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(72) **Inventeurs/Inventors**:
Mühlebach, Andreas, CH;
Simon, Hubert, FR
(73) **Propriétaire/Owner**:
VANTICO AG, CH
(74) **Agent**: FETHERSTONHAUGH & CO.

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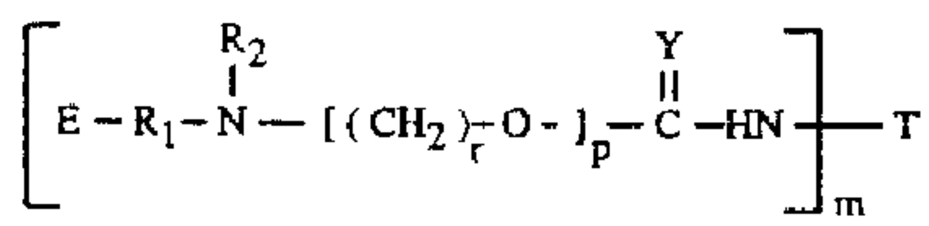
(54) **Title**: ADHESION PROMOTERS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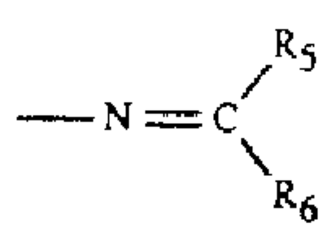
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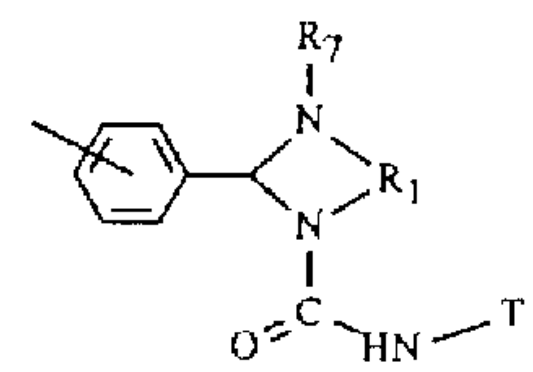
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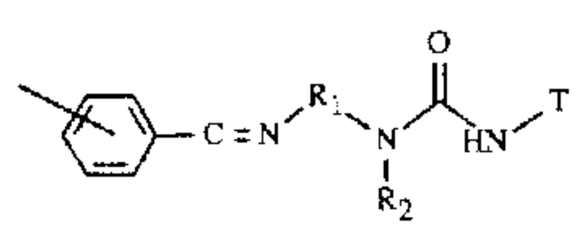
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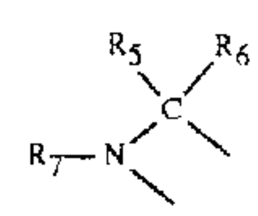
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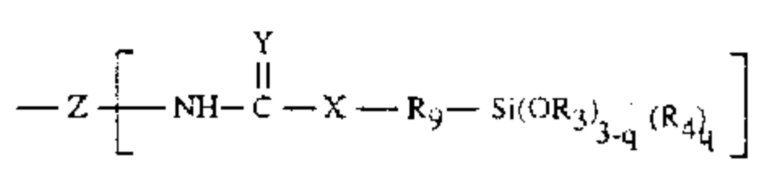

(IV)

(57) **Abrégé/Abstract**:
Compounds of the general formula I (see formula I) in which R_1 is C_2-C_3alkylene and R_2 is hydrogen, C_1-C_6alkyl which is unsubstituted or substituted by -OH, -CN or -$Si(OR_3)_{3-q}(R_4)_q$ or is C_2-C_6alkenyl, in which R_3 is C_1-C_4alkyl or two radicals R_3 together are C_1-C_4alkylene, R_4 is C_1-C_4alkyl or phenyl and q can have values from 0 to 2, furthermore E is a radical of the formula (see formula II) in which R_5 and R_6, independently of one another, are hydrogen, C_1-C_4alkyl, aryl, ethenyl which is substituted by aryl, heteroaryl or radicals of the formulae IIa or IIb (see formula IIa or IIb) with the proviso that at least one of the radicals R_5 or R_6 is aryl, ethenyl which is substituted by aryl, heteroaryl or a radical of the formulae IIa or IIb or E together with R_2 is a radical of the formula (see formula III) in which R_7 is hydrogen, C_1-C_4alkyl or -R_9-$Si(OR_3)_{3-q}(R_4)_q$ and R_3,R_4 and q are as defined above, and R_9 is C_1-C_8alkylene, and Y is oxygen or sulfur; furthermore, T is a radical of the formulae -R_9-$Si(OR_3)_{3-q}(R_4)_q$ or (see formula IV) or, if R_7 is a radical of the formula -R_9-$Si(OR_3)_{3-q}(R_4)_q$ and m is greater than or equal to 2, is an m-valent radical Z in which R_3, R_4, R_9, Y and q are as defined above, X is -S- or -NH- and Z is an organic radical which is derived from a polyisocyanate or a polyisothiocyanate having at least 2 NCO or NCS groups, and r is 1, 2 or 3 and p is 0 or l and m can have values of greater than or equal to 1 and n can have values of greater than or equal to 1, are suitable, for example, as adhesion promoters, in particular for one- and two-component polyurethane resin systems.

30043-36

Adhesion promoters

Abstract

Compounds of the general formula I

$$\left[E-R_1-\overset{\overset{\displaystyle R_2}{|}}{N}-[(CH_2)_r-O-]_p-\overset{\overset{\displaystyle Y}{\|}}{C}-HN \right]_m T \quad , \qquad (I)$$

in which

R_1 is C_2-C_3alkylene and

R_2 is hydrogen, C_1-C_6alkyl which is unsubstituted or substituted by -OH, -CN or $-Si(OR_3)_{3-q}(R_4)_q$ or is C_2-C_6alkenyl, in which

