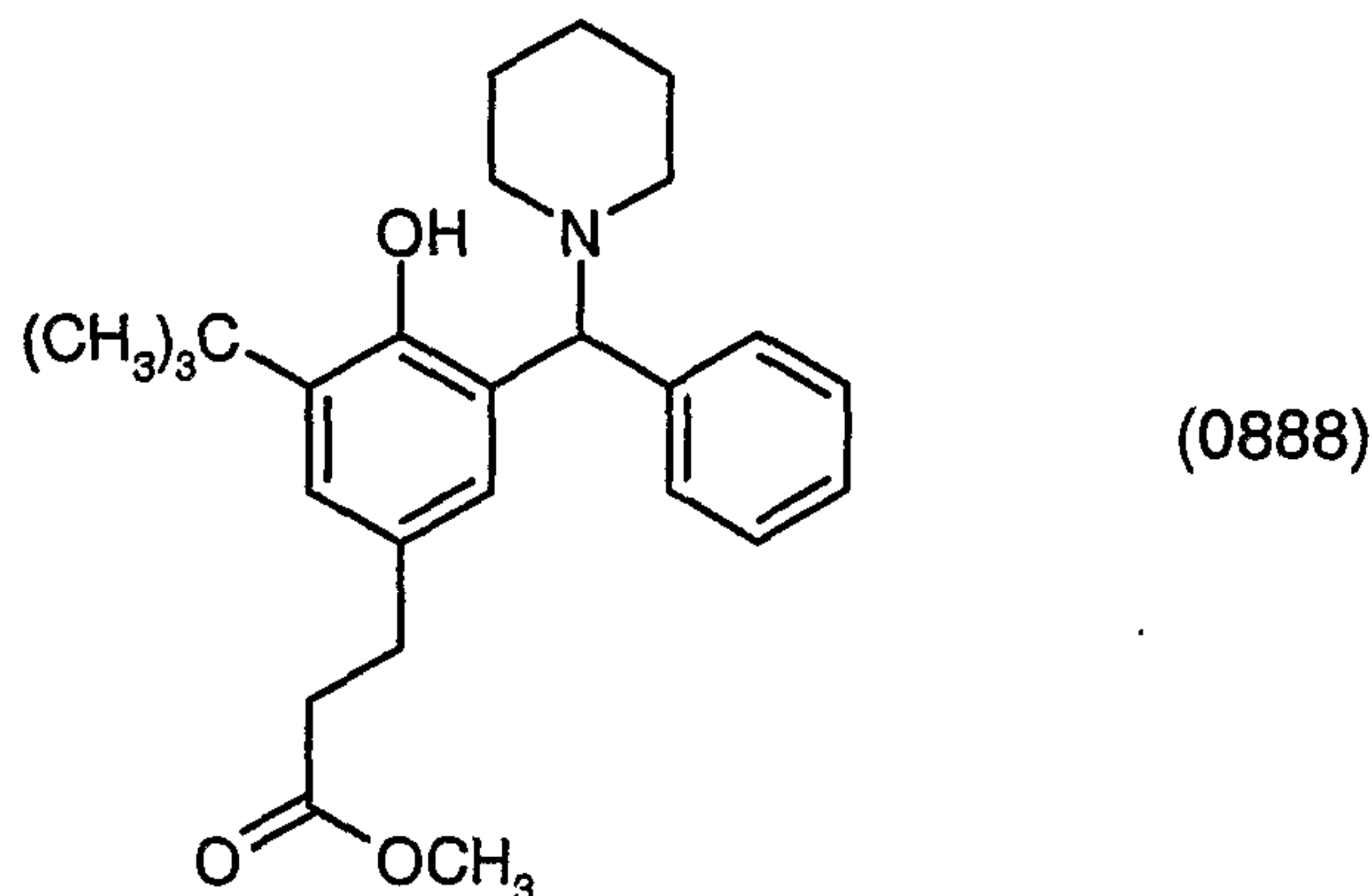
Example E: Preparation of 2,6-di-tert-butyl-4-piperidin-1-yl-methyl-phenol (0867).



2,6-Di-tert-butylphenol (70 g, 0.34 mol), piperidine (70 ml, 0.714 mol), a formaldehyde solution (35% in water) (27 ml, 0.34 mol) and ethanol (1 L) are added to a flask. The slightly yellow-coloured solution is stirred under reflux for 5 hours. The reaction mixture is concentrated *in vacuo*. The resulting red oil is purified by chromatography (SiO_2 , hexane/ethylacetate = 1:9) to yield 84 g (80 %) of the title compound as a white solid. Molecular weight $C_{20}H_{33}NO$ (303.49). ^1H NMR (400 MHz, $CDCl_3$, ppm): 1.5 (s, 18H); 1.6 (m, 5H); 2.5 (s, 5H); 3.45 (s, 2H); 5.62 (s, 1H); 7.1 (s, 2H).

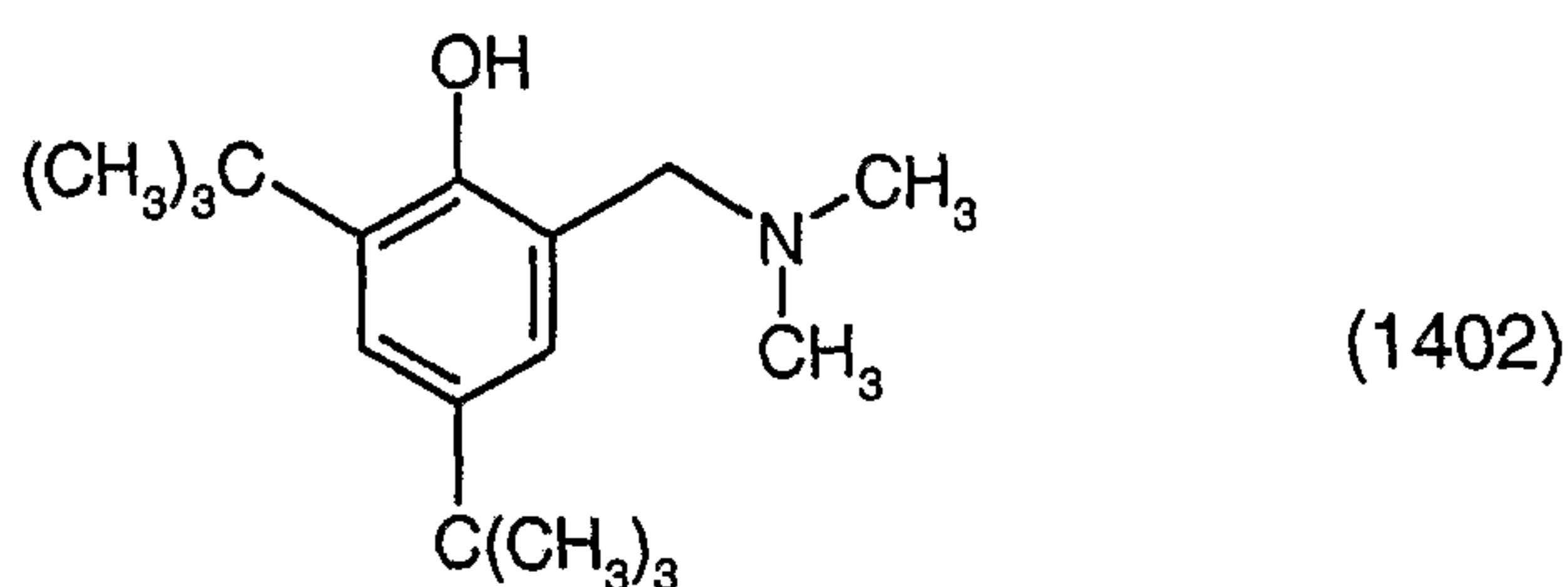
Example F: Preparation of 3-[3-tert-butyl-4-hydroxy-5-(phenyl-piperidin-1-yl-methyl)-phenyl]-propionic acid methyl ester (0888).

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A solution of piperidine (60ml, 0.63 mol) in toluene (250 ml) is added dropwise at room temperature during a time of 5 minutes to a solution of benzaldehyde (36ml, 0.36 mol) in 500 ml of toluene. An exothermicity to 40°C is observed. The pale yellow solution is stirred under reflux for 2.5 hours; whereas approximately 8.5 ml of water separated in a water separator. A solution of 3-(3-tert-butyl-4-hydroxy-phenyl)-propionic acid methyl ester (70 g, 0.3 mol) in toluene (500 ml) is then added dropwise over a period of 20 minutes. The reaction mixture is stirred at reflux for 14 hours and then cooled to room temperature. The mixture is concentrated *in vacuo*, and hexane is added to the residual red oil. The solid material is filtered and washed with cold hexane to yield 78 g (63 %) of the title compound as a white solid. Molecular weight $C_{26}H_{35}NO_3$ (409,57). ^1H NMR (400 MHz, $CDCl_3$, ppm): 1.3-1.4 (s, 9H); 2.3-2.5 (t, 2H); 2.6-2.7 (t, 2H); 3.5 (s, 3H); 4.4 (s, 1H); 6.5-7.4 (m, 7H).

Example G: Preparation of 2,4-di-tert-butyl-6-dimethylaminomethyl-phenol (1402).

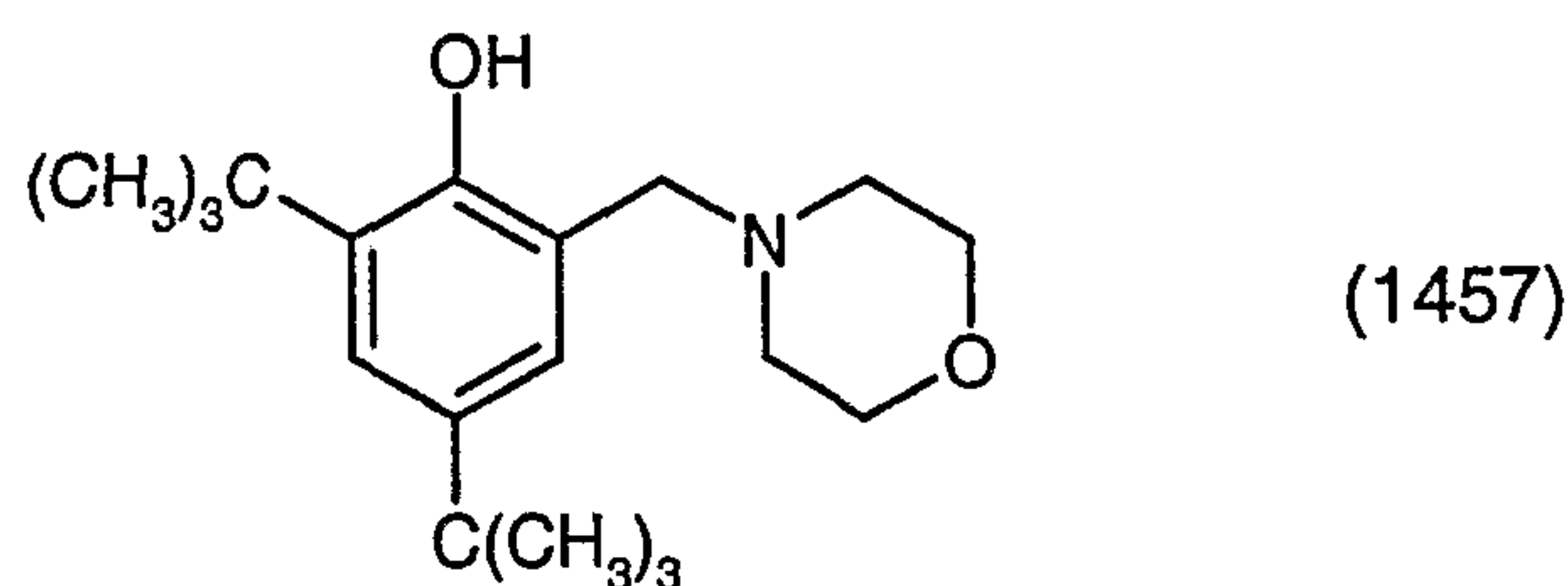


A mixture of 1.5 l ethanol, 300 g (1.5 mol) of 2,4-di-tert-butylphenol, 193 g (2.25 mol) of aqueous formaldehyde (35%) and 253 g (2.25 mol) of aqueous dimethylamine (40 %) is stirred for 2 days at room temperature. The product crystallizes slowly as the reaction proceeds and is eventually filtered-off to afford 250 g (0.95 mol) of the title compound as a white solid; m.p. 54 - 56 °C. After partial removal of the residual ethanol in *vacuo*, another 40 g of

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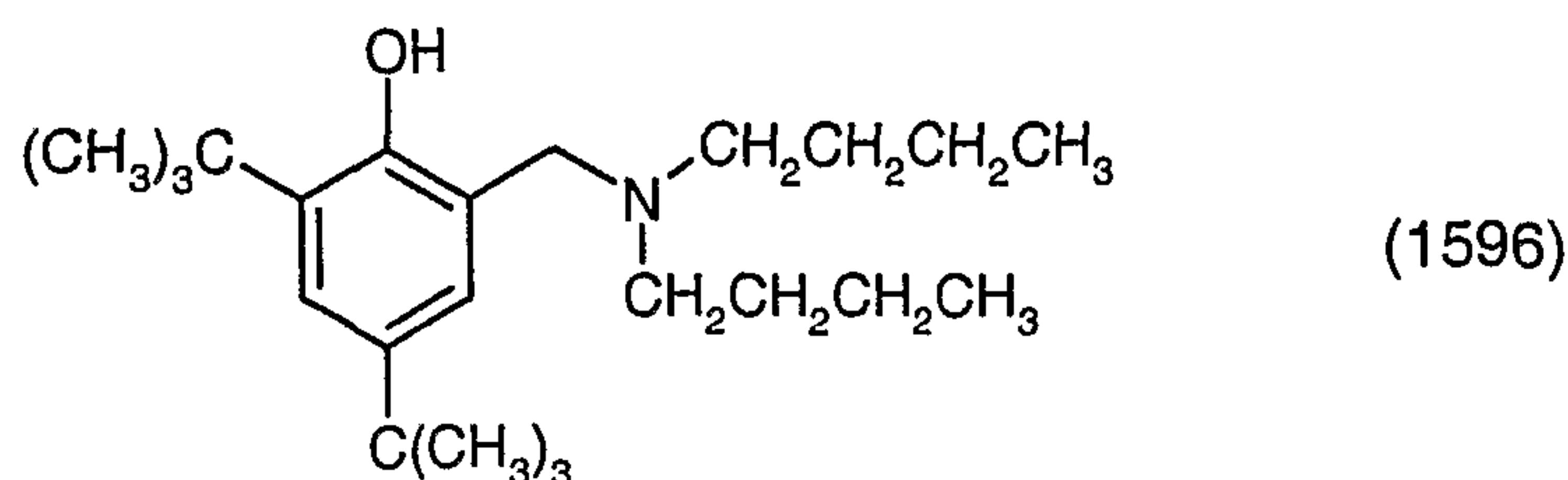
the title compound can be isolated from the filtrate. Total yield: 290 g (1.1 mol), molecular weight 263.43 ($C_{17}H_{29}NO$). ^1H -NMR (400 MHz, $CDCl_3$, ppm): 1.35 (s, 9H); 1.48 (s, 9H); 2.38 (s, 6H); 3.65 (s, 2H); 6.88 (s, 1H); 7.18 (s, 1H); >10 (broad s, -OH).

Example H: Preparation of 2,4-di-tert-butyl-6-N-morpholino-4-ylmethyl-phenol (1457).



A mixture of 700 ml of toluene, 46.2 g (0.539 mol) of aqueous formaldehyde (35%) and 47 g (0.539 mol) of morpholine is refluxed at a water separator for approximately 2 hours, until the water separation is complete. Then, a solution of 100 g (0.49 mol) 2,4-di-tert-butylphenol in 300 ml of toluene is slowly added under these conditions, which are maintained for approximately 16 hours. After cooling to room temperature, the solvent is removed in vacuo, and the obtained yellowish, oily residue dispersed in 200 ml of iso-propanol. The product crystallizes during cooling with methanol/dry-ice and is filtered-off to afford 85 g (0.323 mol) of the title compound as a white solid. M.p. 108 - 109 °C, molecular weight 305.46 ($C_{19}H_{31}NO_2$). ^1H -NMR (400 MHz, $CDCl_3$, ppm): 1.25 (s, 9H); 1.4 (s, 9H); 2.5 (m, 4H); 3.6 (s, 2H); 3.7 (m, 4H); 6.8 (s, 1H); 7.2 (s, 1H); >10 (broad s, -OH).

Example I: Preparation of 2,4-di-tert-butyl-6-di-n-butylaminomethyl-phenol (1596).