R_3 is C_1-C_4alkyl or two radicals R_3 together are C_1-C_4alkylene,

R_4 is C_1-C_4alkyl or phenyl and

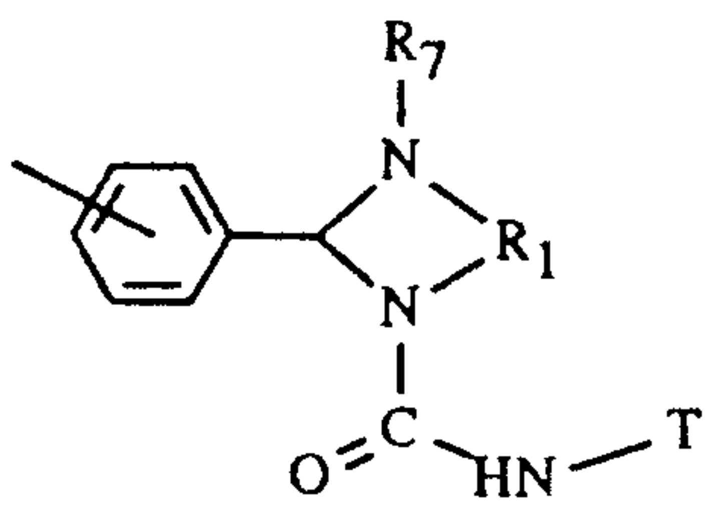
q can have values from 0 to 2, furthermore

E is a radical of the formula

$$-N=C\begin{matrix} R_5 \\ R_6 \end{matrix} \quad ,$$

in which

R_5 and R_6, independently of one another, are hydrogen, C_1-C_4alkyl, aryl, ethenyl which is substituted by aryl, heteroaryl or radicals of the formulae IIa or IIb



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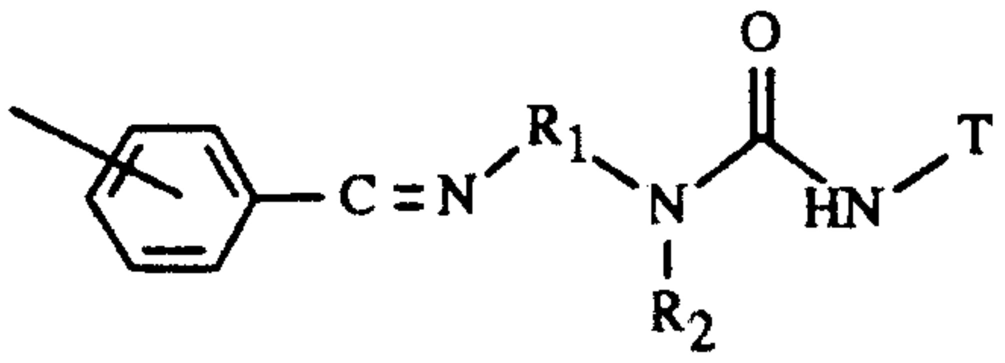
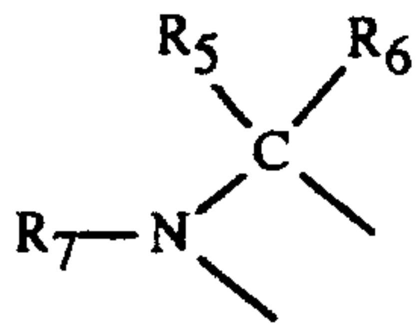


(IIb)

with the proviso that at least one of the radicals R_5 or R_6 is aryl, ethenyl which is substituted by aryl, heteroaryl or a radical of the formulae IIa or IIb or

E together with R_2 is a radical of the formula



in which R_7 is hydrogen, C_1-C_4alkyl or $-R_9-Si(OR_3)_{3-q}(R_4)_q$ and R_3,R_4 and q are as defined above, and

R_9 is C_1-C_8alkylene,

and

Y is oxygen or sulfur; furthermore,

T is a radical of the formulae $-R_9-Si(OR_3)_{3-q}(R_4)_q$ or

$$-Z\left[-NH-\overset{\overset{\displaystyle Y}{\|}}{C}-X-R_9-Si(OR_3)_{3-q}(R_4)_q\right]_n$$

or, if R_7 is a radical of the formula $-R_9-Si(OR_3)_{3-q}(R_4)_q$ and m is greater than or equal to 2, is an m-valent radical Z in which R_3, R_4, R_9, Y and q are as defined above,

X is -S- or -NH- and

Z is an organic radical which is derived from a polyisocyanate or a polyisothiocyanate having at least 2 NCO or NCS groups, and

r is 1, 2 or 3 and

p is 0 or 1 and

m can have values of greater than or equal to 1 and

n can have values of greater than or equal to 1,

are suitable, for example, as adhesion promoters, in particular for one- and two-component polyurethane resin systems.

K-18444/A

Adhesion promoters

The present invention relates to nitrogen-containing silane compounds and polyurethane resins containing these silane compounds as adhesion promoters.

The adhesion of cured polyurethanes to various substrates, such as glass, plastic or metal, is in many industrial applications unsatisfactory, which has led to the use of primers. This makes it possible to obtain a good bond between the polyurethane and the substrate. This bond is hardly impaired by high moisture, elevated temperatures and high mechanical stress. Examples of primers which have proven suitable are aminoalkylalkoxysilanes (cf. Plueddemann et al. "Silane Coupling Agents", Plenum Press, NY [1982]). However, the most effective aminosilane adhesion promoters cannot be used as incorporated adhesion promoters in moisture-curing polyurethanes in unmodified form, since the amine groups react completely with isocyanate groups. Therefore, DE-A 34 14 877 has described ketimines and aldimines of aminoalkylsilanes, which can be added to polyurethane adhesives without impairing their shelf life.

Furthermore, US-A 3,787,416 and 4,289,869 have described cyclic aminals as hardeners for polyurethane resins. Furthermore, the reaction of cyclic aminals with isocyanates to give adducts which are suitable as hardeners for polyurethane resins is disclosed in US-A 4,404,379. However, these aminals or aminal adducts do not contain silane-containing groups.

A group of compounds has now been found which can be added to 1- or 2-component polyurethane resin adhesives, sealing compositions, coating compositions and insulating materials, resulting in significantly improved adhesion to glass, metal, coated steel and plastics while at the same time not impairing or even increasing the curing rate.

The present invention relates to compounds of the general formula I

$$\left[E-R_1-\overset{\overset{\displaystyle R_2}{|}}{N}-[(CH_2)_r-O-]_p-\overset{\overset{\displaystyle Y}{\|}}{C}-HN \right]_m T \quad , \qquad (I)$$

in which

R_1 is C_2-C_3alkylene and

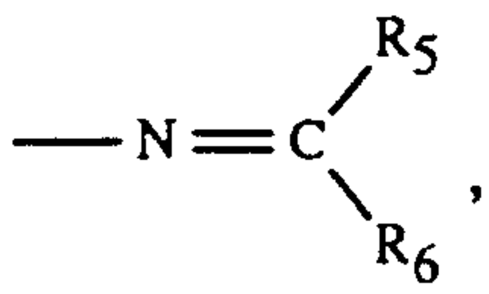
R_2 is hydrogen, C_1-C_6alkyl which is unsubstituted or substituted by -OH, -CN or $-Si(OR_3)_{3-q}(R_4)_q$ or is C_2-C_6alkenyl, in which

R_3 is C_1-C_4alkyl or two radicals R_3 together are C_1-C_4alkylene,

R_4 is C_1-C_4alkyl or phenyl and

q can have values from 0 to 2, furthermore

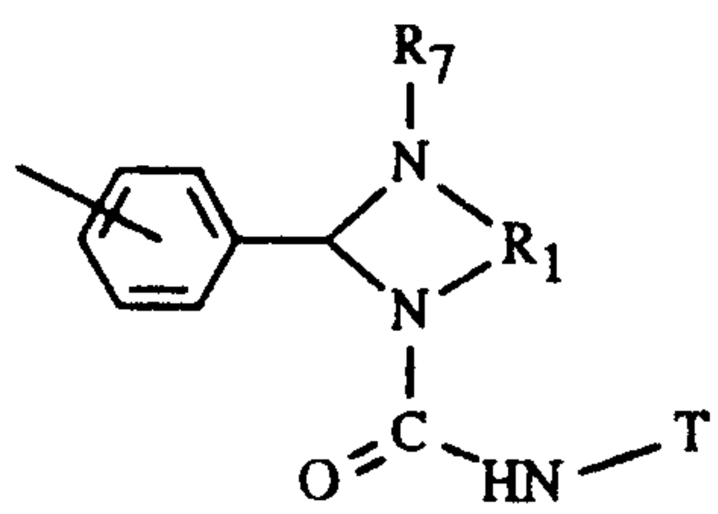
E is a radical of the formula



,

in which

R_5 and R_6, independently of one another, are hydrogen, C_1-C_4alkyl, aryl, ethenyl which is substituted by aryl, heteroaryl or radicals of the formulae IIa or IIb



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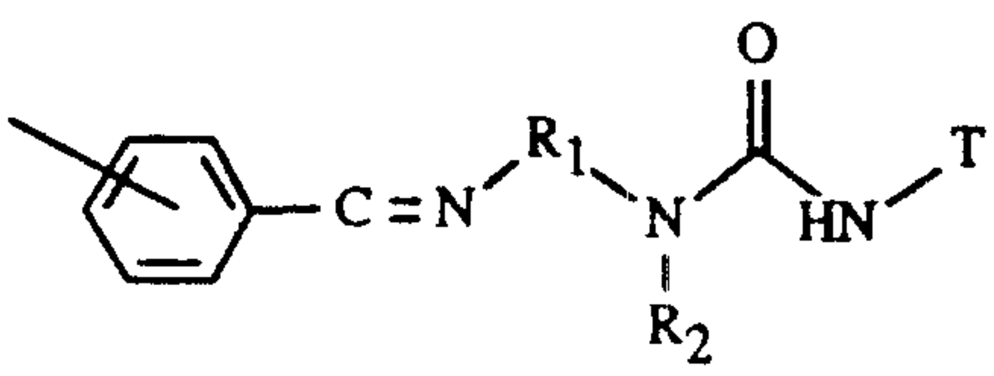
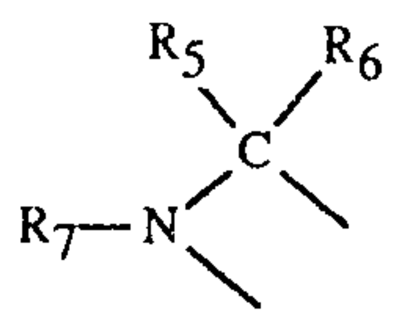


(IIb)

with the proviso that at least one of the radicals R_5 or R_6 is aryl, ethenyl which is substituted by aryl, heteroaryl or a radical of the formulae IIa or IIb or

E together with R_2 is a radical of the formula



in which R_7 is hydrogen, C_1-C_4alkyl or -R_9-$Si(OR_3)_{3-q}(R_4)_q$ and R_3, R_4, R_5, R_6 and q are as defined above, and

R_9 is C_1-C_8alkylene,

and

Y is oxygen or sulfur; furthermore,

T is a radical of the formulae -R_9-$Si(OR_3)_{3-q}(R_4)_q$ or

$$-Z\left[NH-\overset{\overset{\displaystyle Y}{\|}}{C}-X-R_9-Si(OR_3)_{3-q}(R_4)_q\right]_n$$

or, if R_7 is a radical of the formula -R_9-$Si(OR_3)_{3-q}(R_4)_q$ and m is greater than or equal to 2, is an m-valent radical Z in which R_3, R_4, R_9, Y and q are as defined above,

X is -S- or -NH- and

Z is an organic radical which is derived from a polyisocyanate or a polyisothiocyanate having at least 2 NCO or NCS groups, and

r is 1, 2 or 3 and

p is 0 or 1 and

m can have values of greater than or equal to 1 and

n can have values of greater than or equal to 1.

R_3, R_4, R_5, R_6 and R_7 as C_1-C_4alkyl or R_2 as C_1-C_6alkyl are, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl and tert-butyl and in the case of R_2 additionally n-pentyl or n-hexyl.

The preferred meaning of R_3 and R_4 as alkyl is methyl and ethyl, in particular methyl.

Examples of R_5 and R_6 as aryl are phenyl or naphthyl, which can be unsubstituted or substituted by C_1-C_4alkyl, C_2-C_4alkenyl, in particular -$CH=CH_2$, C_1-C_4alkoxy, -NO_2 and halogen, in particular chlorine or bromine. Examples are methylphenyl, ethylphenyl, propylphenyl, isopropylphenyl, butylphenyl, isobutylphenyl and tert-butylphenyl; methoxyphenyl, ethoxyphenyl and butoxyphenyl; nitrophenyl, fluorophenyl, chlorophenyl, bromophenyl, dichlorophenyl and dibromophenyl and styryl.