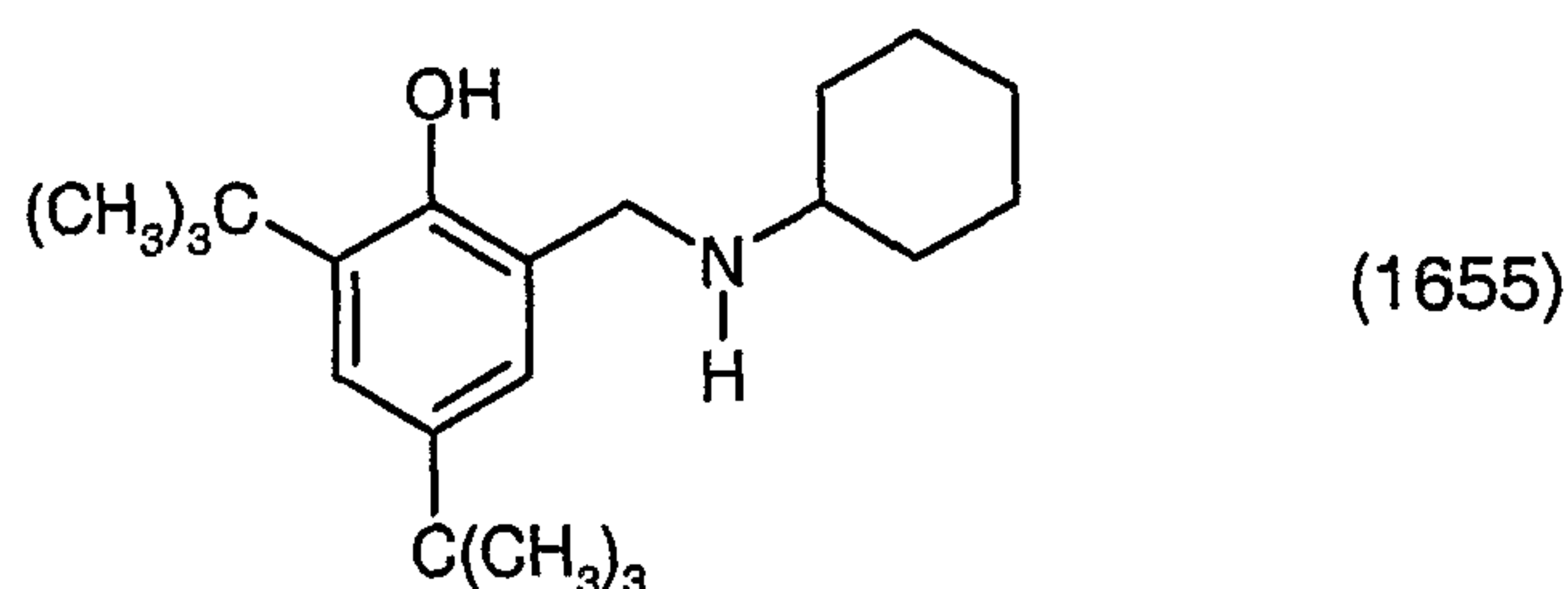


To a solution of 39.5 g (0.31 mol) of di-n-butylamine and 60 g (0.29 mol) of 2,4-di-tert-butylphenol in 150 ml of ethanol, 26.1 g (0.31 mol) of aqueous formaldehyde (35%) are added within 10 minutes, then stirred at 50°C for 2 days. After cooling to room temperature, two phases are formed (upper ethanol-water phase over the product layer). Addition of some ml

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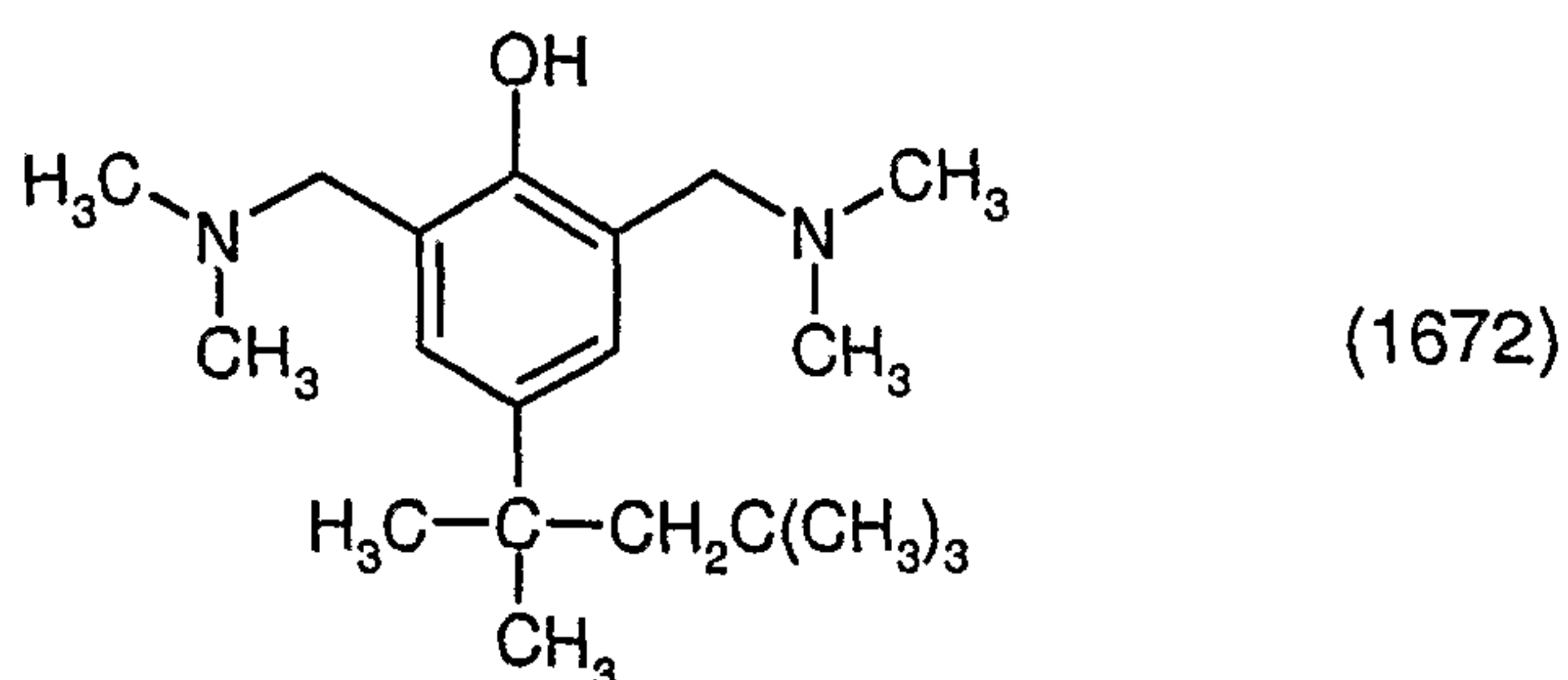
of n-hexane facilitates the phase separation. The lower product phase is dried over Na_2SO_4 , filtered and the solvent removed in vacuo to yield 88 g (0.25 mol) of the title compound as slightly yellowish oil, which solidifies upon standing over several days to form colorless crystals of the product with m.p. $33 - 35\text{ }^\circ\text{C}$; molecular weight $\text{C}_{23}\text{H}_{41}\text{NO}$ (347.59). $^1\text{H-NMR}$ (400 MHz, CDCl_3 , range 0 -10 ppm): 0.7 - 0.9 (t, 6H), 1.28 (s, 9H), 1.28 - 1.32 (m, 4H), 1.4 (s, 9H), 1.45 - 1.55 (m, 4H), 2.43 - 2.49 (t, 4H), 3.7 (s, 2H), 6.8 (s, 1H), 7.18 (s, 1H) ; >10 (broad s, -OH).

Example J: Preparation of 2,4-di-tert-butyl-6-cyclohexylaminomethyl-phenol (1655).



120 g (0.46 mol) of 2,4-di-tert-butyl-6-dimethylaminomethyl-phenol in 150 ml of cyclohexylamine are heated to 140°C for 16 hours; the dimethylamine formed is allowed to evaporate. After removal of all volatiles in vacuo, the remaining yellow oil is dispersed in approximately 200 ml of iso-propanol. During cooling to about $-25\text{ }^\circ\text{C}$, the product crystallizes and is filtered-off to yield 70 g (0.22 mol) of the title compound as a white powder. M.p. $67 - 70\text{ }^\circ\text{C}$, molecular weight 317.52 ($\text{C}_{21}\text{H}_{35}\text{NO}$). $^1\text{H-NMR}$ (400 MHz, CDCl_3 , range 0 -10 ppm): 1.16 (m, 2H); 1.23 (m, 3H); 1.28 (s, 9H); 1.4 (s, 9H); 1.61 (m, 1H); 1.75 (m, 2H); 1.97 (m, 2H); 2.56 (m, 1H); 3.97 (s, 2H), 6.88 (s, 1H); 7.21 (s, 1H) ; >10 (broad s, -OH).

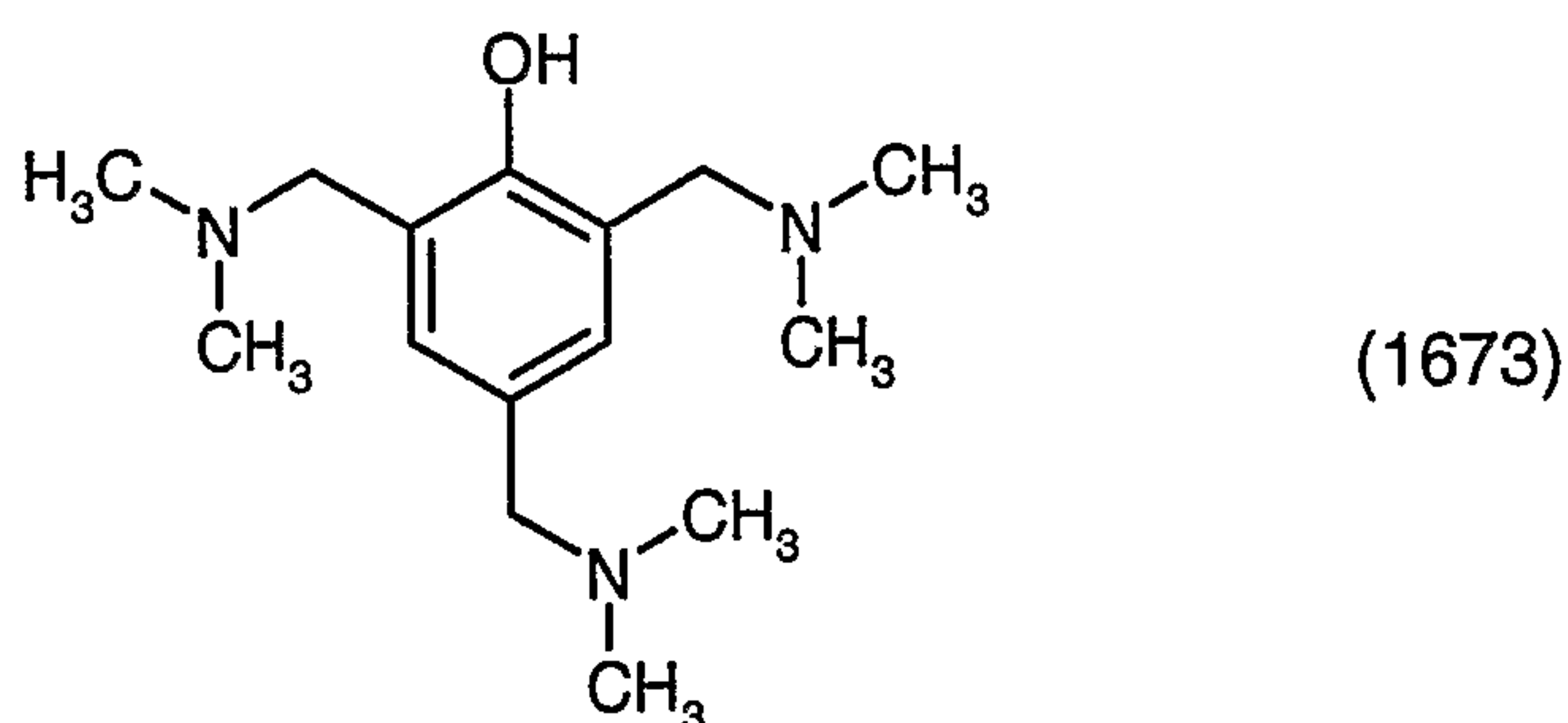
Example K: Preparation of 2,6-bis-dimethylaminomethyl-4-(1,1,3,3-tetramethyl-butyl)-phenol (1672).



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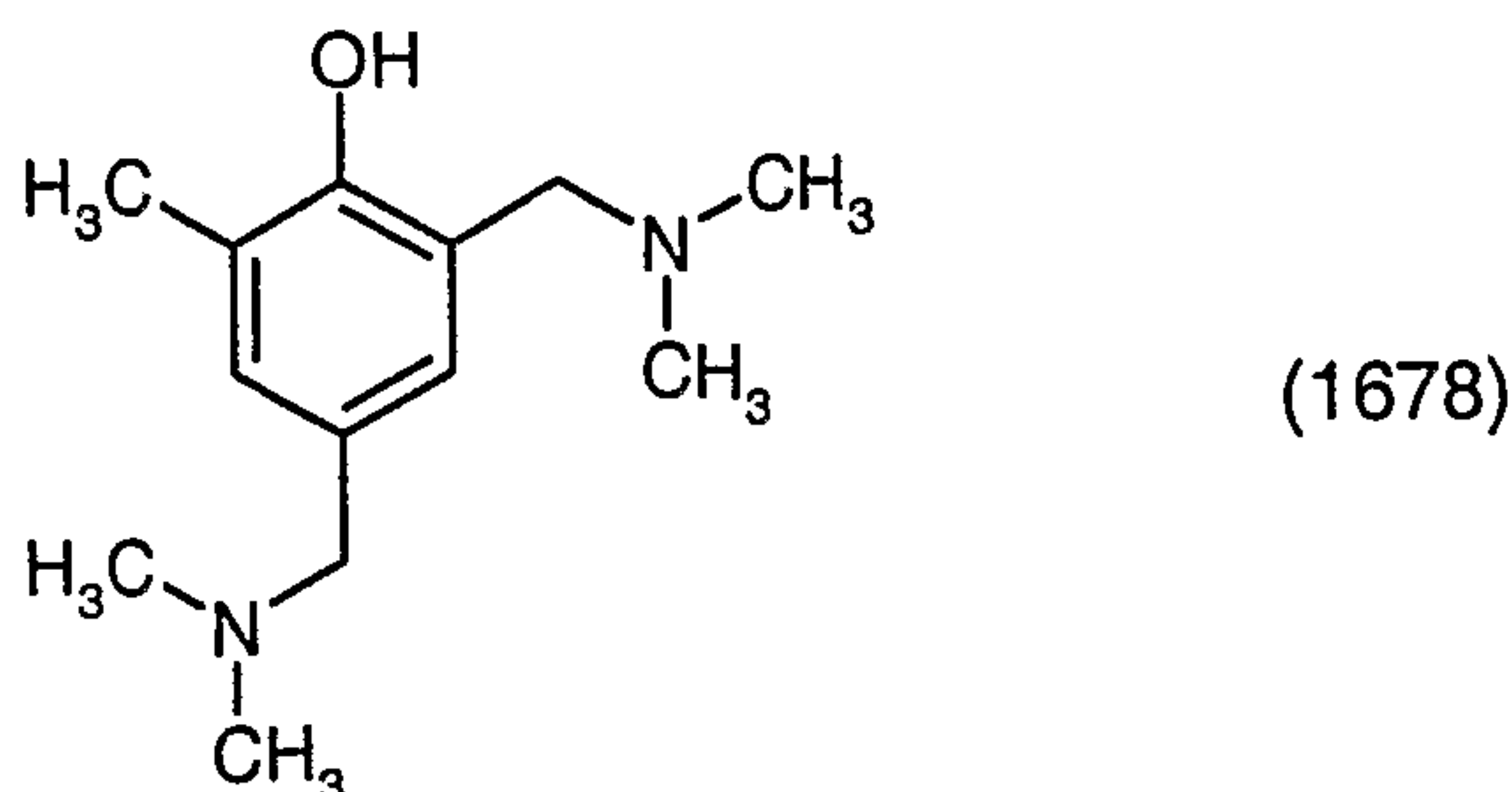
87.5 g (1.02 mol) of aqueous formaldehyde (35 %) is added to solution of 100 g (0.486 mol) of 4-tert-octylphenol in 450 ml of ethanol. During the subsequent, slow addition of 114.8 g (1.02 mol) of aqueous dimethylamine (40%), the temperature rises from 25 to 37 °C. The colorless solution is then heated to reflux for 5 to 7 hours. After removal of approximately 300 ml of the solvent in vacuo, two liquid phases are formed. The phase separation is improved by addition of about 300 ml of n-hexane so that the lower product phase can be easily separated from the upper ethanol-water layer. The product solution is then dried over Na₂SO₄, filtered and remaining solvent removed in vacuo to afford 134 g (0.42 mol) of the title compound as a slightly yellowish oil; molecular weight 320.52 (C₂₀H₃₆N₂O). ¹H-NMR (400 MHz, CDCl₃, range 0 -10 ppm): 0.67 (s, 9H), 1.26 (s, 6H), 1.65 (s, 2H), 2.25 (s, 12H), 3.5 (s, 4H), 6.96 (s, 2H) ; >10 (broad s, -OH).

Example L: 2,4,6-tris-dimethylaminomethyl-phenol (1673).



2,4,6-tris-dimethylaminomethyl-phenol (1673) is available for example from Aldrich Chemical Company Inc.: Molecular weight 265.40 (C₁₅H₂₇N₃O); ¹H-NMR (400 MHz, CDCl₃, ppm): 2.18 (s, 6H); 2.25 (s, 12H); 3.26 (s, 2H); 3.49 (s, 4H); 6.91 (s, 2H); >10 (broad s, -OH).

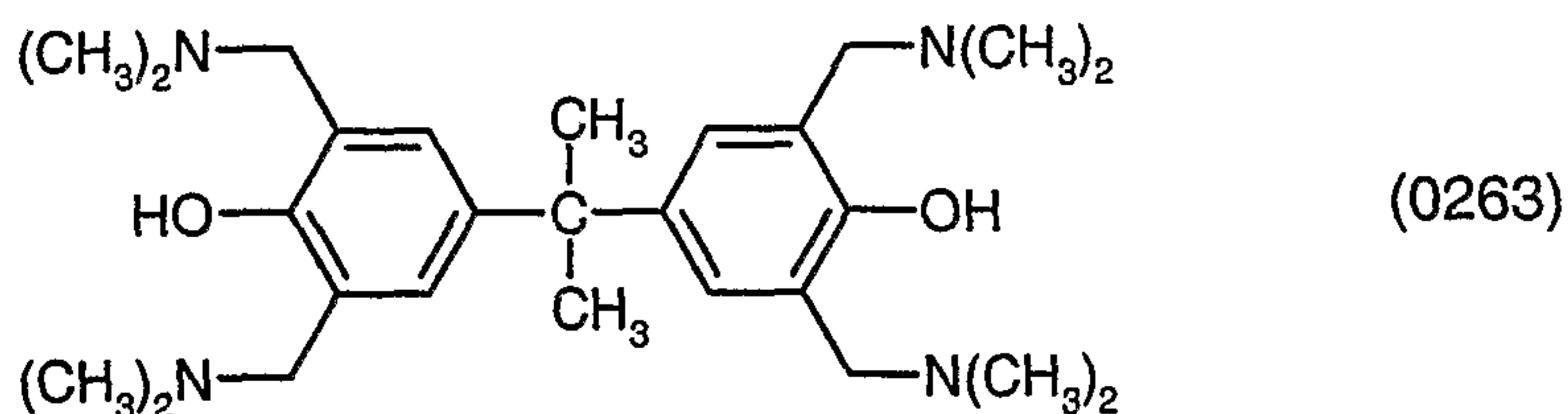
Example M: Preparation of 2,4-bis-dimethylaminomethyl-6-methyl-phenol (1678).



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A solution of 49.2 g (0.46 mol) of o-cresol and 500 ml of ethanol is slowly mixed with 109 g (1.27 mol) of aqueous formaldehyde (35 %). During the subsequent addition of 133.5 g (1.19 mol) of aqueous dimethylamine (40 %), the temperature increases from 24 °C to 33 °C. The homogeneous reaction mixture is then heated to reflux for 3.5 hours. After cooling to room temperature, approximately 300 ml of the solvent is removed in vacuo and two liquid phases are formed. The phase separation is facilitated by addition of about 200 ml of n-hexane so that the lower product phase can be easily separated from the upper ethanol-water layer. The product solution is then dried over Na₂SO₄, filtered and the remaining solvent removed to give 88 g (0.4 mol) of the title compound as pale yellowish oil; molecular weight 222.33 (C₁₃H₂₂N₂O). ¹H-NMR (400 MHz, CDCl₃, ppm): 2.14 (s, 6H), 2.15 (s, 3H), 2.23 (s, 6H), 3.2 (s, 2H), 3.52 (s, 2H), 6.7 (s, 1H), 6.9 (s, 1H) ; >10 (broad s, -OH).