R_5 and R_6 as heteroaryl are in particular heteroaromatics having 5 or 6 ring members and one or two N, O or S atoms, which, if desired, can be benzo-fused, such as pyridyl, thienyl, benzothienyl, furyl, pyrrolyl, imidazolyl, pyrazolyl, pyrazinyl, pyrimidinyl and quinolyl.

R_1 as C_2-C_3alkylene, two radicals R_3 together as C_1-C_4alkylene and R_9 as C_1-C_8alkylene are straight-chain or branched alkylene, the straight-chain alkylene being preferred. Examples are methylene, ethylene, propylene, trimethylene, tetramethylene, 2-methyl-1,3-trimethylene for R_3 and R_9 and in the case of R_9 additionally pentamethylene, 2-methyl-1,4-tetramethylene, 3-propyl-1,3-trimethylene, 1,6-hexamethylene, 1,7-heptamethylene, 1,8-octamethylene or 2-ethyl-1,2-hexamethylene, the meaning of R_1 being limited to ethylene, propylene and trimethylene.

Preferably, R_9 is C_1-C_4alkylene, in particular trimethylene or ethylene.

R_2 as C_2-C_6alkenyl is straight-chain or branched alkenyl, preferably straight-chain alkenyl containing one or more, but preferably one, double bond, such as ethenyl (vinyl), 2-propenyl (allyl), n-butenyl, 1,3-butadienyl, i-pentenyl, n-pentenyl or n-hexenyl.

R_2 as C_1-C_6alkyl substituted by OH, CN or $-Si(OR_3)_{3-q}(R_4)_q$ groups can be mono- or polysubstituted, monosubstitution being preferred. The substitution can be present in any possible position, although the terminal position is preferred.

Preferably, R_2 is C_1-C_4alkyl, in particular methyl.

Preferably, the parameter p in formula I has the value 0.

Also preferably, the parameter q has the value 0.

The radical Z is derived from a polyisocyanate or polyisothiocyanate having at least 2 NCO or NCS groups. This NCO or NSC functionality of greater than or equal to 2 of the polyisocyanate or polyisothiocyanate which is possible according to the invention is achieved by converting, for example, polyamines, such as amino-terminal polyether polyols, to polyisocyanates or polyisothiocyanates having a functionality of greater than or equal to 2 by phosgenation or thiophosgenation. The polyisocyanates or polyisothiocyanates thus obtainable can either be used directly or first converted with diols, polyols, dithiols, diamines or polyamines to NCO- or NCS-terminal prepolymers. The polyisocyanates obtainable in the manner described below can also be reacted in this way.

A further possibility to prepare polyisocyanates having an NCO functionality of greater than/equal to 2 consists in oligomerisation of diisocyanates. Thus, for example, diisocyanates, such as hexamethylene diisocyanate, can be converted by partial hydrolysis to products containing biuret groups (for example Desmodur® N100 from Bayer).

Furthermore, diisocyanates, such as hexamethylene diisocyanate, can be partially trimerised, leading to the formation of higher functional polyisocyanates containing isocyanurate rings (for example Desmodur® N3200 from Bayer).

Chain-lengthening by reaction of diisocyanates with polyfunctional compounds having acidic hydrogen and a functionality of greater than or equal to 2, such as triols, tetrols, pentols, triamines, polyamines or polythiols, also leads to polyisocyanates having an NCO functionality of greater than/equal to 2. There, the NCO/OH ratio is greater than 1, but preferably greater than 3:1, in particular greater than 10:1.

Suitable diisocyanates are not only aromatic but also aliphatic, heterocyclic or monocyclic and polycyclic bifunctional isocyanate compounds. Examples of compounds of this type are toluylene diisocyanate, diphenylmethane diisocyanate, napthylene diisocyanate, xylylene diisocyanate, hexamethylene diisocyanate, trimethylhexamethylene diisocyanate, isophorone diisocyanate or dicyclohexylmethane diisocyanate.

The parameters m and n have, advantageously independently of one another, values from 1 to 49, preferably 1 to 9, particularly preferably 1 to 5 and very particularly preferably 1, 2 and 3. The sum of n + m is advantageously 2 to 50, preferably 2 to 10, in particular 2 to 6.

The radical Z has preferably an average molecular weight M_n of less than 10 000, in particular an M_n of less than 4000.

Preference is given to compounds of the formula I in which Y is oxygen.

Preferred compounds have the formula I in which Z is derived from an aliphatic, cycloaliphatic, aliphatic/aromatic, aromatic or heterocyclic polyisocyanate or polyisothiocyanate having 2 or more than 2 NCO or NCS groups, it being possible for this radical Z to contain, if desired, one more ester, ether, urethane, thiourethane, isocyanurate, urea or biuret functions.

Particularly preferred compounds have the formula I in which Z is derived from an aliphatic or mixed aliphatic/aromatic polyisocyanate having ≥ 2 NCO groups, it being possible for this radical Z to contain, if desired, a total of one or two ester, ether, urethane, thiourethane, isocyanurate, urea or biuret functions.

In the compounds of the formula I in which Z has ether oxygen atoms, Z can be a monoether or oligoether, for example a group of the formula $-(CH[CH_3]-CH_2-O)_y-$ or $-(CH_2-CH_2-CH_2-CH_2-O)_y-$, in which y is a number from 1 to 80, preferably from 1 to 20.

In the compounds of the formula I in which the radical Z comprises urethane or thiourethane groups, Z is a derivative which is obtainable by reaction of polyols with compounds containing isocyanate or isothiocyanate groups. This is also understood to include radicals which contain not only one or more urethane groups but also one or more thiourethane groups, for example those containing a bridging member of the formula

$$—O-\overset{O}{\overset{\|}{C}}-HN—D—NH-\overset{O}{\overset{\|}{C}}-O— \quad \text{or} \quad —S-\overset{O}{\overset{\|}{C}}-HN—D—NH-\overset{O}{\overset{\|}{C}}-S— \quad \text{or}$$

$$—S-\overset{O}{\overset{\|}{C}}-HN—D—NH-\overset{O}{\overset{\|}{C}}-O—$$

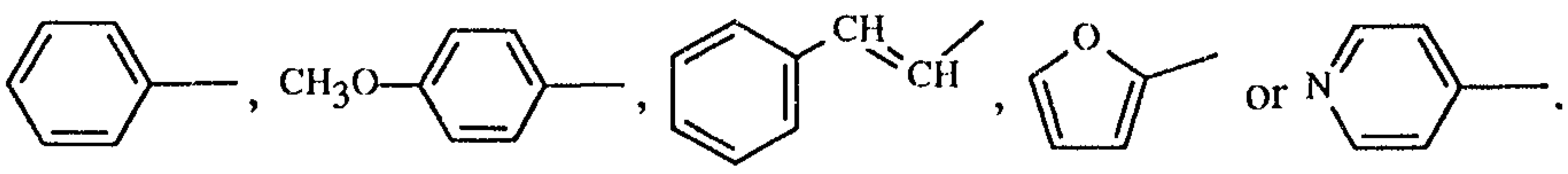
, in which D is the radical of the polyol.

Examples of polyols which can also be used are OH-terminal polyethers or polyesters.

The radical Z in preferred compounds of the formula I contains two ester, urethane, isocyanurate, urea or biuret functions, but particularly preferred compounds only one. The ether functions represent a certain exception, since, as shown above, they are capable of forming oligoether bridging members. Compounds of this type can therefore contain up to 80, preferably up to 20, ether functions.

Preference is given to compounds of the formula I in which R_1 is propylene.

Particular preference is given to compounds of the formula I in which at least one of the radicals R_5 or R_6 is a group of the formulae



A further preferred embodiment relates to compounds of the formula I in which T is a radical of the formulae $-R_9-Si(OR_3)_{3-q}(R_4)_q$ or

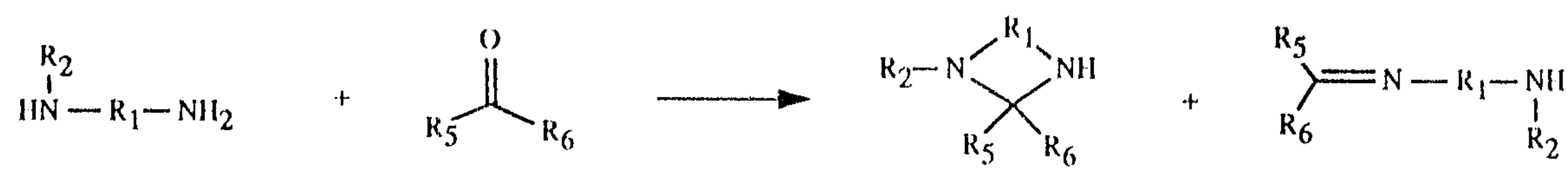
$$-Z\left[-NH-\overset{\overset{\displaystyle Y}{\|}}{C}-X-R_9-Si(OR_3)_{3-q}(R_4)_q\right]_n,$$

in particular those in which at least one radical X is -S-.

Special preference is given to compounds of the formula I in which p and q are 0, m is 1 and n is 2, Y is oxygen, X is -S-, R_1 and R_9 are propylene, R_2 and R_3 are methyl, R_5 is phenyl and R_6 is hydrogen.

The compounds of the formula I are prepared by processes known per se, which can be most simply illustrated by means of the following reaction schemes.

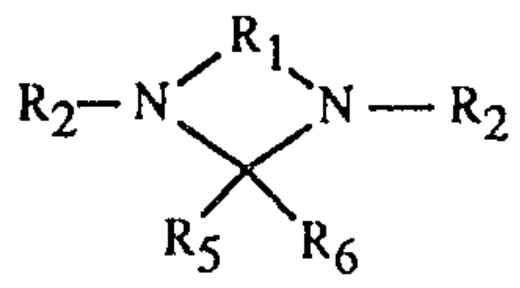
I. Amine portion of the aminal or imine



(A) (B) (C) (D)

This preparation is carried out, for example, in the manner described in US-A 4,404,379. Starting materials (A) and (B) are known compounds, some of them being commercially available, or can be prepared in a simple, known manner. Suitable starting materials (A) are in particular 3-methylaminopropylamine and 3-(2-aminoethylamino)propyltrimethoxy-silane. Examples of suitable starting materials (B) are the carbonyl compounds benzaldehyde, 4-pyridinecarboxaldehyde, benzophenone, cinnamaldehyde, furfural, p-anisaldehyde or also terephthaldehyde.

Aminals of the formula (E)



(E)

can be prepared by reaction of (C) with suitable compounds containing reactive double bonds, for example acrylonitrile, using the process described in EP-A 70 536.

Aminals (C) and (E) thus prepared can be reacted in a further step with a polyisocyanate Z-$(NCO)_n$ or a polyisothiocyanate Z-$(NCS)_n$, in which n is greater than or equal to 2.

II. Silane portion

The amino- or mercaptoalkoxysilanes used according to the invention are compounds which are known per se. Some are commercially available, or they can be prepared by methods known per se. Compounds of this type are described in detail, for example, in "Silane Coupling Agents" by E.P. Plueddemann, Plenum Press, New York (1982).

III. Polyisocyanate Z-$(NCO)_{\geq 2}$ or polyisothiocyanate Z-$(NCS)_{\geq 2}$

These isocyanates are prepared by methods known from the literature, such as are described in US-A 3,492,330; 3,394,164 and 3,567,763; in DE-A 19 29 034 and 20 04 048; in German patents 10 22 789; 12 22 067; 11 01 394; 10 27 394 and 12 31 688; in British patents 994,890; 889,050; 956,474 and 1,072,956 or in Belgian patent 723,640.

The polyisothiocyanates can be prepared analogously. Instead of the diisocyanates, the corresponding diisothiocyanates are used as starting materials. Aliphatic starting materials can be prepared by the methods described in US-A 3,787,472 and aromatic starting materials by the methods described in "Org. Syntheses"; Collective Volume 1, p. 447, John Wiley, New York (1948).

IV. Conversion of the polyisocyanates obtained by the above process III with the aminals (C) and/or (E) and with the silanes obtained by process II to the compounds of the formula I.

The reaction of the polyisocyanates or polyisothiocyanates with the other two components can be carried out in succession or simultaneously. In the stepwise reaction, first the aminal compound can be reacted with the polyisocyanate or polyisothiocyanate and then the adduct can be reacted with the alkoxysilane or vice versa. In this reaction, it is also possible to form polyisocyanate or -thiocyanate adducts with different aminal or silane components, it being possible to react the various components alternately with one another, i.e., for example, first adduct formation with a silane, then adduct formation with the aminal and finally adduct formation with the second silane.