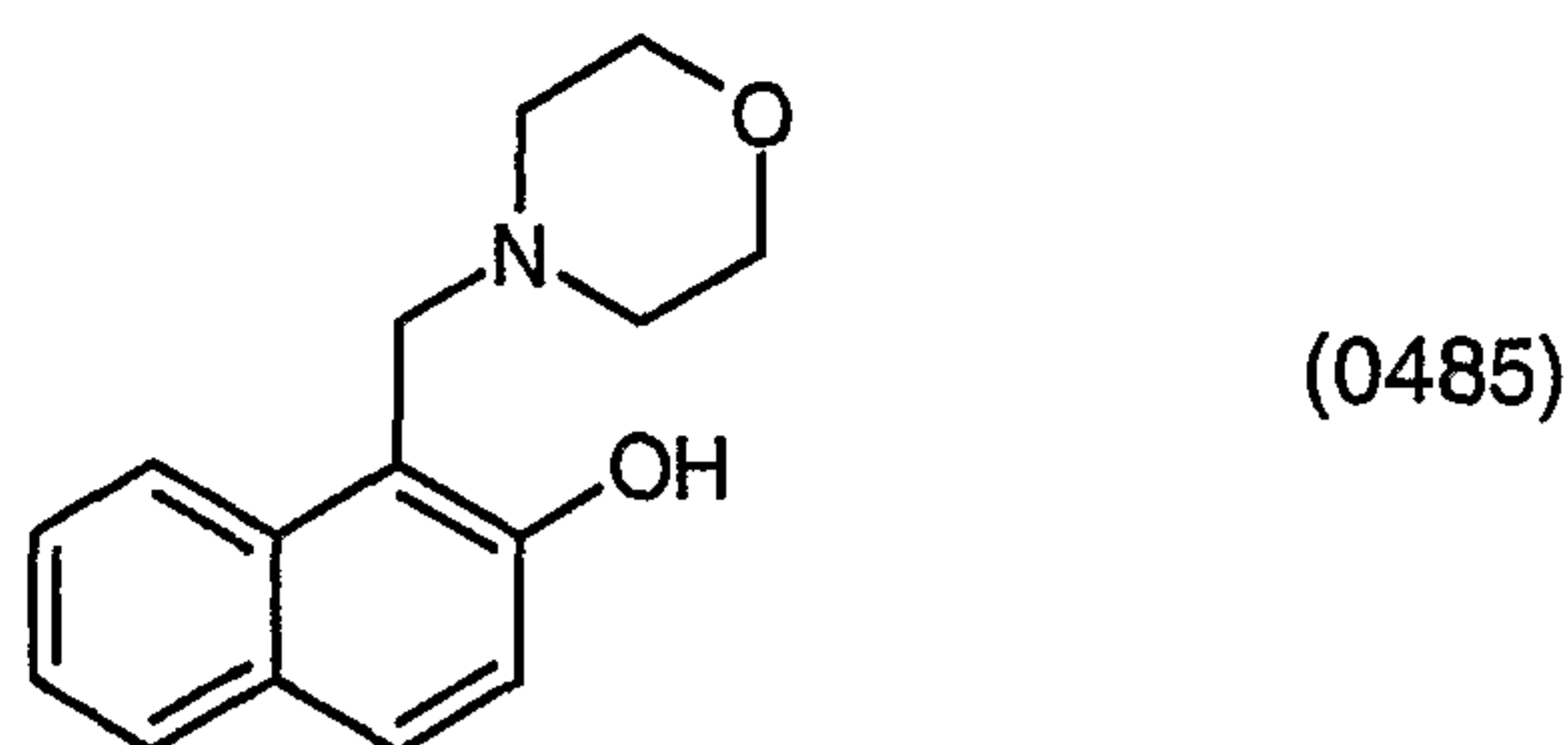
Example N: Preparation of 2,6,2',6'-Tetrakis(dimethylaminomethyl)-4,4'-isopropylidene-diphenol (0263).



95 ml (1.14 mol) of aqueous formaldehyde (35 %) is added to a solution of 60 g (0.26 mol) of bisphenol A in 130 ml of ethanol. During the subsequent, slow addition of 150 ml (1.14 mol) of aqueous dimethylamine (d = 0.89; 40 %), the temperature rises from 22°C to 60°C. The slightly yellowish solution is then heated to reflux for 15 hours. After complete removal of the ethanol in vacuo, two liquid phases are formed. The addition of 400 ml of n-hexane facilitates the phase separation, so that the upper product phase can easily be removed from the ethanol water layer. The product solution is dried over Na₂SO₄, filtered and the remaining solvent stripped-off in vacuo. The yellowish oily residue is treated again with 530 ml of n-hexane; while stirring the mixture the product crystallizes to give 60 g (0.13 mol) of the title compound as a white powder; molecular weight 456.68 (C₂₇H₄₄N₄O₂), m.p. 88 – 90°C. ¹H-NMR (400 MHz, CDCl₃, ppm): 1.61 (s, 6H), 2.26 (s, 24H), 3.48 (s, 8H), 6.83 (s, 4H), >10 (broad s, -OH).

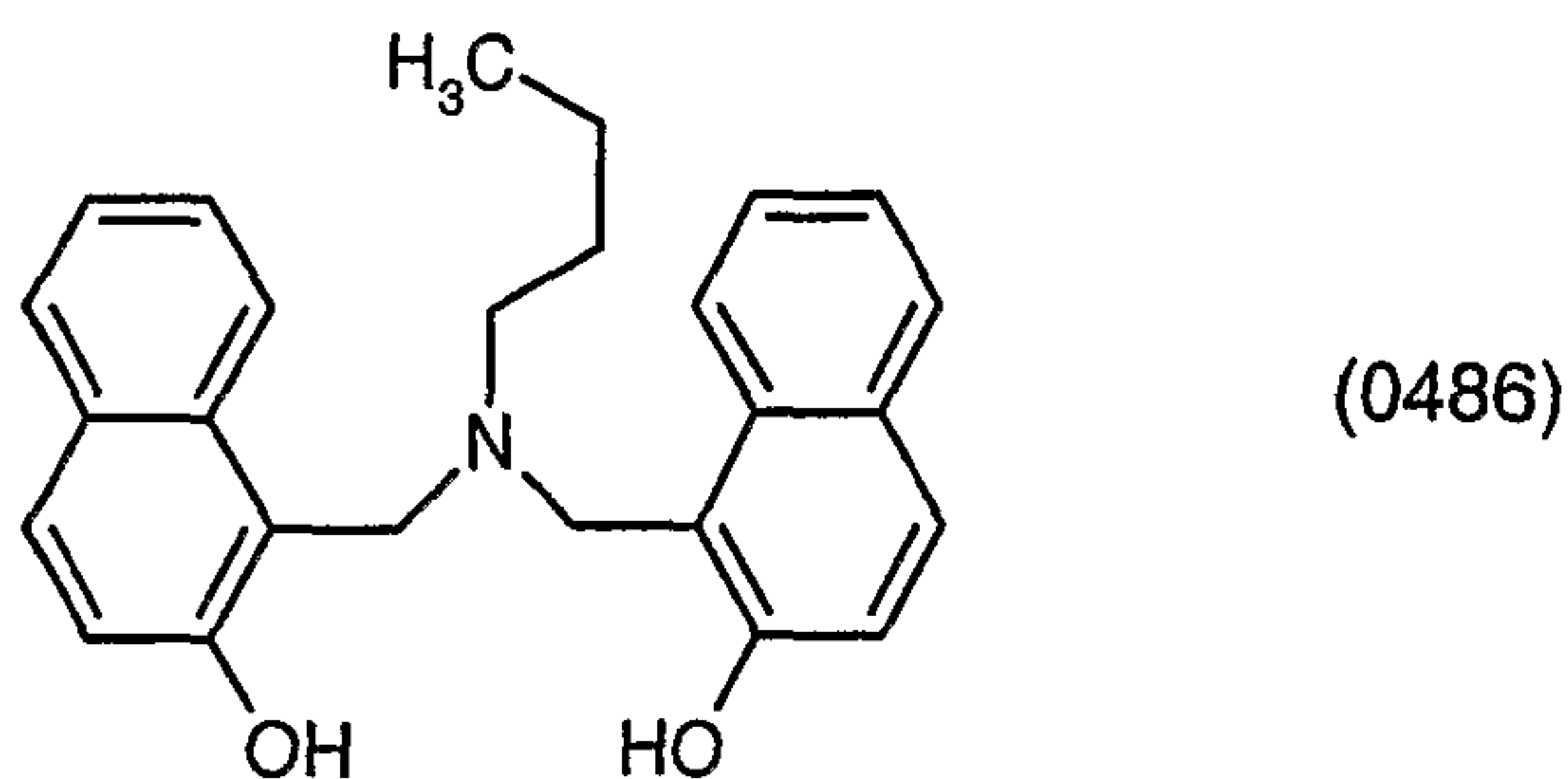
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Example O: Preparation of 1-(N-morpholino-4-yl-methyl)-2-naphthol (0485).



66 ml of aqueous formaldehyde ($d = 1.09$ g/ml; 35 %, 0.83 mol) is added to a solution of 120 g (0.83 mol) of β -naphthol in 500 ml of ethanol. During the subsequent, slow addition of 73 ml (0.83 mol) of morpholine ($d = 1.0$ g/ml) the temperature rises up to 38°C. The slightly brownish solution is then heated at 55°C for 3 hours. The product crystallizes during cooling, is filtered-off and washed with cold ethanol (raw yield: 185 g). After recrystallization from 700 ml of *n*-hexane, 177 g (0.73 mol) of the title compound is obtained as a white powder; molecular weight 243.31 ($C_{15}H_{17}NO_2$), m.p. 115 – 116°C. ^1H -NMR (400 MHz, $CDCl_3$, ppm): 2.68 (m, 4H), 3.8 (m, 4H), 4.2 (s, 2H), 7.1 – 7.85 (m, 6H), >10 (broad s, -OH).

Example P: Preparation of *n*-butyl-bis-(2-hydroxy-1-naphthylmethyl)-amine (0486).

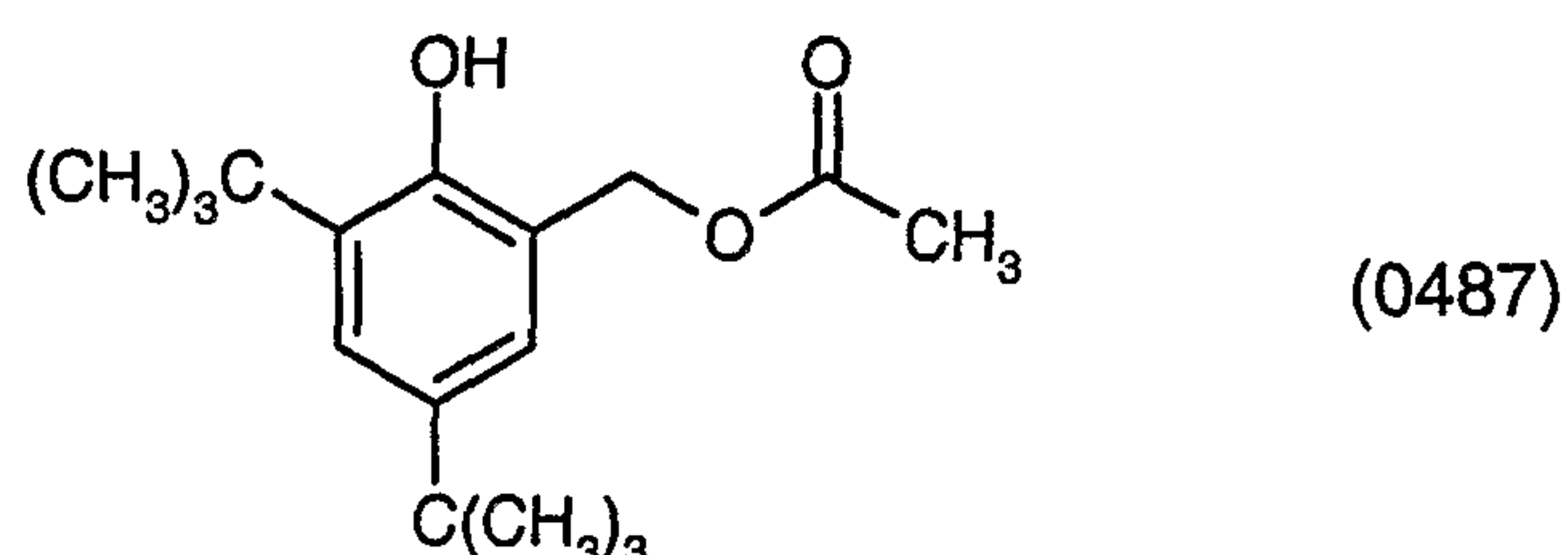


82 ml (1.04 mol) of aqueous formaldehyde ($d = 1.09$ g/ml; 35 %) is slowly added to a solution of 150 g (1.04 mol) of β -naphthol in 350 ml of methanol. During the subsequent, slow addition of 52 ml (0.52 mol) of *n*-butylamine in 350 ml of methanol the temperature rises to 32°C. Already during addition of the *n*-butylamine the product starts to crystallize slowly from the reaction mixture. The slightly brownish suspension is further stirred at room temperature for 30 hours. Afterwards the product is filtered-off, washed with 100 ml of methanol and dried [raw yield 164 g (0.42 mol)]. After recrystallization from 1400 ml of acetone/methanol = 1 : 1, 140 g (0.36 mol) of the title compound is obtained as a white powder; molecular weight

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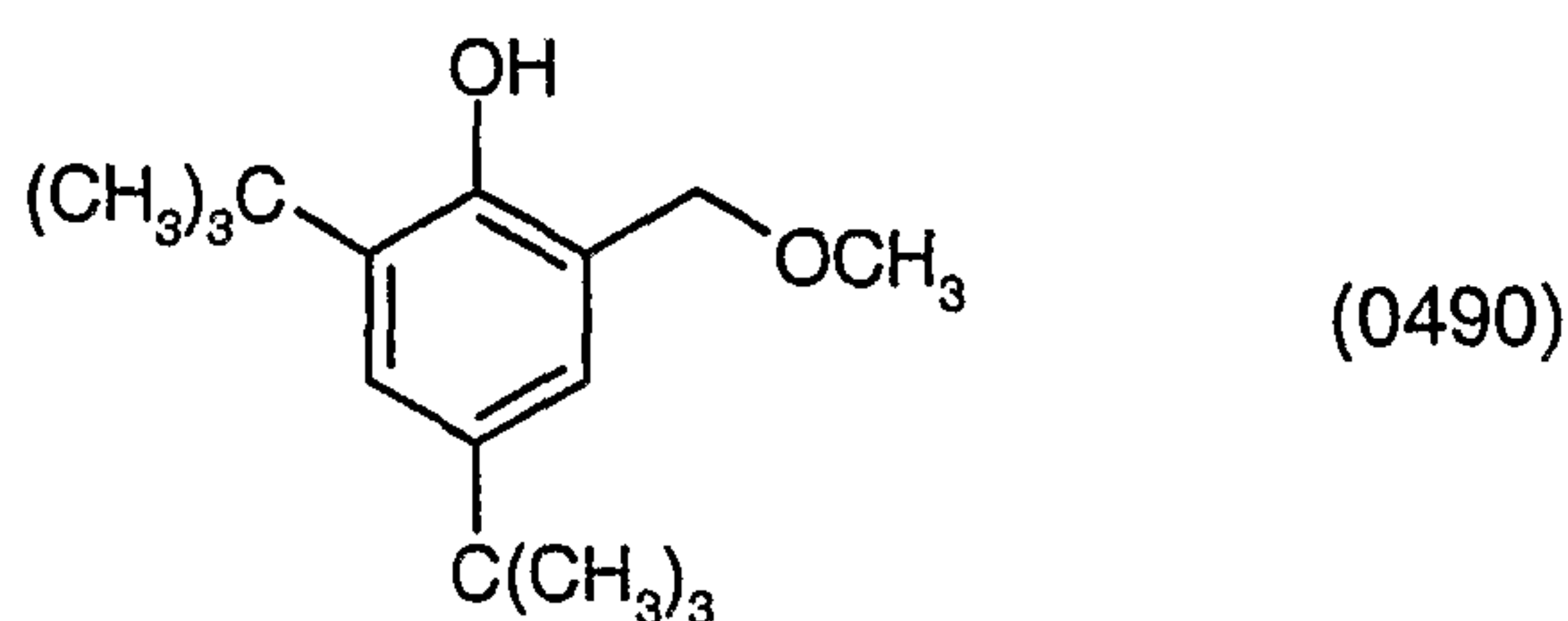
385.51 ($C_{26}H_{27}NO_2$), m.p. 130 – 131°C. ^1H -NMR (400 MHz, $CDCl_3$, ppm): 0.6 – 0.69 (t, 3H), 1.05 – 1.17 (m, 2H), 1.58 – 1.68 (m, 2H), 2.55 – 2.64 (m, 2H), 4.14 (s, 4H), 6.8 – 7.75 (m, 12H), >10 (broad s, 2H -OH).

Example Q: Preparation of 3,5-di-tert-butyl-2-hydroxy-benzyl-acetate (0487).



54.61 g (1.82 mol) of paraformaldehyde and 25 ml (0.242 mol; $d = 0.704$ g/ml) of diethylamine is added to a solution of 250 g (1.21 mol) of 2,4-di-tert-butyl phenol in 800 ml of acetic acid. The temperature increases slightly from 19 to 25°C. The mixture is heated to reflux for 40 hours. Afterwards, the excess of acetic acid is removed in vacuo, the yellow oily residue crystallizes on standing over night. The mixture is then treated with 100 ml of methanol for 2 hours, the crystals filtered-off, washed twice with 10 ml of very cold (-20 °C) methanol and dried in vacuo at 40°C to afford 124 g (0.45 mol) of the title compound as a white powder; molecular weight 278.39 ($C_{17}H_{26}O_3$), m.p. 71 - 72°C. ^1H -NMR (400 MHz, $CDCl_3$, ppm): 1.32 (s, 9H), 1.44 (s, 9H), 2.13 (s, 3H), 5.14 (s, 2H), 7.15 (m, 1H), 7.4 (m, 1H), >10 (broad s, -OH).

Example R: Preparation of 2,4-di-tert-butyl-6-methoxymethyl-phenol (0490).