The reaction can be carried out in the absence of solvents, although, as a rule, one or all components are diluted with a suitable inert solvent, for example xylene, in order, for example, to adjust the viscosity to the requirements.

The addition reaction itself is advantageously carried out at temperatures of between 15°C and 200°C, but preferably at temperatures of between 30°C and 140°C.

The course of the reaction can be monitored by infrared spectroscopy or titration.

It is also possible to use catalysts of the type known per se in the addition reactions, for example tertiary amines such as triethylamine, N-methylmorpholine, N,N,N',N'-tetramethylethylenediamine or 1,4-diazabicyclo[2.2.2]octane. Organometallic compounds, in particular organic tin compounds, can also be used as catalysts.

Examples of organic tin compounds are tin(II) salts of carboxylic acids, for example tin(II) acetate, tin(II) octanoate and tin(II) laurate, or the dialkyltin salts of carboxylic acids, for example dibutyltin diacetate, dibutyltin dilaurate or dioctyltin diacetate.

The stoichiometric ratios during the addition reaction of the aminal and silane components with the polyisocyanates or -thiocyanates are maintained at such a value that the ratio of the NH groups of the aminals and the NH_2 or SH groups of the silanes is approximately equimolar with respect to the NCO or NCS groups of the polyisocyanates or -thiocyanates. The adduct can still contain free NCO or NCS groups. Preferably, however, no free NCO or NCS group is present.

The ratio of aminal or urea imine radicals to silane radicals in the compounds according to the invention of the formula I can be controlled by the stoichiometric ratio of the starting materials during the addition reaction. For this purpose, the aminal or silane compound is reacted with the polyisocyanate or -thiocyanate in separate steps. As a rule, the first step takes place at a ratio of NH or SH groups to NCO or NCS groups of less than 1. The preferred aminal-NH/NCO or NCS ratio is between 1:2 and 1:6, in particular between 1:3 and 1:5. The preferred ratio of silane-NH_2/NCO or silane-SH/NCO or NCS groups is between 2:3 and 1:5, in particular between 2:3 and 1:2.

As a rule, the remaining free NCO or NCS groups are reacted completely in the second step with the aminal-NH or silane-NH_2 or -SH groups. To this end, the stoichiometric ratio of the groups containing acidic hydrogen to the NCO or NCS groups is greater than or equal to 1, preferably 4:1 to 1:1, in particular 2:1 to 1:1.

However, it is also possible to react only a portion of the remaining free NCO or NCS groups in the second step. In this case, the same stoichiometric ratios as in the first addition step apply. Such a procedure is preferably used when two or more different aminal or silane compounds are added.

The compounds according to the invention can be used as adhesion promoters in substrates such as polyurethane resins. Their use is particularly effective in moisture-curing polyurethane resins which are used as adhesives, sealing compositions, coating compositions or insulating materials. If used in adhesives, the compounds according to the invention have properties which enable them to be used in two-component and very particularly in one-component systems. By using the compounds according to the invention as adhesion promoters in the substrates mentioned, a pretreatment of the surfaces to be bonded with a primer is made superfluous. Suitable use examples are the bonding of windscreens and headlights in automobile construction. Compounds of the formula I in which m is greater than or equal to 2 can furthermore be used as moisture-activated curing agents for the substrates mentioned. Moreover, compounds of the formula I can be used as primers for the pretreatment of the substrate.

A moisture-curing polyurethane as the substrate contains, as the main component, polyfunctional isocyanates and/or polyurethane prepolymers. Suitable compounds are both aromatic as well as aliphatic, monocyclic as well as polycyclic, polyfunctional isocyanate compounds. Thus, according to a first embodiment, the aromatic isocyanate compound used is toluylene diisocyanate or diphenylmethane diisocyanate. Technical grade diphenylmethane diisocyanate containing higher functional diisocyanates and having an isocyanate group functionality of greater than 2 is particularly suitable. A further suitable aromatic diisocyanate is xylylene diisocyanate. In addition to these, a large number of aliphatic isocyanates having a functionality of 2 and higher can be used. Examples of these in the form of cyclic aliphatic diisocyanates are isophorone diisocyanate and dicyclohexylmethane diisocyanate. Further examples are aliphatic, straight-chain diisocyanates, such as are obtained by phosgenation of diamines, for example tetramethylene diisocyanate or hexamethylene diisocyanate.

According to a preferred embodiment of the invention, polyurethane prepolymers are used instead of the polyfunctional isocyanate compounds. Prepolymers are understood in this context to mean adducts of an excess of polyfunctional isocyanates with polyfunctional alcohols, for example the reaction products of one of the abovementioned aromatic or aliphatic diisocyanates with ethylene glycol, propylene glycol, glycerol, trimethylolpropane or pentaerythritol. Reaction products of diisocyanates with polyether polyols, for example polyether polyols based on polyethylene oxide or based on polypropylene oxide, can also be used as prepolymers. Preference is given to polyurethane prepolymers based on polyether polyols having molecular weights of between 200 and 10000, in particular 500 and 3000. A person skilled in polyurethane chemistry is familiar with a large number of polyether polyols of this type; they are offered by many manufacturers and are characterised by their molecular weight (number-average), which can be calculated from end group determinations. Further suitable polyether polyols are polyether polyols based on polytetrahydrofuran.

Instead of polyether polyols, polyester polyols can also be used. Suitable polyester polyols are reaction products of polyfunctional acids with polyfunctional alcohols, for example polyesters based on aliphatic and/or aromatic dicarboxylic acids and polyfunctional alcohols having a functionality of 2-4. Thus, polymers obtained from adipic acid, sebacic acid, phthalic acid, hydrophthalic acid and/or trimellitic acid on the one hand and ethylene glycol, propylene glycol, neopentyl glycol, hexane glycol, glycerol and/or trimethylolpropane on the other hand can be used. In particular polyester polyols having a molecular weight (number-average) of between 500 and 5000, in particular between 600 and 2000, are suitable. Further suitable polyester polyols are the reaction products of caprolactone with alcohols having a functionality of 2-4, for example the adduct of 1-5 moles of caprolactone with 1 mole of ethylene glycol, propylene glycol, glycerol and/or trimethylolpropane.