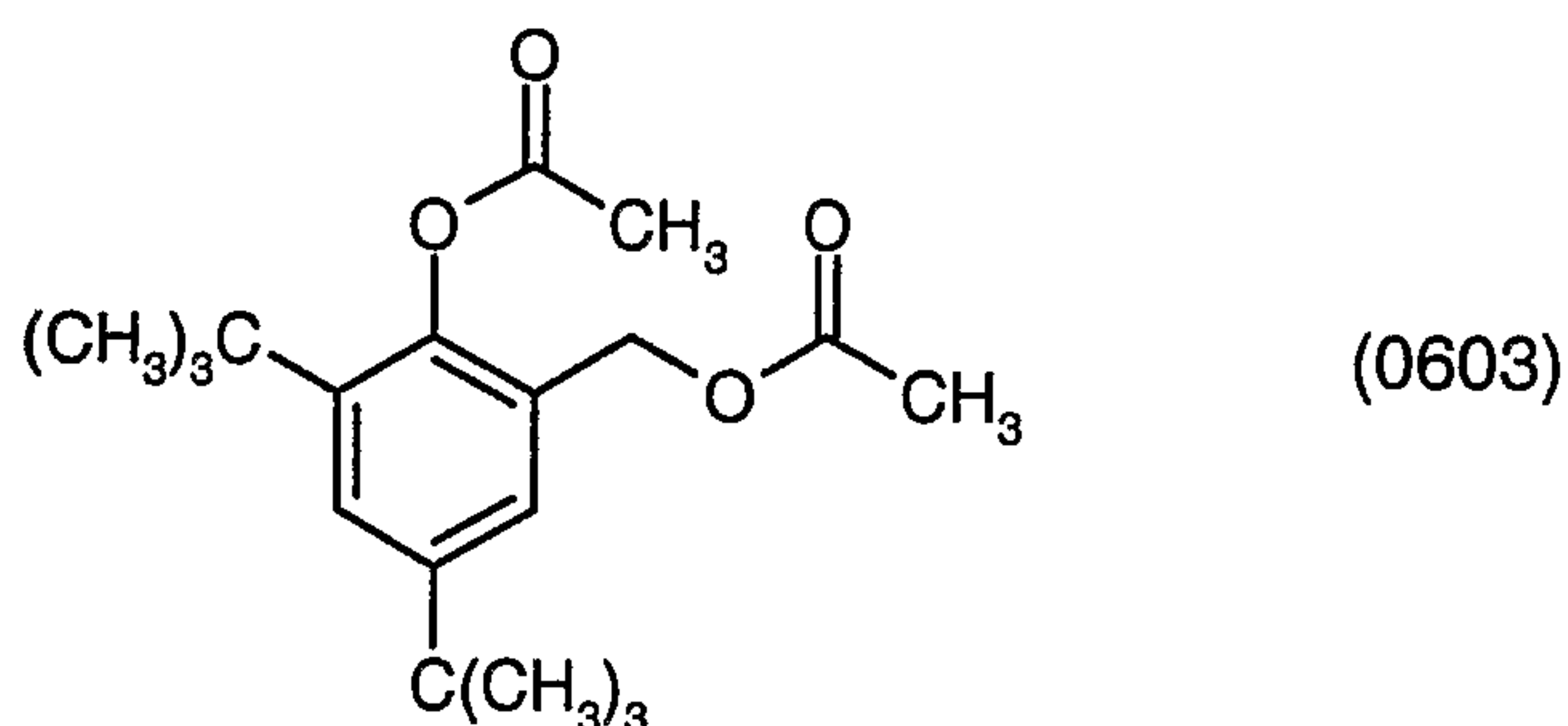


A solution of 100 g (0.36 mol) of acetic acid-3,5-di-tert-butyl-2-hydroxybenzyl-ester in 200 ml of methanol is stirred at 75°C under reflux for 26 hours. The solvent is then stripped-off in vacuo, the residue treated with 200 ml of n-hexane and extracted with 70 ml of water. The organic layer is dried over Na_2SO_4 and filtered; the solvent is again entirely removed in

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vacuo. The orange, oily residue slowly crystallizes overnight. The crystals are dissolved in approximately 100 ml of ethanol and re-precipitated by drop-wise addition of 20 ml of water. The white precipitate is filtered-off and washed with 60 ml of a mixture of water/ethanol (1/5) to give 37 g (0.147 mol) of the title compound as a white powder: molecular weight 250.38 ($C_{16}H_{26}O_2$), m.p. 36 – 39°C. ^1H -NMR (400MHz, $CDCl_3$, ppm): 1.31 (s, 9H), 1.42 (s, 9H), 3.47 (s, 3H), 4.66 (s, 2H), 6.90 (m, 1H), 7.29 (m, 1H), >10 (broad s, -OH).

Example S: Preparation of acetic acid-2-acetoxymethyl-4,6-di-tert-butyl-phenyl-ester (0603).

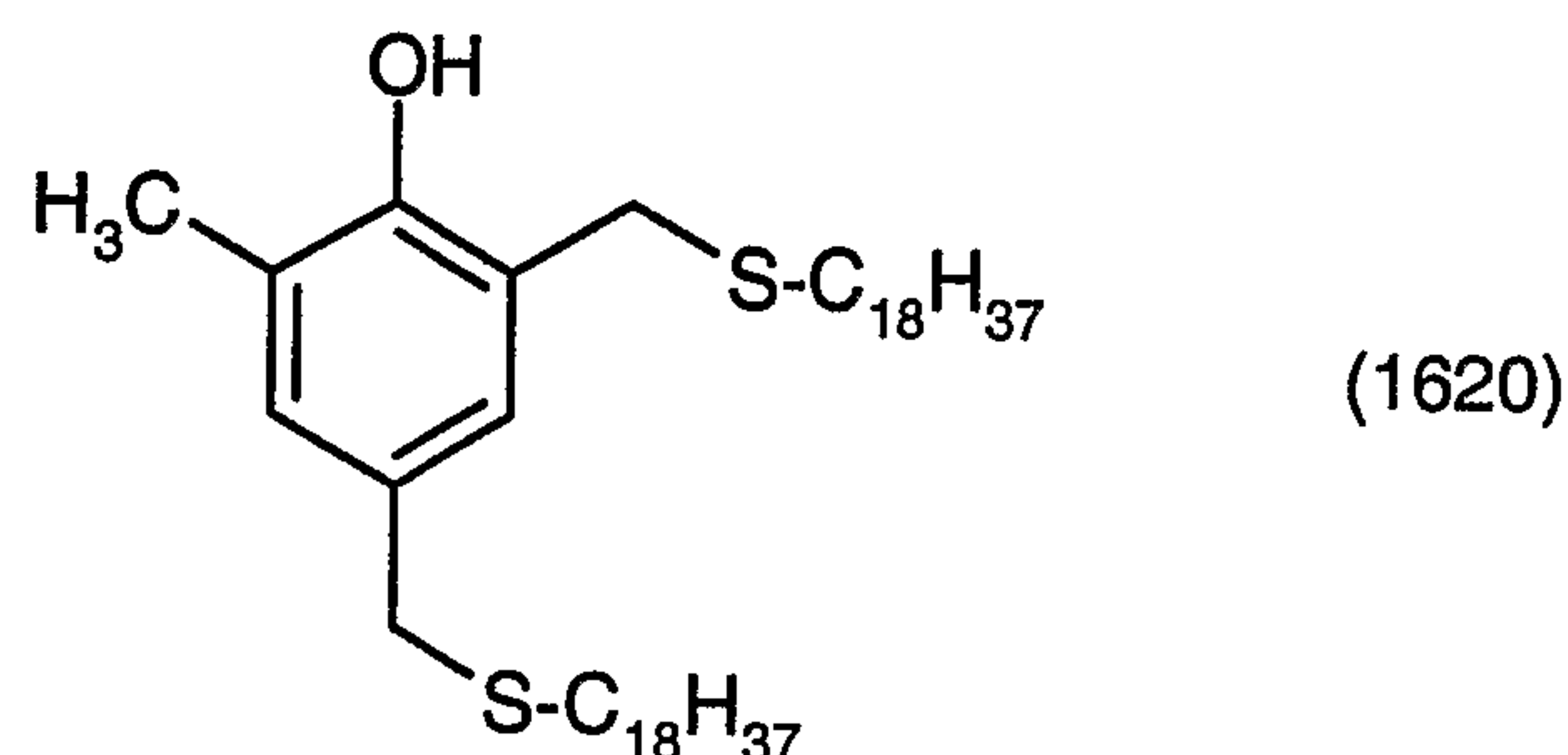


A solution of 200 g (0.72 mol) of 2,4-di-tert-butyl-6-dimethylaminomethyl-phenol in 200 ml (1.44 mol) of triethylamine and 500 ml (5.3 mol) of acetic acid anhydride is stirred at 140°C for 2 hours. After cooling to 40°C, the mixture is poured on ice/water and stirred for 2 hours. The product is then extracted with 300 ml of n-hexane, dried over Na_2SO_4 and filtered. The solvent and volatiles are removed in vacuo. The orange, oily residue is purified by distillation under reduced pressure to yield 162 g (0.51 mol) of the title compound as a faintly yellowish oil; molecular weight 320.43 ($C_{19}H_{28}O_4$), b.p. 121 °C (0.098 mbar). ^1H -NMR (400MHz, $CDCl_3$, ppm): 1.35 (s, 9H), 1.38 (s, 9H), 2.1 (s, 3H), 2.36 (s, 3H), 5.00 (s, 2H), 7.32 (m, 1H), 7.45 (m, 1H).

It is contemplated that “capping” off the phenolic -OH as in this Mannich base compound will result in another class of organic compounds that are active as stabilizers against aldehyde formation. Phenolic hydroxyls may be capped off by known methods, for example by acylating or alkylating. Acyl and alkyl groups are as defined herein.

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Example T: Preparation of 2,4-bis(n-octadecylthiomethyl)-6-methyl-phenol (1620).



The title compound is prepared in accordance to U.S. 5,116,894; Example 1; after recrystallization, a white powder is obtained: m.p. 42 - 43°C, molecular weight 705.30 (C₄₅H₈₄S₂O).

Example 1: Stabilization of poly(ethylene terephthalate) (PET).

Unstabilized commercial PET (CLEARTUF 8006, M&G) is used as a control PET. The PET as received from M&G had an initial AA (acetaldehyde) concentration of 0.4 ppm as reported by the supplier. Upon a single extrusion heat history, the unstabilized PET increases in acetaldehyde content to an average of 3.4 ppm, indicating that PET produces undesirable AA upon heated melt processing. When PET is extrusion compounded, a significant reduction in the amount of acetaldehyde (AA) is observed in samples stabilized with additives of the present invention compared to unstabilized PET. The % AA reduction is the amount less compared to the amount of AA in the control, all measured by GC-FID. The results are summarized in Table 1. Additive levels are in parts per million (ppm) based on PET.

Table 1:

Formulation	Additive	Additive Level (ppm)	% AA Reduction	GC-FID avg. ppm, AA
Control	none	none	none	3.41
Example 1a	1071	500	74	0.88
Example 1b	1071	5000	92	0.26

It is seen that the additives of the present invention provide significant reduction of acetaldehyde versus the control in PET.

Example 2: Stabilization of poly(ethylene terephthalate) (PET).

Unstabilized commercial PET (CLEARTUF 8006, M&G) is used as a control PET. The PET as received from M&G had an initial AA concentration of 0.4 ppm as reported by the supplier. Upon a single extrusion heat history, the unstabilized PET increases in acetaldehyde (AA) content to an average of 2.8 ppm, indicating that PET produces undesirable AA upon heated melt processing. When PET is extrusion compounded, a significant reduction in the amount of acetaldehyde (AA) is observed in samples stabilized with additives of the present invention compared to unstabilized PET. The % AA reduction is the amount less compared to the amount of AA in the control, all measured by GC-FID. The results are disclosed in Table 2. Additive levels are in parts per million (ppm) based on PET.

Table 2:

Formulation	Additive	Additive Level (ppm)	% AA Reduction	GC-FID avg. ppm AA	Haze
Control	none	none	none	2.84	2.3
Example 2a	1071	250	43.3	1.61	2.0
Example 2b	1071	500	65.5	0.98	1.7
Example 2c	1071	1000	85.9	0.40	1.7

Example 3: Stabilization of poly(ethylene terephthalate) (PET).

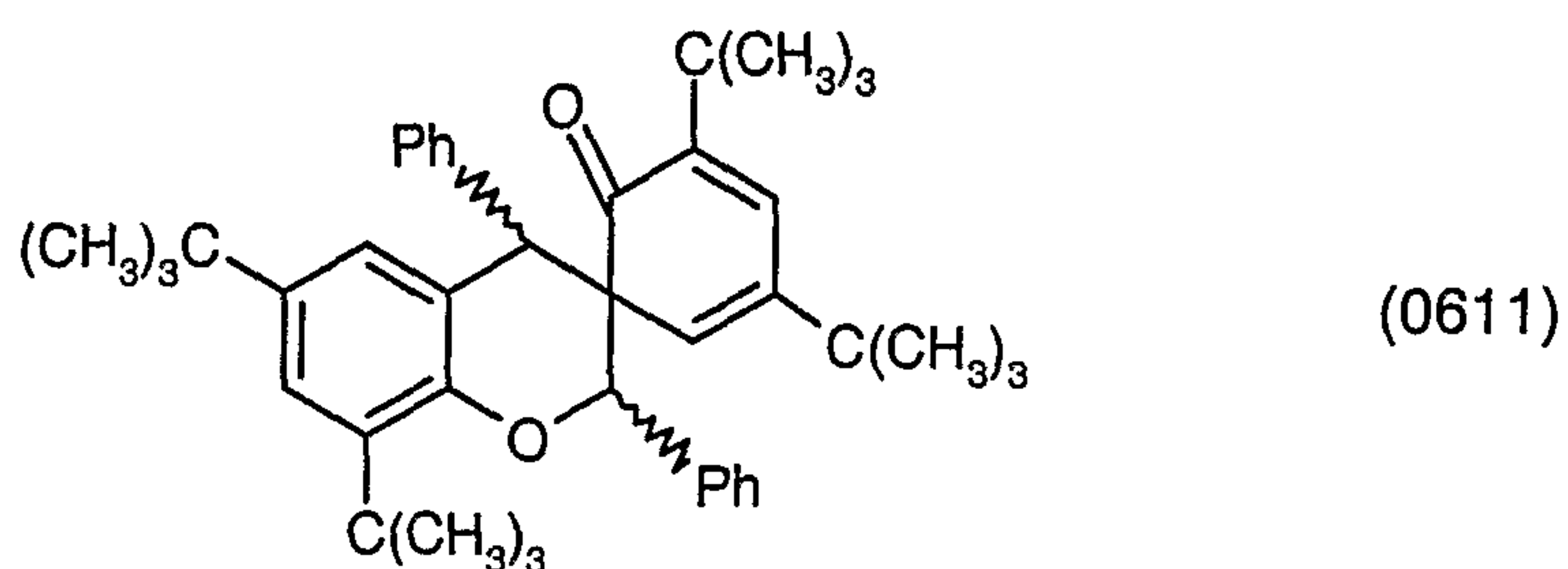
An extruder evaluation as in the previous Examples is conducted. Upon a single extrusion heat history, the unstabilized PET increases in acetaldehyde (AA) content to an average of 3.34 ppm, indicating that PET produces undesirable AA upon heated melt processing. The additive compound 0611 is a thermally produced dimer from the compound 1071. The dimer itself is active in AA reduction by itself at 1000 ppm loading. Additive levels are in weight percent based on PET. The results are summarized in Table 3.

Table 3:

Formulation	Additive	Additive Level (ppm)	% AA Reduction	GC-FID avg. ppm AA
Control 3a	none	none	none	3.34
Control 3b	amine ^{a)}	1000	none	4.40
Control 3c	amine ^{a)}	2500	none	4.70
Example 3a	0611 ^{b)}	1000	10.2	3.00
Example 3b	0611 ^{b)} amine ^{a)}	1000 500	56.0	1.47
Example 3c	0611 ^{b)} amine ^{a)}	1000 1000	58.7	1.38
Example 3d	0611 ^{b)} amine ^{a)}	1000 2000	42.8	1.91
Example 3e	0611 ^{b)} amine ^{a)}	5000 2500	88.6	0.38
Example 3f	0611 ^{b)} amine ^{a)}	5000 5000	71.0	0.97

a) amine is trimethylene-dipiperidine, available from Adrich Chem. Co., CAS# [16898-52-5].

b) 0611 is a thermal product of the Mannich base 1071 (Example A) with the formula 0611



These results show that the thermal products of the present Mannich bases are effective as AA scavengers, especially in the presence of an amine.

Example 4: Stabilization of poly(ethylene terephthalate) (PET).

In this study the efficacy of Mannich base compounds with either a 2-substitution or 4-substitution is evaluated. Upon a single extrusion heat history, the unstabilized PET increases in acetaldehyde (AA) content to an avg. of 3.07 ppm, indicating that PET produces undesirable AA upon heated melt processing. In all cases where compounds of the invention are evaluated, a high AA reduction is observed with either the 4-substituted or 2-substituted Mannich base compounds. The results are summarized in Table 4.

Table 4:

Formulation	Additive	Additive Level (ppm)	% AA Reduction	GC-FID avg. ppm AA
Control	none	none	none	3.07
Example 4a	1071	1000	94.1	0.18
Example 4b	0888	1000	90.9	0.28
Example 4c	0888	5000	94.1	0.18
Example 4d	0867	1000	47.6	1.61
Example 4e	0868	5000	48.9	1.57
Example 4f	0858	1000	91.2	0.27
Example 4g	0858	5000	88.6	0.35

Example 5: Stabilization of poly(ethylene terephthalate) (PET).

Unstabilized commercial PET (CLEARTUF 8006, M&G) is used as a control PET. Upon a single extrusion heat history, the unstabilized PET increases in acetaldehyde (AA) content to an average of 3.27 ppm, indicating that PET produces undesirable AA upon heated melt processing. When PET is extrusion compounded, a significant reduction in the amount of acetaldehyde (AA) is observed in samples stabilized with additives of the present invention compared to unstabilized PET. The % AA reduction is the amount less compared to the amount of AA in the control, all measured by GC-FID. The results are summarized in Table 5.

Table 5:

Formulation	Additive	Additive Level (ppm)	% AA Reduction	GC-FID avg. ppm AA
Control	none	none	none	3.27
Example 5a	1070	250	39.4	1.98
Example 5b	1070	500	65.4	1.13
Example 5c	1070	1000	80.7	0.63
Example 5d	1070	5000	96.3	0.12
Example 5e	1071	1000	83.8	0.53

Example 6: Color stabilization of poly(ethylene terephthalate) (PET) with a pigment.

In this example the b^* color of the polyester is improved when a certain pigment is used in combination with an additive of the instant invention (compound 1071). The pigment is first prepared as a 0.025% masterbatch in Shell 8006 PET via extrusion compounding. The pigment is then let-down into virgin Shell 8006 PET, along with compound 1071, and extrusion compounded. Test plaques of 60 mm thickness are prepared by injection molding on a BOY 50 machine. Color (b^*) is measured per the experimental. It is seen that a b^* color value for the composition of PET, compound 1071 and Ciba Chromophtal Violet B pigment close to the control PET is achieved. The lower the b^* color value, the less yellow or discolored is the PET. Ciba Chromophtal Violet B is of the dioxazine class. The results are summarized in Table 6.

Table 6:

Formulation	Additive	Additive Level (ppm)	Color b^*
Control 6a	none	none	2.74
Control 6b	1071	500	4.24
Example 6a	1071 Violet B	500 2	3.26
Example 6b	1071 Violet B	500 5	1.68
Example 6c	1071 Violet B	500 7	0.83
Example 6d	1071 Violet B	500 10	-1.20

Example 7: Color stabilization of poly(ethylene terephthalate) in the presence of a dye.