A further suitable group of polyfunctional alcohols are polybutadienols. These are oligomers based on butadiene and containing OH groups as end groups. Of these, suitable products are those in the molecular weight range 200-4000, in particular 500-3000. Furthermore, siloxane prepolymers, preferably in combination with other prepolymers, are suitable.

When the polyurethane prepolymers are prepared, the ratio of the OH groups of the alcohol component to the isocyanate groups is important. It is in general between 1:2 and 1:10. A high excess of isocyanate tends to give low-viscosity polyurethane prepolymers, while a small excess of isocyanate gives highly viscous preparations, which in most cases can only be applied by trowelling.

It is known to a person skilled in polyurethane chemistry that the crosslinking density and thus the hardness of the polyurethanes increases with the functionality of the isocyanate component or else of the polyol. Reference may be made here to the general technical literature, for example to the monograph by Saunders and Frisch "Polyurethanes, Chemistry and Technology", Volume XVI of the series "High Polymers", Interscience Publishers, New York-London, Part I (1962) and Part II (1964).

The polyurethane preparations according to the invention can furthermore contain various auxiliaries. Examples of auxiliaries which can be used are fillers. Suitable fillers are inorganic compounds which are unreactive towards isocyanates, for example chalk or ground chalk, precipitated and/or pyrogenic silicas, zeolites, bentonites, ground minerals and other inorganic fillers known to a person skilled in this technical field, in particular chopped fibres, and others. For some applications, fillers are preferred which give the preparations thixotropic properties, for example swellable plastics, in particular PVC.

Apart from the compounds mentioned, the polyurethane preparations according to the invention can contain further auxiliaries, for example solvents. Suitable solvents are those which themselves do not react with isocyanate groups, for example halogenated hydrocarbons, esters, ketones and aromatic hydrocarbons. Plasticisers, retardants, dyes and anti-ageing agents, such as are known in polyurethane adhesives and sealing compositions, can also be incorporated.

For some applications, it is desirable to add foam stabilisers to the polyurethane preparations according to the invention. So-called silicosurfactants can be used as foam stabilisers. These are understood to mean block copolymers which are composed of a polysiloxane block and one or more polyoxyethylene and/or polyoxypropylene blocks. The polyurethane preparations according to the invention can furthermore contain flame-retardant and plasticising additives. Compounds containing phosphorus and/or halogen atoms, such as tricresyl phosphate, diphenyl cresyl phosphate, tris(2-chloroethyl) phosphate, tris(2-chloropropyl) phosphate and tris(2,3-dibromopropyl) phosphate are common. In addition, flame retardants can be used, for example chloroparaffins, phosphinic acid halides, ammonium phosphate and halogen- and phosphorus-containing resins. For some applications, plasticisers are important as further additives.

Examples of these which are suitable are esters of phthalic acid or esters of long-chain dicarboxylic acids, for example sebacic or azelaic esters. So-called epoxide plasticisers, for example epoxidized fatty acid derivatives, can also be used.

Further possible additives are basic accelerators. Examples of basic accelerators are tertiary bases, such as bis(N,N'-dimethylamino)diethyl ether, dimethylaminocyclohexane, N,N-dimethylbenzylamine, N-methylmorpholine and the reaction products of dialkyl-(ß-hydroxyethyl)amines with monoisocyanates and esterification products of dialkyl-(ß-hydroxyethyl)amines with dicarboxylic acids. A further important accelerator is 1,4-diaminobicyclo[2.2.2]octane. Furthermore, non-basic substances can be used as accelerators. Of these, suitable substances are metal compounds, for example iron acetylacetonate and tin(II) 2-ethylhexanoate, dibutyltin dilaurate or molybdenum glycolate.

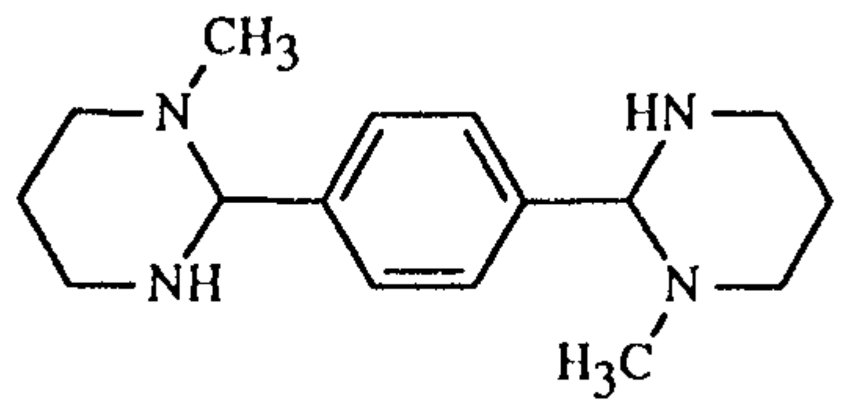
The compounds of the formula I are added to the polyurethane resins in amounts of 0.1-20 % by weight, preferably 0.5-15 % by weight, in particular 2.5-10 % by weight, relative to the prepolymer.

Furthermore, the compounds of the formula I can also be used as hardeners. When used as hardeners, the molar ratio of released secondary NH groups to free isocyanate groups in the resin should be 0.5 to 1.5:1, preferably 0.9 to 1.1:1.

The examples below illustrate the invention.

I. Preparation of the starting materials

Example A: 1,4-Bis(1-methylhexahydropyrimidin-2-yl)benzene



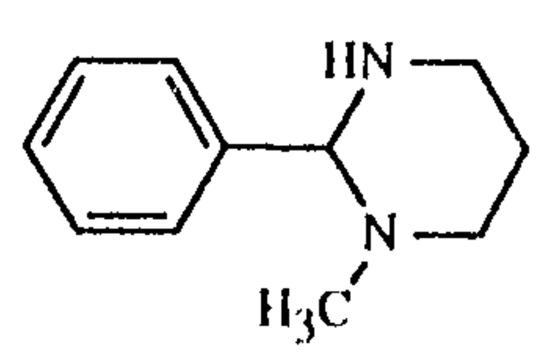
1 mol of terephthalaldehyde in 500 ml of toluene is initially introduced into a 1 l sulfonating flask equipped with stirrer, reflux condenser, thermometer and water separator. An equimolar amount of 3-methylaminopropylamine is then slowly added dropwise under nitrogen, followed by 0.1 % by weight of toluenesulfonic acid as the catalyst. The mixture is then refluxed for some time, during which the extent of the reaction can be monitored by the amount of water separated. The reaction mixture is then concentrated in a rotary evaporator, and the product is then worked up under a high vacuum.