In this example the b^* color of the polyester is improved when a certain dye is used in combination with the additive of the instant invention (compound 1071). The dye is first prepared as a 0.025% masterbatch in Shell 8006 PET via extrusion compounding. The dye is then let-down into virgin Shell 8006 PET, along with compound 1071, and extrusion compounded. Test plaques of 60 mm thickness are prepared by injection molding on a BOY 50 machine. Color (b^*) is measured per the experimental. It is seen that a b^* color value for the composition of PET, compound 1071 and Bayer Macrolex Violet B Gran, SV-13, close to the control PET is achieved. The lower the b^* color value, the less yellow or discolored is the PET. The results are summarized in the Table 7.

Table 7:

Formulation	Additive	Additive Level (ppm)	Color b^*
Control 7a	none	none	2.7
Control 7b	1071	500	4.2
Example 7a	1071 SV-13	500 2	3.4
Example 7b	1071 SV-13	500 5	1.8
Example 7c	1071 SV-13	500 7	1.3
Example 7d	1071 SV-13	500 10	-0.5

Example 8: Stabilization of poly(ethylene terephthalate) (PET).

Unstabilized commercial PET (CLEARTUF 8006, M&G) is used as a control PET. Upon a single extrusion heat history, the unstabilized PET increases in acetaldehyde (AA) content to an average of 4.21 ppm, indicating that PET produces undesirable AA upon heated melt processing. When PET is extrusion compounded, a significant reduction in the amount of

acetaldehyde (AA) is observed in samples stabilized with additives of the present invention compared to unstabilized PET. The % AA reduction is the amount less compared to the amount of AA in the control, all measured by GC-FID. The results are summarized in the Table 8 below.

Table 8:

Formulation	Additive	Additive Level (ppm)	% AA Reduction	GC-FID avg. ppm AA
Control	none	none	none	4.21
Example 8a	1457	250	28.0	3.03
Example 8b	1457	1000	86.0	0.59
Example 8c	1457	2500	85.5	0.61
Example 8d	1402	250	41.3	2.47
Example 8e	1402	1000	87.9	0.51
Example 8f	1402	2500	90.3	0.41

Example 9: Stabilization of poly(ethylene terephthalate) (PET).

Unstabilized commercial PET (CLEARTUF 8006, M&G) is used as a control PET. Upon a single extrusion heat history, the unstabilized PET increases in acetaldehyde (AA) content to an avg. of 5.20 ppm, indicating that PET produces undesirable AA upon heated melt processing. When PET is extrusion compounded, a significant reduction in the amount of acetaldehyde (AA) is observed in samples stabilized with additives of the present invention compared to unstabilized PET. The % AA reduction is the amount less compared to the amount of AA in the control, all measured by GC-FID. The results are summarized Table 9.

Table 9:

Formulation	Additive	Additive Level (ppm)	% AA Reduction	GC-FID avg. ppm AA
Control	none	none	none	5.20
Example 9a	1655	500	31.3	3.57
Example 9b	1655	1000	53.1	2.44
Example 9c	1655	2500	81.5	0.96

Example 10: Stabilization of poly(ethylene terephthalate) (PET).

Unstabilized commercial PET (CLEARTUF 8006, M&G) is used as a control PET. Upon a single extrusion heat history, the unstabilized PET increases in acetaldehyde (AA) content to an avg. of 6.05 ppm, indicating that PET produces undesirable AA upon heated melt processing. When PET is extrusion compounded, a significant reduction in the amount of acetaldehyde (AA) is observed in samples stabilized with additives of the present invention compared to unstabilized PET. The % AA reduction is the amount less compared to the amount of AA in the control, all measured by GC-FID. The results are summarized in Table 10.

Table 10:

Formulation	Additive	Additive Level (ppm)	% AA Reduction	GC-FID avg. ppm AA
Control	none	none	none	6.05
Example 10a	1672	250	66.1	1.89
Example 10b	1672	500	89.4	0.59
Example 10c	1673	250	82.9	0.95
Example 10d	1673	500	95.7	0.24
Example 10e	1678	250	63.7	2.02
Example 10f	1678	500	94.3	0.32
Example 10g	1596	250	63.2	2.05
Example 10h	1596	500	77.7	1.24

The additives in Table 10 are highly effective and at low loading levels (250-500 ppm) which is advantageous.

Example 11: Stabilization of poly(ethylene terephthalate) (PET).

This example illustrates the general concept where the novel compounds provide efficacy in reducing the acetaldehyde content in a lower molecular weight, non-bottle grade of PET. The utility of this example indicates that it is possible to take a lower molecular weight polyester such as the fiber grade of PET below and reduce the acetaldehyde content to a level approaching usefulness for the beverage bottling market. Unstabilized commercial PET (IMPET 100, Hoechst Celanese Corp., CAS# 25038-59-9) is used as a control PET. Upon a single extrusion heat history, the unstabilized PET increases in acetaldehyde (AA) content to an avg. of 4.21 ppm, indicating that PET produces undesirable AA upon heated melt processing. When PET is extrusion compounded, a significant reduction in the amount of acetaldehyde (AA) is observed in samples stabilized with additives of the present invention compared

to unstabilized PET. The % AA reduction is the amount less compared to the amount of AA in the control, all measured by GC-FID. The results are summarized in Table 11.

Table 11:

Formulation	Additive	Additive Level (ppm)	% AA Reduction	GC-FID avg. ppm AA
Example 11a	1071	500	66.8	23.5
Example 11b	1071	1000	93.7	4.5

The IMPET 100 polyester is analyzed to contain approximately 154 ppm of acetaldehyde, as received and prior to any thermal processing. The compound of the instant invention (1071) provided excellent reduction in acetaldehyde content after thermal processing of the polyester.

Example 12: Stabilization of poly(ethylene terephthalate) (PET).

Unstabilized commercial PET (CLEARTUF 8006, M&G) is used as a control PET. Upon a single extrusion heat history, the unstabilized PET increases in acetaldehyde (AA) content to an avg. of 3.79 ppm, indicating that PET produces undesirable AA upon heated melt processing. When PET is extrusion compounded, a significant reduction in the amount of acetaldehyde (AA) is observed in samples stabilized with additives of the present invention compared to unstabilized PET. The % AA reduction is the amount less compared to the amount of AA in the control, all measured by GC-FID. The results are summarized in Table 12.

Table 12:

Formulation	Additive	Additive Level (ppm)	% AA Reduction	GC-FID avg. ppm AA
Control	none	none	none	3.79
Example 12a	0263	125	48.0	1.97
Example 12b	0263	250	79.7	0.77
Example 12c	0263	500	89.4	0.40
Example 12d	0486	125	18.5	3.09
Example 12e	0486	250	34.8	2.47
Example 12f	0486	500	53.6	1.76
Example 12g	0485	125	29.8	2.66
Example 12h	0485	250	20.6	3.01
Example 12i	0485	500	37.5	2.37

Example 13: Stabilization of poly(ethylene terephthalate) (PET).

The compounds of the present invention are incorporated into polyester with either a solid or liquid carrier as a masterbatch. Samples of PET (M&G Cleartuf® 8006) are admixed with the compounds 1070 and 1071, respectively, as dispersions in a liquid carrier, into an Arburg 420C injection molder operated at 268 - 271°C. AA is measured on cryogenically ground molded preforms by gas chromatography. Significant reduction in AA formation is observed in molded preforms. Blow molding is done on a Sidel SBO-2/3, to produce 20 ounce bottles with mid-panel thickness of 0.012 inches. The b* yellowness color measurements are made on bottle sidewall cutouts. Bottle sidewall color is not changed significantly by the addition of the additives as a masterbatch. The results are summarized in Table 13.

Table 13:

Formulation	Additive	Additive Level (ppm)	% AA Reduction	GC-FID avg. ppm AA	b* color bottle sidewall
Control	none	none	none	10.15	2.64
Example 13a	1071	250	28.0	7.32	3.34
Example 13b	1071	500	70.6	2.98	3.48
Example 13c	1070	250	31.5	6.95	3.02
Example 13d	1070	500	63.1	3.75	3.30

Example 14: Stabilization of poly(ethylene terephthalate) (PET) bottles.

The additives of the invention are incorporated into PET and injection molded into 24 gram weight bottle preforms which are in turn subsequently blow molded into 20 fluid ounce bottles. Measurement of AA in the preforms indicated that the additives are effective at reducing the level of AA to a significant extent as desired by the bottling industry. Measurement of 24 hour headspace AA in the freshly blown bottles (ASTM D4509) likewise indicates a significant reduction in AA.

Example 15: The previous Examples are repeated with the further inclusion of polyols selected from the group consisting of pentaerythritol, dipentaerythritol and trimethylolpropane. The co-use of the Mannich base compounds of this invention and a polyol provides significant reduction of acetaldehyde vs. a control sample of PET without any undesirable side effects.

Example 16: The previous Examples are repeated with the further inclusion of additives selected from the group consisting of the N,N-di(alkyl)hydroxylamine produced by the direct oxidation of N,N-di(hydrogenated tallow)amine (Irgastab[®] FS-042), O-allyl-N,N-dioctadecylhydroxylamine, N-octadecyl- α -heptadecylnitrone, and Genox[™] EP, a di(C₁₆-C₁₈)alkyl methyl amine oxide, CAS# 204933-93-7. The co-use of the Mannich bases of this invention and an additional additive as above provides significant reduction of acetaldehyde vs. a control sample of PET without any undesirable side effects.

Example 17: Polyamide 4; 6,6; 6; 12; and 6,4 molded articles, fibers and films and PET fibers and films, are prepared by melt extrusion with additives as in the previous Examples. Significant reduction in aldehydic contaminants is observed.

Example 18: Stabilization of polyester during synthesis.

1621.3 g of ethylene glycol, 3338.5 g of terephthalic acid, 66.8 g of isophthalic acid, 1.36 g of antimony trioxide and 1000 ppm (0.1 %) of the stabilizer according to Table 14 are mixed within a metal container. The mixture is transferred into a 10 liter stainless steel reactor fitted with stirrer, refluxing unit and an outlet-die at the bottom of the reactor. The reaction mixture is heated to 250°C within 30 minutes. The pressure increases to 4 bars. A water/ethylene glycol mixture is distilled off during 3.5 hours. The temperature is increased consecutively to 280°C. During the next 5 hours the pressure is continuously reduced to further distill off water and ethylene glycol. The polyester product is then extruded through the bottom die, cooled to room temperature in a water bath and pelletized to yield clear PET granules. The Intrinsic Viscosity (I.V.) is measured by dissolving 1 g of formed the polyester in 100 g of a mixture of phenol/dichlorobenzene = 1 : 1. The viscosity of this solution is measured at 30°C in an Ubelodeviscosimeter and recalculated to the intrinsic viscosity. The results are summarized in Table 14.

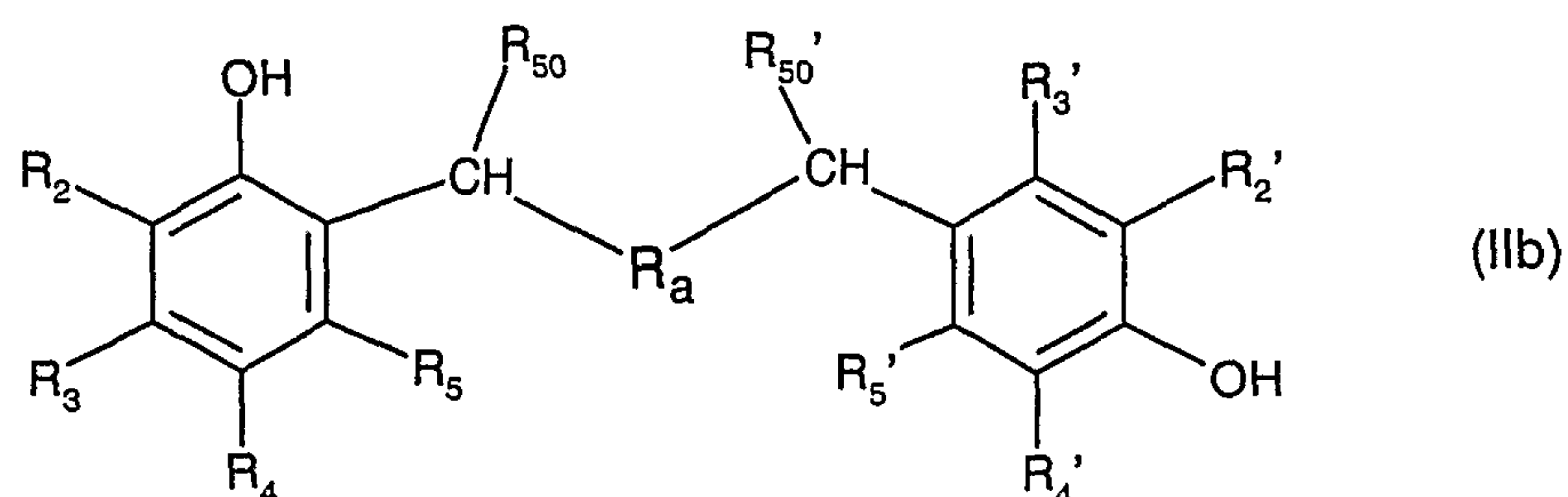
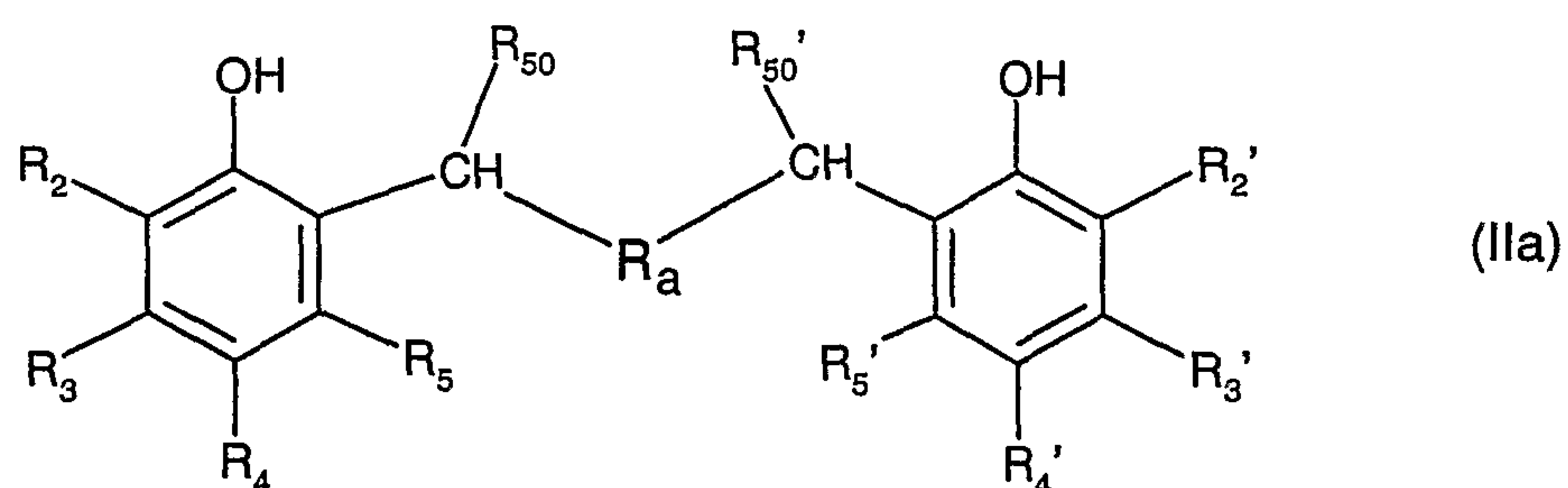
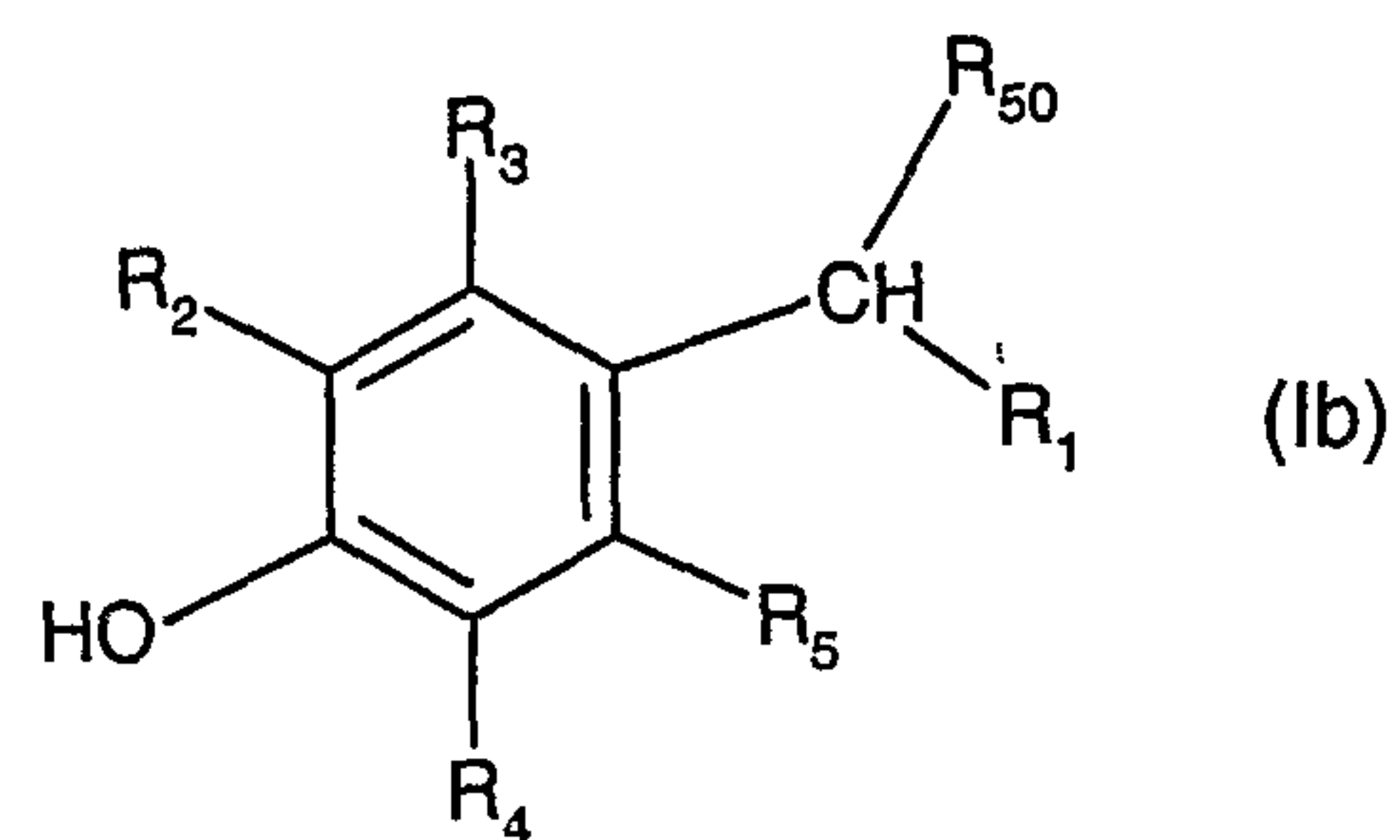
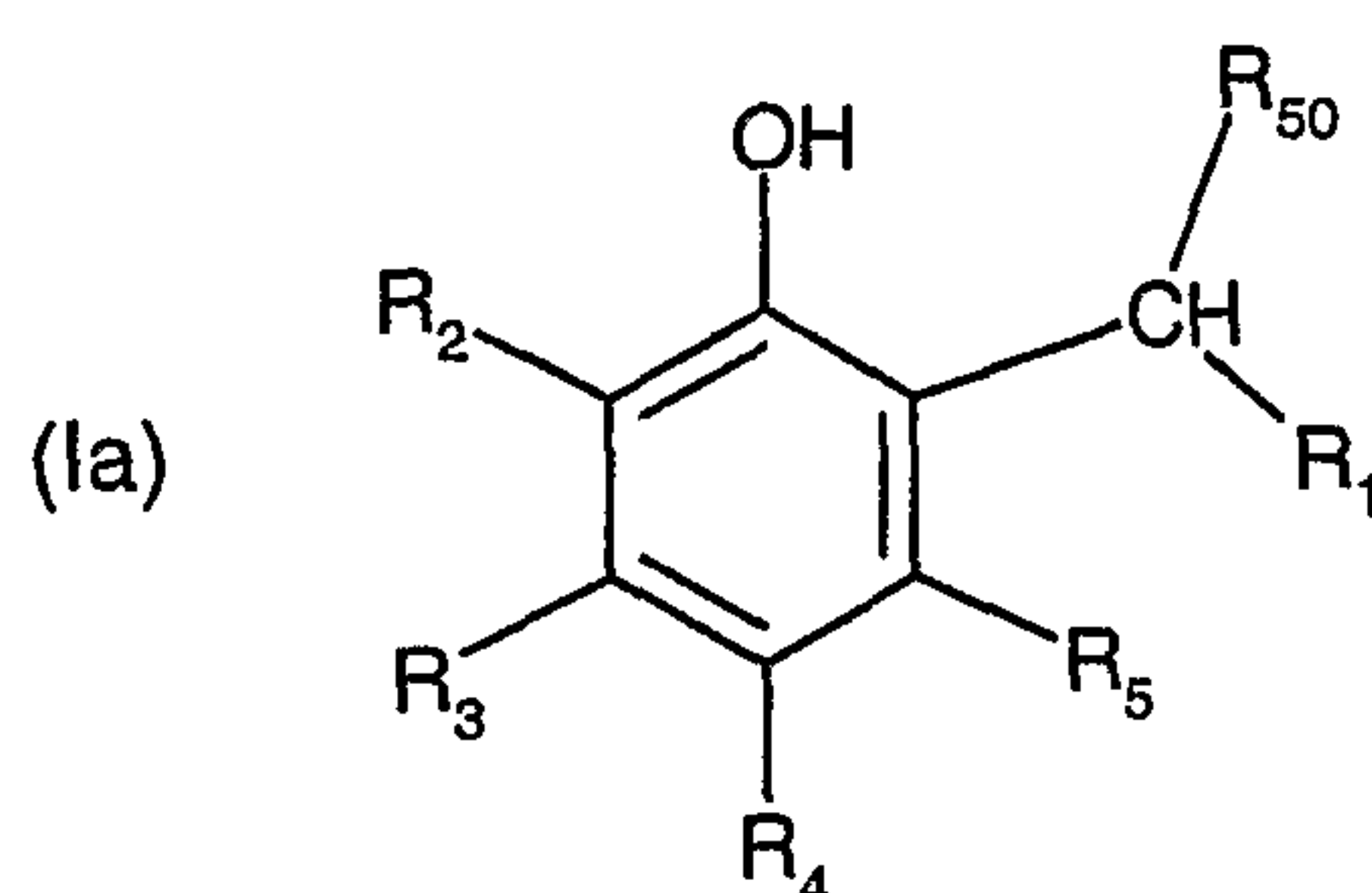
Table 14:

Formulation	Additive	Additive Level (ppm)	I.V. dl/g	GC-FID avg. ppm AA
Control	none	none	0.75	170
Example 18a	1071	1000	0.45	53
Example 18b	0888	1000	0.33	30

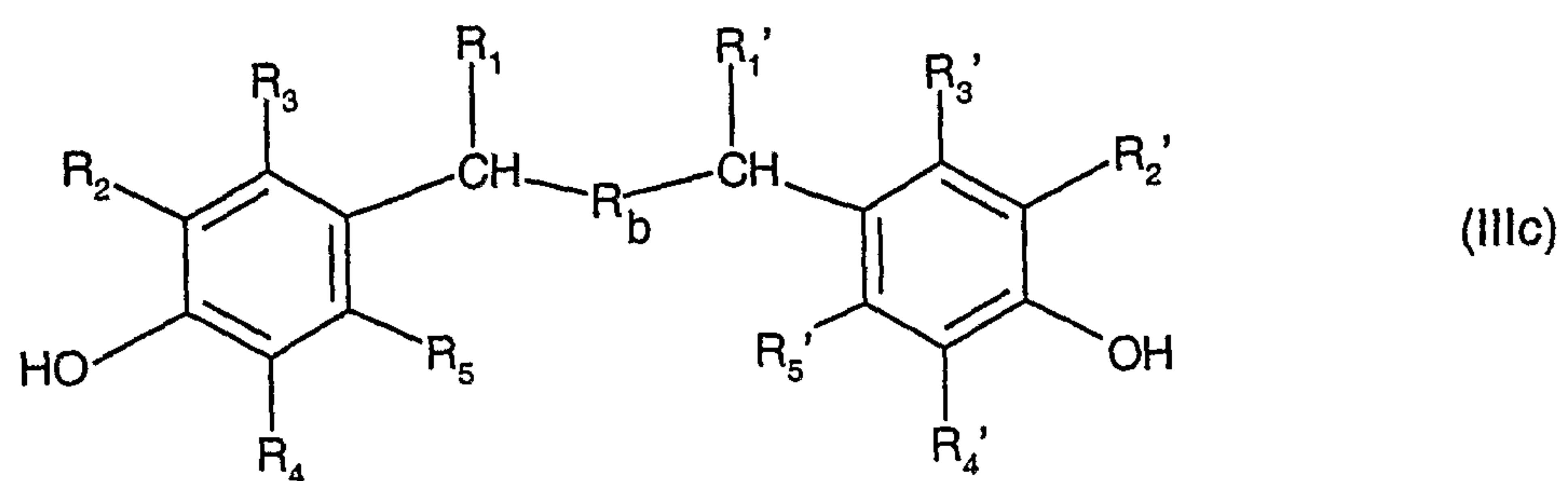
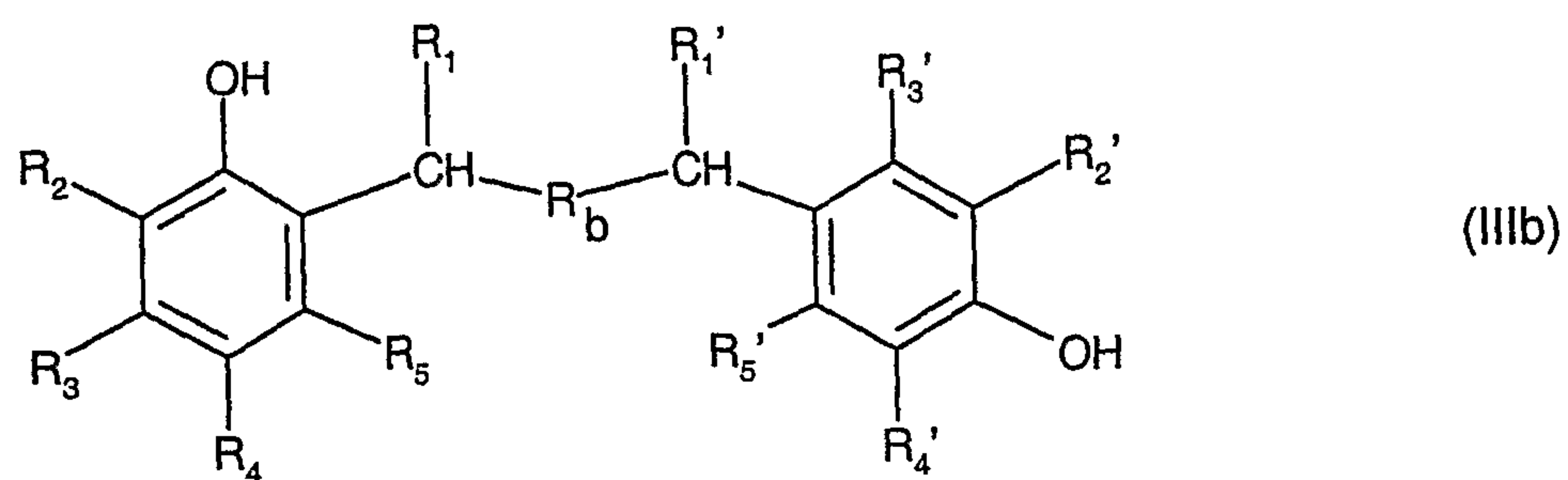
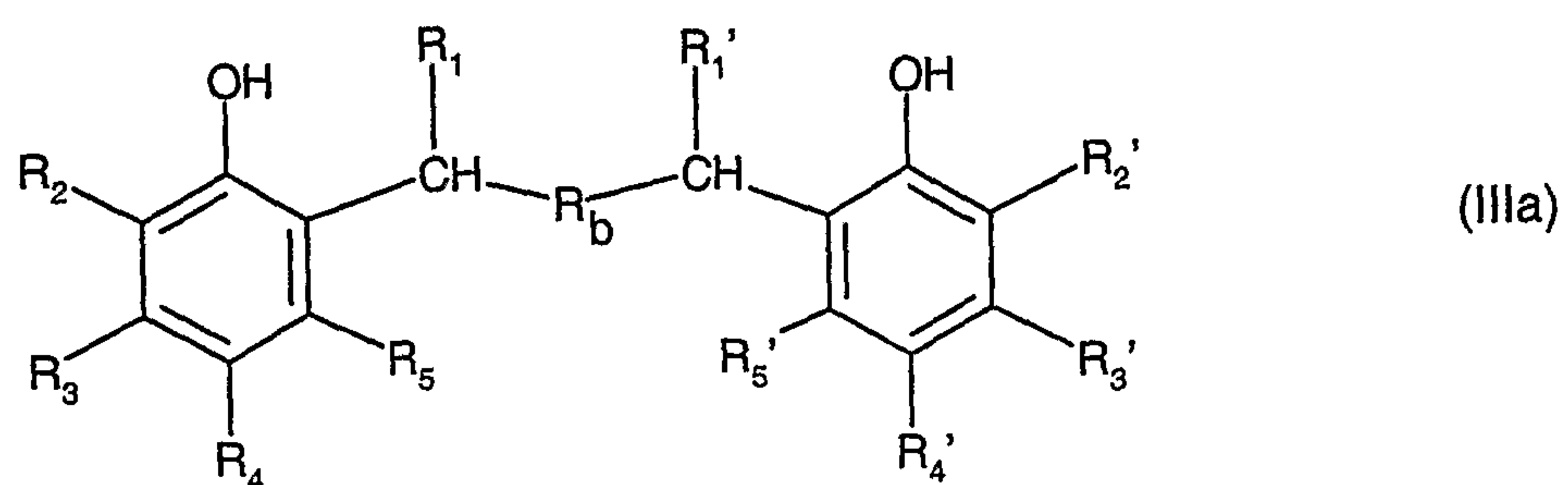
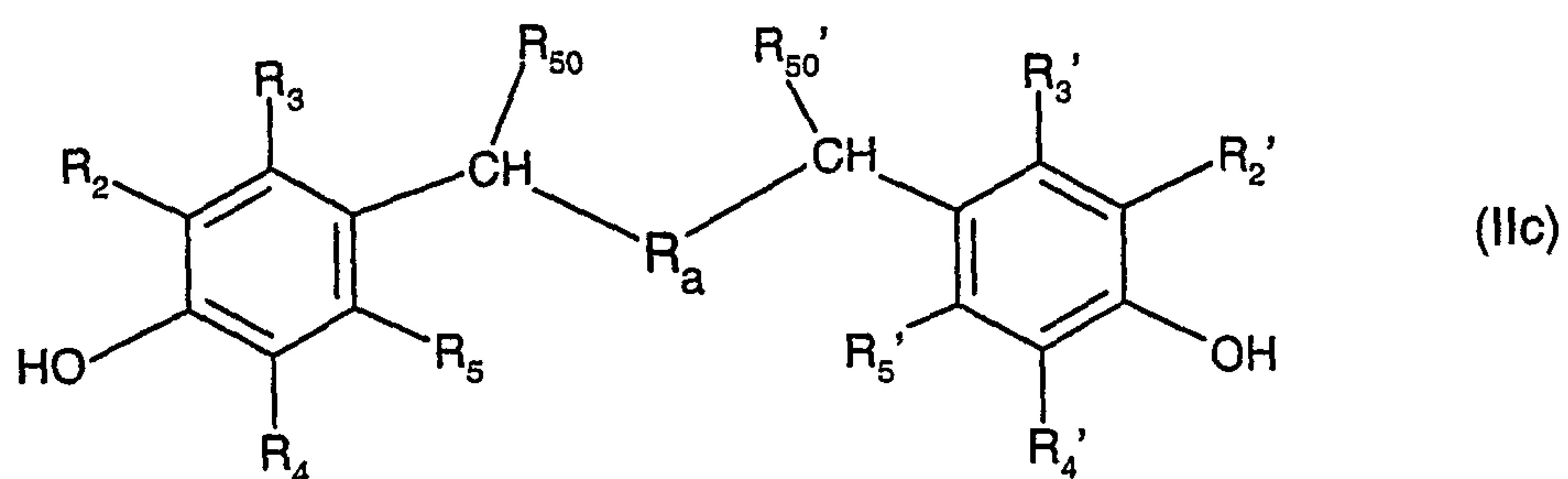
What is claimed is:

1. A composition, stabilized against the formation of aldehydic contaminants during melt processing of said composition, which comprises

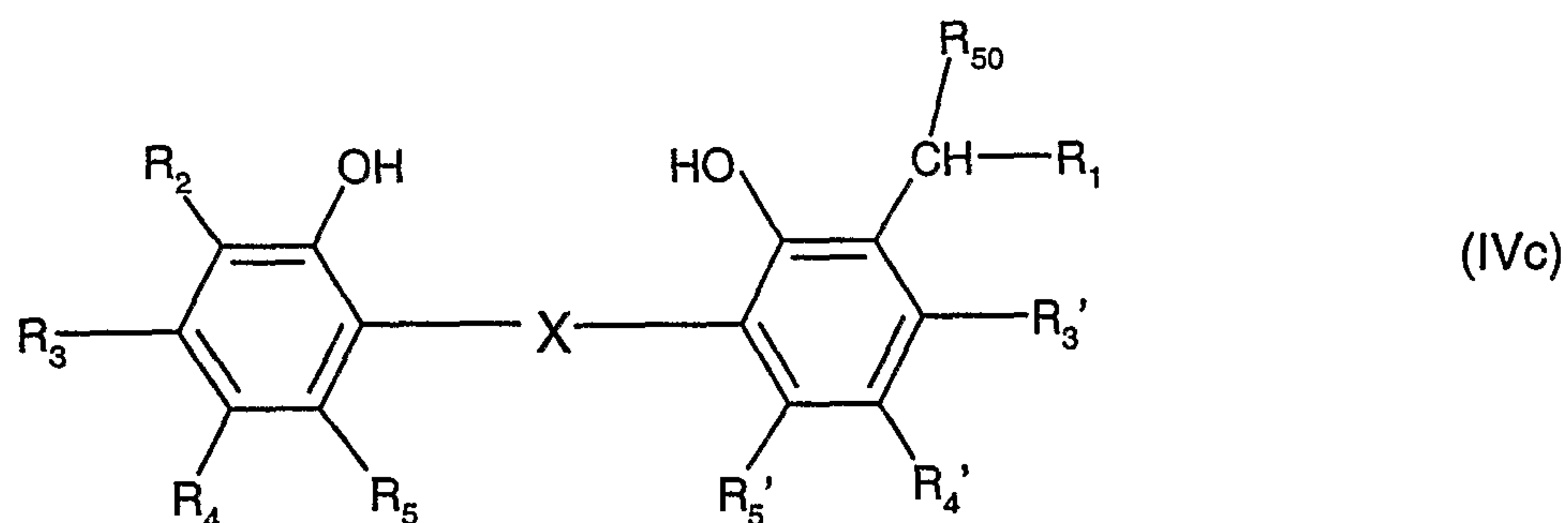
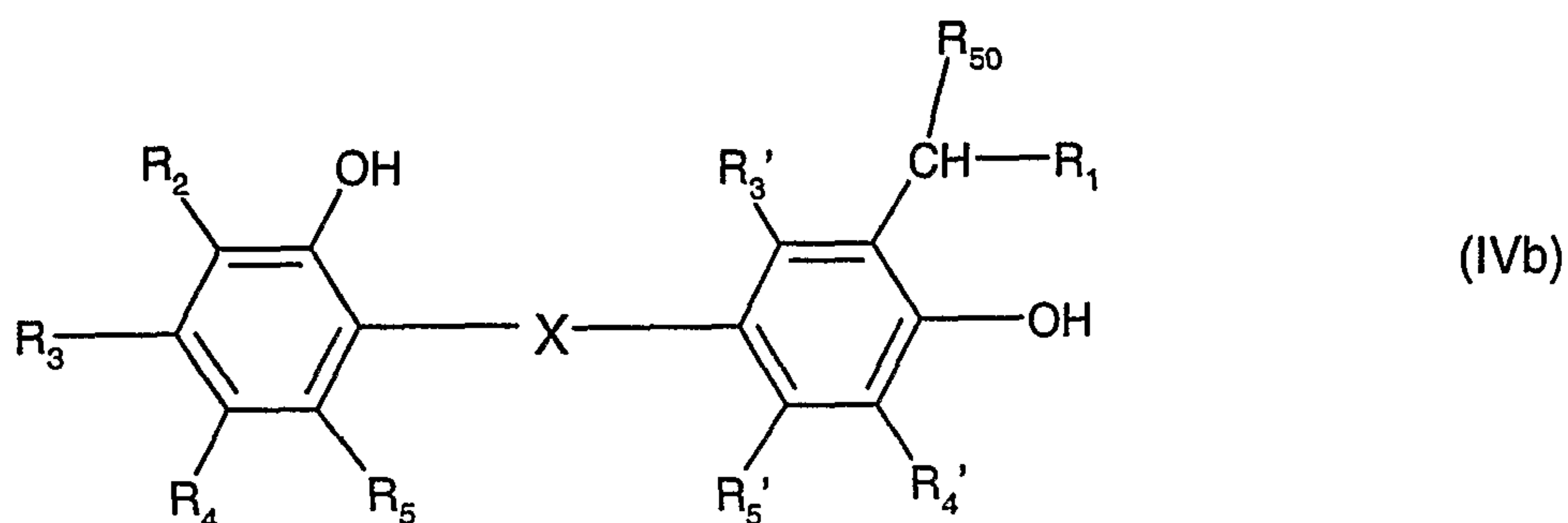
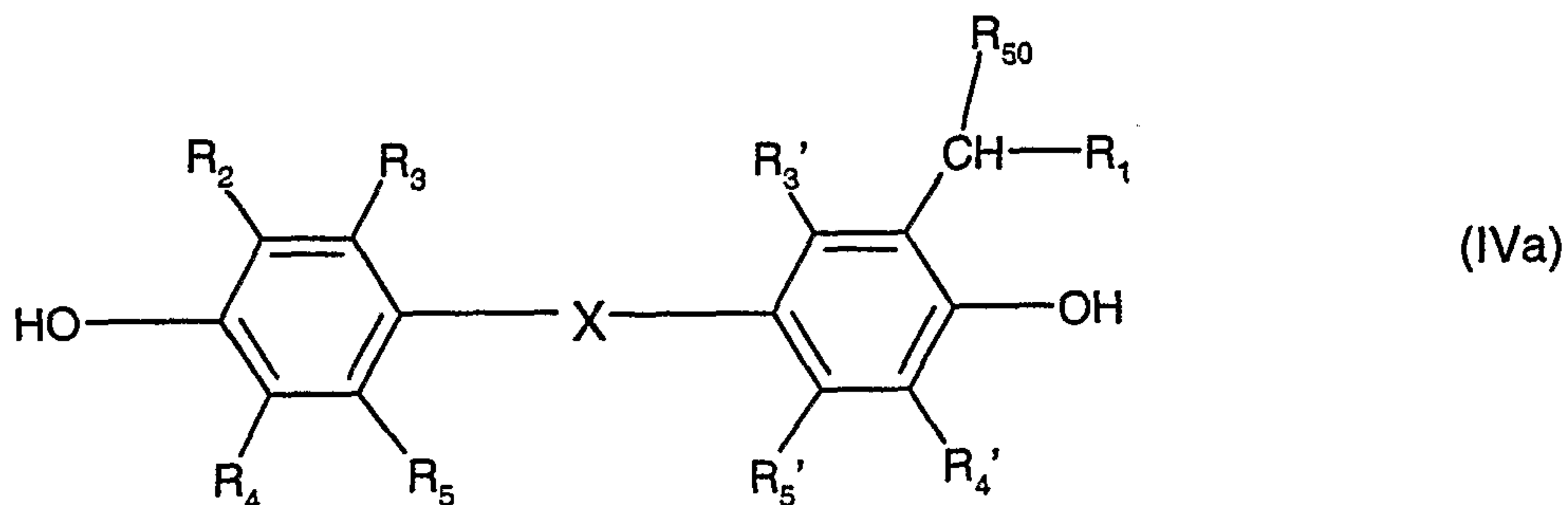
- (a) a polyester or polyamide, and
- (b) an effective stabilizing amount of at least one effective stabilizing amount of at least one compound selected from the group consisting of the Mannich base compounds of formulae (Ia), (Ib), (IIa), (IIb), (IIc), (IIIa), (IIIb), (IIIc) (IVa), (IVb) and (IVc)



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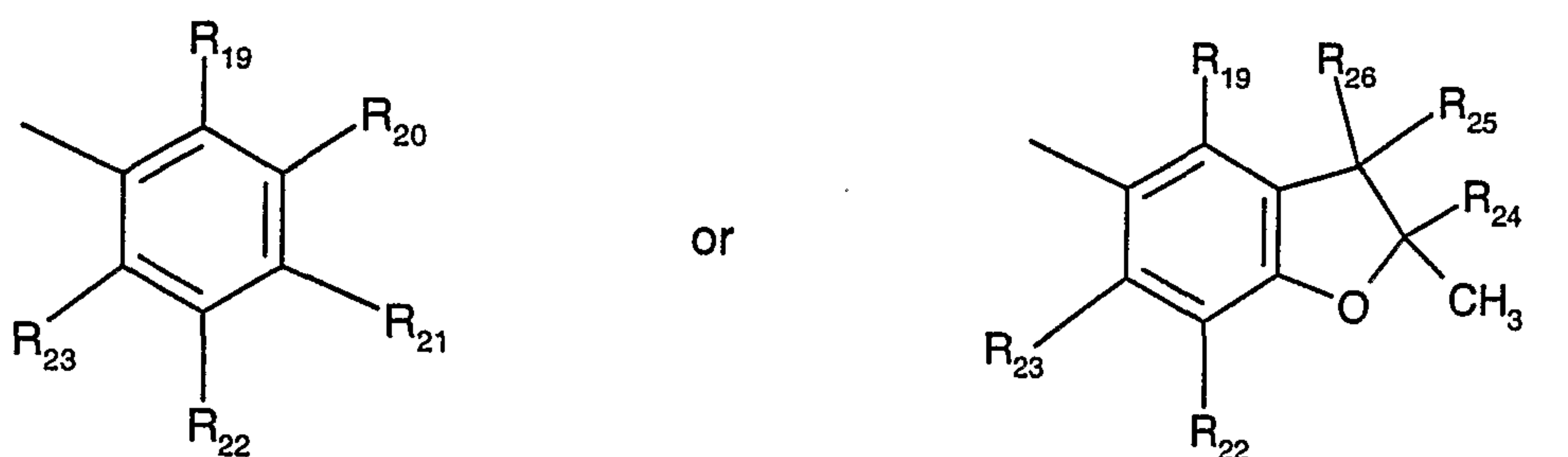


wherein

R_1 is hydrogen, hydroxy, C_1 - C_{25} alkyl, C_7 - C_9 phenylalkyl, unsubstituted or C_1 - C_4 alkyl-substituted C_5 - C_8 cycloalkyl; naphthyl, phenanthryl, anthryl, 5,6,7,8-tetrahydro-2-naphthyl, thienyl, benzo[b]thienyl, naphtho[2,3-b]thienyl, thianthrenyl, furyl, benzofuryl, isobenzofuryl, dibenzofuryl, xanthenyl, phenoxathiinyl, pyrrolyl, imidazolyl, pyrazolyl, pyridinyl, pyrazinyl, pyrimidinyl, pyridazinyl, indolizynyl, isoindolyl, indolyl, indazolyl, purinyl, quinolizynyl, isoquinolyl, quinolyl, phthalazinyl, naphthyridinyl, quinoxalinyl, quinazolinyl, cinnolinyl, pteridinyl, carbazoyl, β -carbonyl, phenanthridinyl, acridinyl, perimidinyl, phenanthrolinyl, phenazinyl, isothiazolyl, phenothiazinyl, isoxazolyl, furazanyl, biphenyl, terphenyl, fluorenyl or phenoxazinyl, each of

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which is unsubstituted or substituted by fluorine, hydroxy, C₁-C₁₈alkyl, C₁-C₁₈alkoxy, C₁-C₁₈alkylthio, di(C₁-C₄alkyl)amino, phenyl, benzyl, benzoyl or by benzoyloxy or R₁ is a radical of formula



R₂, R₃, R₄ and R₅ are each independently hydrogen, fluorine, hydroxy, C₁-C₂₅alkyl, C₁-C₂₅alkenyl, C₇-C₉phenylalkyl, C₇-C₉phenylalkenyl, unsubstituted or C₁-C₄alkyl- or alkenyl- substituted phenyl, unsubstituted or C₁-C₄alkyl-substituted C₅-C₈cycloalkyl, C₁-C₁₈alkoxy, C₁-C₁₈alkylthio, C₁-C₄alkylamino, di(C₁-C₄alkyl)amino, C₁-C₂₅alkanoyloxy, C₁-C₂₅alkanoylamino, C₃-C₂₅alkanoyloxy interrupted by oxygen, sulfur or by >NR₈; -(CH₂)_p-C(O)OR₈, C₆-C₉cycloalkylcarbonyloxy, benzoyloxy or C₁-C₁₂alkyl-substituted benzoyloxy, or adjacent radicals R₂ and R₃ or R₃ and R₄ or R₄ and R₅, together with the carbon atoms to which they are bonded, form a benzo ring, or R₂ and R₄ may each be -(CH₂)_p-COR₉ or -(CH₂)_qOH, or

R₂ and R₄ may each be -CH(R₁)R₅₀;

R₁' , R₂' , R₃' , R₄' and R₅' are independently defined as for R₁, R₂, R₃, R₄ and R₅ respectively;

R_a is C₁-C₁₈alkylene; C₂-C₁₈alkylene interrupted by oxygen, sulfur or by >NR₁₄; or R_a is C₂-C₂₀alkylidene, C₇-C₂₀phenylalkylidene, C₅-C₈cycloalkylene, C₇-C₈bicycloalkylene, phenylene or naphthylene each unsubstituted or substituted by C₁-C₄alkyl or by fluorine; or is -R₆-Y-R₇;

R_b is -NR₅₃, C₁-C₂₅alkylenediimino, C₁-C₂₅alkylenetriimino, C₁-C₂₅alkylenetetraimino, or C₅-C₈cycloalkylenediimino;

X is defined as for R_a or is a direct bond, -CR₁R₂-, -O-, -NR₁₀- or -S-, or X is phenylene substituted by R₂, R₃, R₄ and R₅, or X is alkylene substituted by -CF₃, C₁-C₁₂alkyl or phenyl, or X is a C₅-C₈cycloalkylene ring unsubstituted or substituted by 1 to 3 C₁-C₄alkyl groups;

Y is a direct bond, oxygen, sulfur or -NR₁₀;

R₆ and R₇ are each independently of the other phenylene or naphthylene each unsubstituted or substituted by C₁-C₄alkyl;

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R₈ is C₁-C₂₅alkyl;

R₉ is hydroxy, $\left[-\text{O}^- \frac{1}{r} \text{M}^{r+} \right]$, C₁-C₁₈alkoxy or $-\text{N} \begin{matrix} \text{R}_{12} \\ \text{R}_{13} \end{matrix}$;

R₁₀ is hydrogen, hydroxy, C₁-C₂₅alkyl or said alkyl unsubstituted or substituted by -OH, -OR₈, -NH(R₈) or -N(R₈)₂; C₂-C₂₅alkyl interrupted by oxygen or by sulfur, C₇-C₉phenylalkyl, unsubstituted or C₁-C₄alkyl-substituted C₅-C₈cycloalkyl, or a dendrimeric, oligomeric or polymeric C₄-C₁₀₀hydrocarbon radical;

R₁₂ and R₁₃ are each independently of the other hydrogen or C₁-C₁₈alkyl;

R₁₄ is hydrogen or C₁-C₁₈alkyl;

R₁₉, R₂₀, R₂₁, R₂₂ and R₂₃ are each independently hydrogen, cyano, perfluoroalkyl of 1 to 12 carbon atoms, fluoro, chloro, hydroxy, C₁-C₂₅alkyl; C₂-C₂₅alkyl interrupted by oxygen, sulfur or by >NR₈; C₁-C₂₅alkoxy; C₂-C₂₅alkoxy interrupted by oxygen, sulfur or by >NR₈; C₁-C₄alkylamino, di(C₁-C₄alkyl)amino, C₁-C₂₅alkanoyl, C₁-C₂₅alkanoyloxy, C₁-C₂₅alkanoylamino; C₁-C₂₅alkylthio, C₇-C₉phenylalkyl, C₇-C₉phenylalkoxy, unsubstituted or C₁-C₄alkyl-substituted phenyl; unsubstituted or C₁-C₄alkyl-substituted phenoxy; unsubstituted or C₁-C₄alkyl-substituted C₅-C₈cycloalkyl; unsubstituted or C₁-C₄alkyl-substituted C₅-C₈cycloalkoxy; C₃-C₂₅alkanoyl interrupted by oxygen, sulfur or by >NR₈; C₁-C₂₅alkanoylcarbonyl; C₃-C₂₅alkanoylcarbonyl interrupted by oxygen, sulfur or by >NR₈; C₁-C₂₅alkylaminocarbonyl; C₃-C₂₅alkylaminocarbonyl interrupted by oxygen, sulfur or by >NR₈; di-C₁-C₂₅alkylaminocarbonyl; di-C₃-C₂₅alkylaminocarbonyl interrupted by oxygen, sulfur or by >NR₈; C₁-C₂₅alkanoyloxy; C₃-C₂₅alkanoyloxy interrupted by oxygen, sulfur or by >NR₈; C₁-C₂₅alkanoylamino, C₆-C₉cycloalkylcarbonyl, C₆-C₉cycloalkylcarbonyloxy, benzoyl or C₁-C₁₂alkyl-substituted benzoyl; benzoyloxy or

C₁-C₁₂alkyl-substituted benzoyloxy; $-\text{O}-\overset{\overset{\text{R}_{27}}{|}}{\underset{\underset{\text{R}_{28}}{|}}{\text{C}}}-\overset{\overset{\text{O}}{||}}{\text{C}}-\text{R}_9$ or $-\text{O}-\overset{\overset{\text{R}_{29}}{|}}{\underset{\underset{\text{H}}{|}}{\text{C}}}-\overset{\overset{\text{R}_{30}}{|}}{\underset{\underset{\text{R}_{31}}{|}}{\text{C}}}-\text{O}-\text{R}_{32}$;

R₂₄ is hydrogen, C₁-C₄alkyl, or unsubstituted or C₁-C₄alkyl-substituted phenyl;

R₂₅ and R₂₆ are hydrogen, C₁-C₄alkyl or phenyl, with the proviso that at least one of the radicals R₂₅ and R₂₆ is hydrogen;

R₂₇ and R₂₈ are each independently of the other hydrogen, C₁-C₄alkyl or phenyl;

R₂₉ is hydrogen or C₁-C₄alkyl;

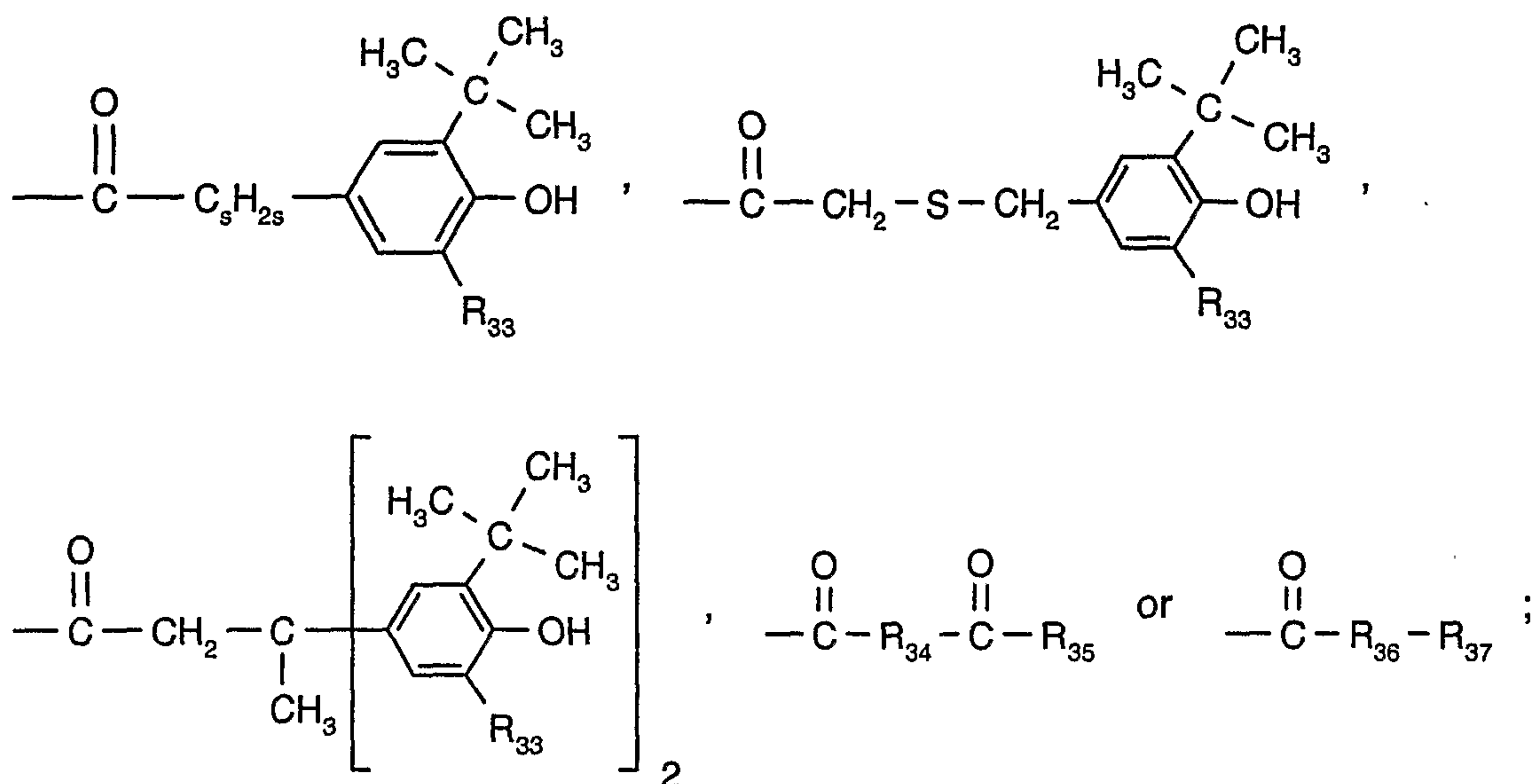
R₃₀ is hydrogen, unsubstituted or C₁-C₄alkyl-substituted phenyl; C₁-C₂₅alkyl; C₂-C₂₅alkyl interrupted by oxygen, sulfur or by >NR₈; C₇-C₉phenylalkyl unsubstituted or substituted on

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the phenyl radical by from 1 to 3 C₁-C₄alkyl groups; or C₇-C₂₅phenylalkyl interrupted by oxygen, sulfur or by >NR₈ and unsubstituted or substituted on the phenyl radical by from 1 to 3 C₁-C₄alkyl groups;

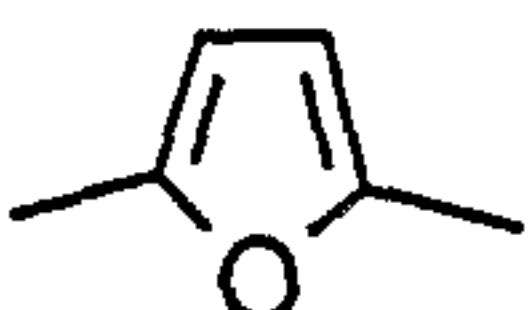
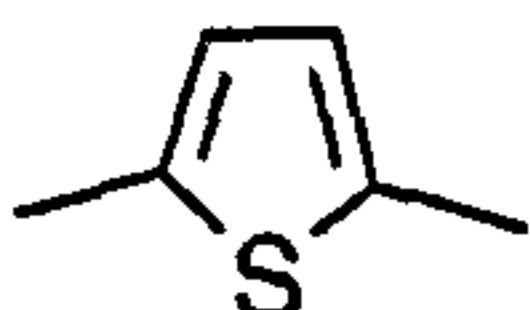
R₃₁ is hydrogen or C₁-C₄alkyl;

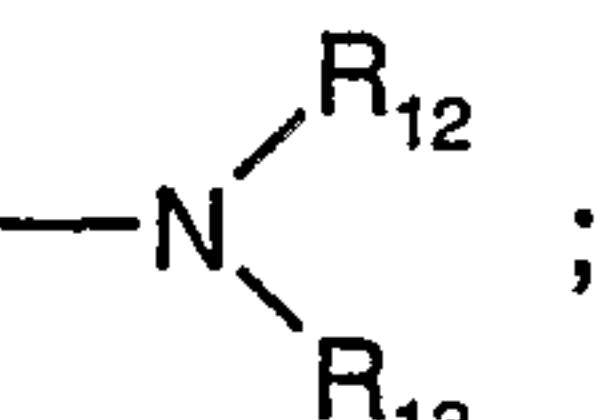
R₃₂ is hydrogen, C₁-C₂₅alkanoyl; C₃-C₂₅alkanoyl interrupted by oxygen, sulfur or by >NR₈; C₂-C₂₅alkanoyl substituted by a di(C₁-C₆alkyl) phosphonate group; C₆-C₉cycloalkylcarbonyl, thenoyl, furoyl, benzoyl or C₁-C₁₂alkyl-substituted benzoyl,

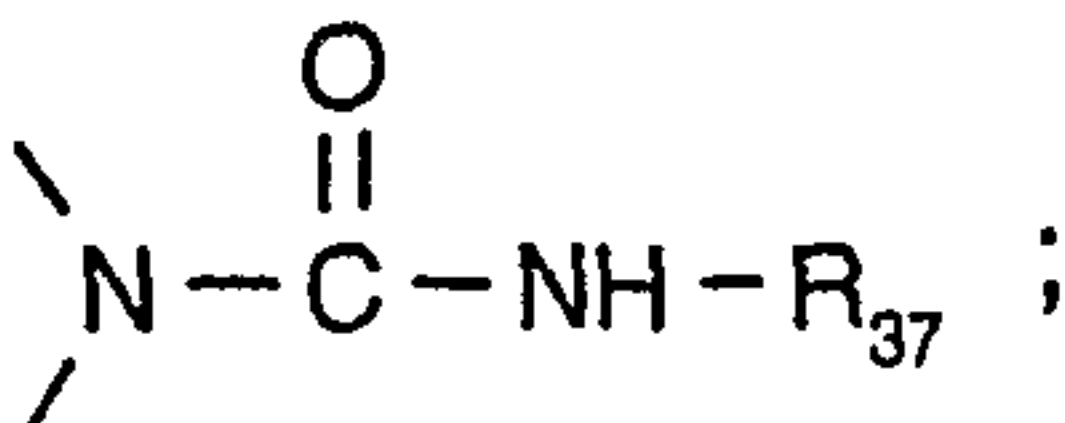


R₃₃ is hydrogen or C₁-C₈alkyl;

R₃₄ is a direct bond, C₁-C₁₈alkylene; C₂-C₁₈alkylene interrupted by oxygen, sulfur or by >NR₈; C₂-C₂₀alkylidene, C₇-C₂₀phenylalkylidene, C₅-C₈cycloalkylene, C₇-C₈bicycloalkylene,

unsubstituted or C₁-C₄alkyl-substituted phenylene,  or  ;

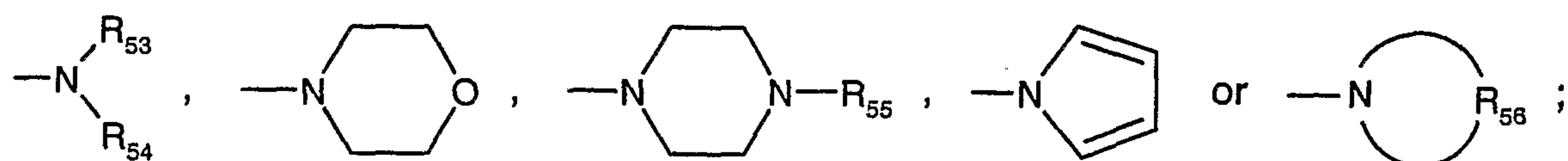
R₃₅ is hydroxy, $\left[\text{---O}^- \frac{1}{r} \text{M}^{r+} \right]$, C₁-C₁₈alkoxy or  ;

R₃₆ is oxygen, -NH- or  ;

R₃₇ is C₁-C₁₈alkyl or phenyl;

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R₅₀ is -OR₅₁, -O-C(O)-R₅₁, -SR₅₂, -S(O)R₅₂, -S(O)₂R₅₂, -N(H)R₅₃, pyrrolino, pyrrolidino,



R₅₀' is independently defined as for **R₅₀**;

R₅₁ is C₁-C₂₅alkyl, unsubstituted or substituted by -OH, -OR₈, -NH(R₈) or -N(R₈)₂; C₂-C₂₅alkyl interrupted by oxygen or by sulfur; C₇-C₉phenylalkyl, unsubstituted or C₁-C₄alkyl-substituted C₅-C₈cycloalkyl; unsubstituted or C₁-C₄alkyl-substituted phenyl;

R₅₂ is C₁-C₂₅alkyl, unsubstituted or substituted by -OH, -OR₈, -NH(R₈) or -N(R₈)₂; C₂-C₂₅alkyl interrupted by oxygen or by sulfur; C₇-C₉phenylalkyl, unsubstituted or C₁-C₄alkyl-substituted C₅-C₈cycloalkyl; unsubstituted or C₁-C₄alkyl-substituted phenyl;

R₅₃ and **R₅₄** are each independently of the other hydrogen, hydroxy; C₁-C₂₅alkyl, unsubstituted or substituted by -OH, -OR₈, -NH(R₈) or -N(R₈)₂; C₂-C₂₅alkyl interrupted by oxygen or by sulfur; C₇-C₉phenylalkyl, unsubstituted or C₁-C₄alkyl-substituted C₅-C₈cycloalkyl; or a dendrimeric, oligomeric or polymeric C₄-C₁₀₀hydrocarbon radical;

R₅₅ is C₁-C₂₅alkyl; C₂-C₂₅alkyl interrupted by oxygen or by sulfur; C₇-C₉phenylalkyl, unsubstituted or C₁-C₄alkyl-substituted C₅-C₈cycloalkyl; unsubstituted or C₁-C₄alkyl-substituted phenyl;

R₅₆ is unsubstituted or C₁-C₄alkyl-substituted C₂-C₁₂alkylene;

M is an r-valent metal cation;

p is 0, 1 or 2;

q is 1, 2, 3, 4, 5 or 6;

r is 1, 2 or 3; and

s is 0, 1 or 2.

2. A composition according to claim 1 wherein component (b) is a compound selected from the group consisting of the Mannich base compounds of formulae (Ia), (Ib), (IIa), (IIb) and (IIc).

3. A composition according to claim 1 wherein the polyester or polyamide of component (a) is 95-99.99 % by weight and the stabilizers of component (b), in total, are 5 to 0.01 % by weight, based on the total weight of (a) and (b).

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4. A composition according to claim 1 wherein the polyester of component (a) is poly(ethylene terephthalate) PET or poly(ethylene 2,6-naphthalene-2,6-dicarboxylate).
5. A composition according to claim 1 in which in the compounds of formulae (Ia), (Ib), (IIa), (IIb), (IIc), (IIIa), (IIIb), (IIIc), (IVa), (IVb) and (IVc)
 R_1 is hydrogen, C_1 - C_{25} alkyl or C_1 - C_{18} alkylene;
 R_a is C_1 - C_{18} alkylene, phenylene or naphthylene each unsubstituted or substituted by C_1 - C_4 alkyl or by fluorine; or is $-R_6-Y-R_7-$;
 R_b is $-NR_{53}$, C_1 - C_{25} alkylenedimino or C_5 - C_8 cycloalkylenediimino; and
 X is C_1 - C_{18} alkylene, $-O-$, $-NR_{10}-$ or $-S-$.
6. A composition according to claim 1 in which R_2 , R_3 , R_4 and R_5 are each independently hydrogen, fluorine, hydroxy or C_1 - C_{25} alkyl.
7. A composition according to claim 1 in which R_2 , R_3 , R_4 and R_5 are each hydrogen or tert-butyl.
8. A composition according to claim 1 in which the compounds of formulae (Ia)-(IVc) are selected from the group consisting of
 2,4-di-tert-butyl-6-(phenyl-piperidin-1-yl-methyl)-phenol,
 2,4-di-tert-butyl-6-(dimethylamino-phenyl-methyl)-phenol,
 2,6-bis-dimethylaminomethyl-4-(1,1,3,3-tetramethyl-butyl)-phenol,
 2,4-di-tert-butyl-6-piperidin-1-ylmethyl-phenol,
 2,6-di-tert-butyl-4-(phenyl-piperidin-1-yl-methyl)-phenol,
 2,6-di-tert-butyl-4-piperidin-1-yl-methyl-phenol,
 3-[3-tert-Butyl-4-hydroxy-5-(phenyl-piperidin-1-yl-methyl)-phenyl]-propionic acid methyl ester,
 2,4-di-tert-butyl-6-dimethylaminomethyl-phenol,
 2,4-di-tert-butyl-6-N-morpholino-4-ylmethyl-phenol,
 2,4-di-tert-butyl-6-di-n-butylaminomethyl-phenol,
 2,4-di-tert-butyl-6-cyclohexylaminomethyl-phenol,
 2,6-bis-dimethylaminomethyl-4-(1,1,3,3-tetramethyl-butyl)-phenol,
 2,4,6-tris-dimethylaminomethyl-phenol,
 2,4-bis-dimethylaminomethyl-6-methyl-phenol,

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2,6,2',6'-tetrakis(dimethylaminomethyl)-4,4'-isopropylidene-diphenol,
1-(N-morpholino-4-yl-methyl)-2-naphthol,
n-butyl-bis-(2-hydroxy-1-naphthylmethyl)-amine,
3,5-di-tert-butyl-2-hydroxy-benzyl-acetate,
2,4-di-tert-butyl-6-methoxymethyl-phenol and
2,4-bis-(n-octadecylthiomethyl)-6-methyl-phenol.

9. A mono- or multi-layered plastic container or film, stabilized against the formation of aldehydic contaminants during melt processing of said container or film, comprising at least one layer which comprises (a) a polyester or polyamide, and (b) an effective stabilizing amount of at least one compound selected from the group consisting of the Mannich base compounds of formulae (Ia), (Ib), (IIa), (IIb), (IIc), (IIIa), (IIIb), (IIIc), (IVa), (IVb) and (IVc) according to claim 1.

10. A plastic container according to claim 9 which is a rigid bottle.

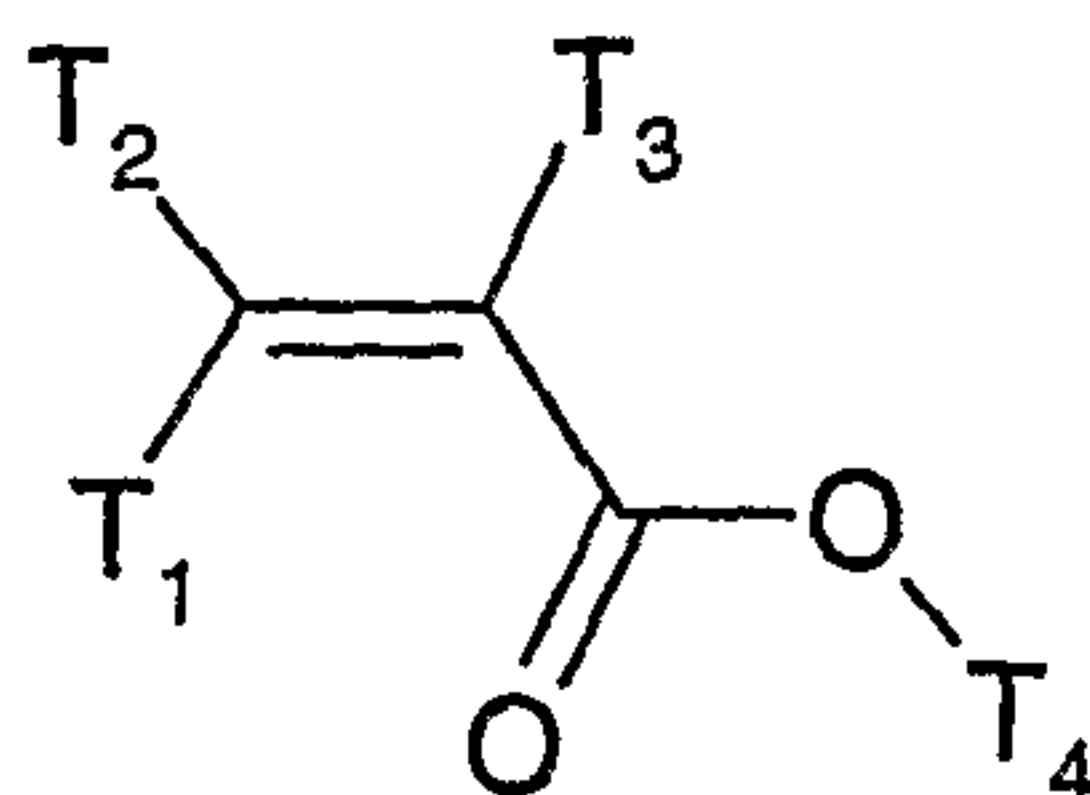
11. A process for preventing the formation of aldehydic contaminants during melt processing of a polyester or polyamide which comprises incorporating into said polyester or polyamide an effective stabilizing amount of at least one compound selected from the group consisting of the Mannich base compounds of formulae (Ia), (Ib), (IIa), (IIb), (IIc), (IIIa), (IIIb), (IIIc), (IVa), (IVb) and (IVc) according to claim 1.

12. A composition, stabilized against the formation of aldehydic contaminants during melt processing of said composition, which comprises

- (a) a polyester or polyamide, and
- (b) an effective stabilizing amount of at least one compound selected from the group consisting of the Mannich base compounds of formulae (Ia), (Ib), (IIa), (IIb), (IIc), (IIIa), (IIIb), (IIIc), (IVa), (IVb) and (IVc) according to claim 1; and optionally
- (c) an effective stabilizing amount of a polymer which is poly(vinyl alcohol) or an ethylene/vinyl alcohol copolymer; and optionally
- (d) an effective stabilizing amount of a polyhydric alcohol; and optionally
- (e) an effective stabilizing amount of a polymer which is polyacrylamide, polymethacrylamide or an acrylamide or methacrylamide copolymer with at least one ethylenically unsaturated comonomer; and optionally

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- (f) an effective stabilizing amount of at least one compound selected from the group consisting of
- i.) hydroxylamine stabilizers,
 - ii.) substituted hydroxylamine stabilizers,
 - iii.) nitron stabilizers, and
 - iv.) amine oxide stabilizers; and optionally
- (g) an effective stabilizing amount of at least one polymer or copolymer derived from at least one 2-propenoic acid ester monomer wherein the polyhydric alcohol of (d) is of the formula $G-(OH)_a$ where a is 2 to 4000, and G is a hydrocarbyl moiety, and wherein the polymer or copolymer of component (g) is of the formula



where T_1 , T_2 and T_3 are independently hydrogen, straight or branched chain alkyl of 1 to 24 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, aralkyl of 7 to 15 carbon atoms, or said alkyl, cycloalkyl or aralkyl which is further substituted by one or more $-OT_5$, $-NT_6T_7$, $-CO_2T_8$ or $-CONT_9T_{10}$ wherein T_5 , T_6 , T_7 , T_8 , T_9 , and T_{10} are independently hydrogen or straight or branched chain alkyl of 1 to 18 carbon atoms; or T_1 , T_2 , T_3 are independently a group $-CO_2T_4$, T_4 is a polyhydric alcohol substituent of the formula $-E-(OH)_a$ where a is 2 to 4000, and E is a hydrocarbylene moiety.

13. A composition according to claim 12 in which the alcohols of component (d) are selected from the group consisting of pentaerythritol, dipentaerythritol and trimethylolpropane and the compounds of component (f) are selected from the group consisting of the N,N-di(alkyl)-hydroxylamine produced by the direct oxidation of N,N-di(hydrogenated tallow)amine, O-allyl-N,N-dioctadecylhydroxylamine, N-octadecyl- α -heptadecylnitron and di(C_{16} - C_{18})alkyl methyl amine oxide.

14. A composition, stabilized against the formation of aldehydic contaminants during melt processing of said composition, which comprises

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- (a) a polyester or polyamide, and
- (b) an effective stabilizing amount of at least one compound selected from the group consisting of the Mannich base compounds of formulae (Ia), (Ib), (IIa), (IIb), (IIc), (IIIa), (IIIb), (IIIc), (IVa), (IVb) and (IVc) according to claim 1, and
- (c) at least one compound selected from the group consisting of the amine compounds.

15. A composition, stabilized against the formation of aldehydic contaminants during melt processing of said composition, which comprises

- (a) a polyester or polyamide, and
- (b) an effective stabilizing amount of at least one compound selected from the group consisting of the thermal products of the Mannich base compounds of formulae (Ia), (Ib), (IIa), (IIb), (IIc), (IIIa), (IIIb), (IIIc), (IVa), (IVb) and (IVc) according to claim 1, and
- (c) at least one compound selected from the group consisting of the amine compounds.

16. A composition, stabilized against the formation of aldehydic contaminants and against yellowing during melt processing of said composition, which comprises

- (a) a polyester or polyamide, and
- (b) an effective stabilizing amount of at least one compound selected from the group consisting of the Mannich base compounds of formulae (Ia), (Ib), (IIa), (IIb), (IIc), (IIIa), (IIIb), (IIIc), (IVa), (IVb) and (IVc) according to claim 1, and
- (c) one or more colorants selected from the group consisting of pigments and dyes.

17. A fiber, film or molded article stabilized against the formation of aldehydic contaminants during melt processing of said fiber, film or article, which comprises

- (a) a polyester or polyamide, and
- (b) an effective stabilizing amount of at least one compound selected from the group consisting of the Mannich base compounds of formulae (Ia), (Ib), (IIa), (IIb), (IIc), (IIIa), (IIIb), (IIIc), (IVa), (IVb) and (IVc) according to claim 1.

18. A process for the preparation of a stabilized polyester or polyamide that is low in the generation of aldehydes during subsequent melt processing, which process comprises preparing the polyester or polyamide from its monomer components in the presence of an effective amount of a stabilizer selected from the group consisting of the Mannich base com-

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pounds of formulae (Ia), (Ib), (IIa), (IIb), (IIc), (IIIa), (IIIb), (IIIc), (IVa), (IVb) and (IVc) according to claim 1.

19. A process according to claim 18 for the preparation of a stabilized polyester that is low in the generation of aldehydes during subsequent melt processing, which process comprises reacting one or more diacids with one or more diols in an esterification process, and/or one or more diesters with one or more diols in a transesterification process in the presence of an effective amount of a stabilizer selected from the group consisting of the Mannich base compounds of formulae (Ia), (Ib), (IIa), (IIb), (IIc), (IIIa), (IIIb), (IIIc), (IVa), (IVb) and (IVc).

20. A polyester or a polyamide obtained by the process according to claim 18.

21. Use of component (b) according to claim 1 for preventing the formation of aldehydic contaminants during melt processing of a polyester or a polyamide.