Yield : 87 %

Melting point : 135°C

Elemental analysis:	calculated:	C 70.03 %; H 9.55 %; N 20.42 %
	found:	C 69.95 %; H 9.74 %; N 20.62 %

Example B: 1-Methyl-2-phenylhexahydropyrimidine



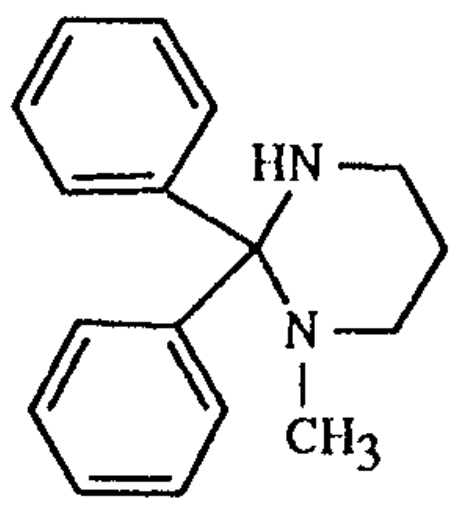
The procedure of Example A is repeated, using 1 mol of benzaldehyde instead of the terephthalaldehyde.

Yield : 91 %

Boiling point : 75°C/0.1 mbar

Elemental analysis:	calculated:	C 74.96 %; H 9.15 %; N 15.89 %
	found:	C 74.94 %; H 9.10 %; N 15.99 %

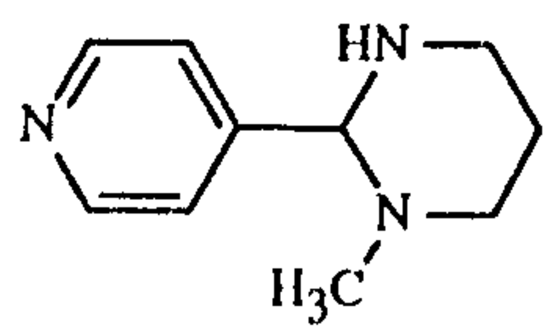
Example C: 1-Methyl-2,2-diphenylhexahydropyrimidine



The procedure of Example A is repeated, using 1 mol of benzophenone instead of the terephthalaldehyde.
Yield : 39 %
Boiling point : 130°C/0.1 mbar

Elemental analysis:	calculated:	C 80.91 %; H 7.99 %; N 11.10 %
	found:	C 81.76 %; H 7.68 %; N 8.85 %

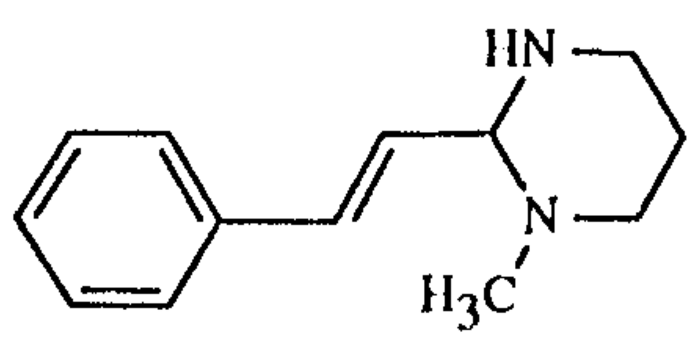
Example D: 1-Methyl-2-pyridin-4-ylhexahydropyrimidine



The procedure of Example A is repeated, using 1 mol of 4-pyridinecarboxaldehyde instead of the terephthalaldehyde.
Yield : 46 %
Boiling point : 70°C/0.05 mbar

Elemental analysis:	calculated:	C 67.76 %; H 8.53 %; N 23.71 %
	found:	C 67.69 %; H 8.73 %; N 23.81 %

Example E: 1-Methyl-2-(2-phenylethenyl)hexahydropyrimidine

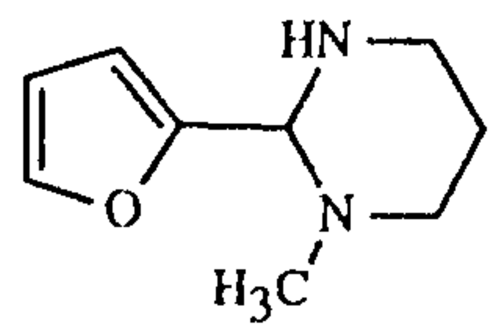


The procedure of Example A is repeated, using 1 mol of cinnamaldehyde instead of the

terephthalaldehyde.
Yield : 28 %
Boiling point : 85°C/0.17 mbar

Elemental analysis:	calculated:	C 77.18 %; H 8.97 %; N 13.85 %
	found:	C 73.27 %; H 9.80 %; N 17.00 %

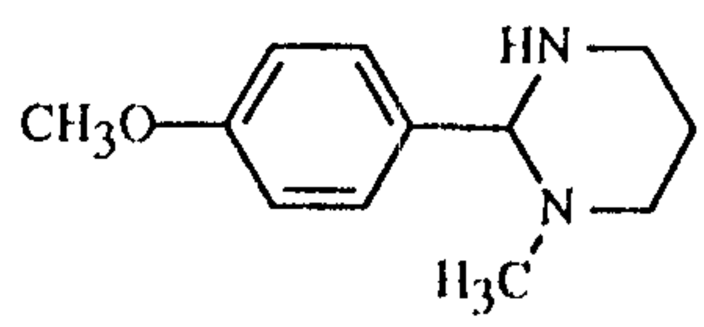
Example F: 1-Methyl-2-furan-2-ylhexahydropyrimidine



The procedure of Example A is repeated, using 1 mol of furfural instead of the terephthalaldehyde.
Yield : 75 %
Boiling point : 110°C/0.12 mbar

Elemental analysis:	calculated:	C 65.03 %; H 8.49 %; N 16.85 %
	found:	C 64.88 %; H 8.51 %; N 16.84 %

Example G: 1-Methyl-2-(4-methoxyphenyl)hexahydropyrimidine

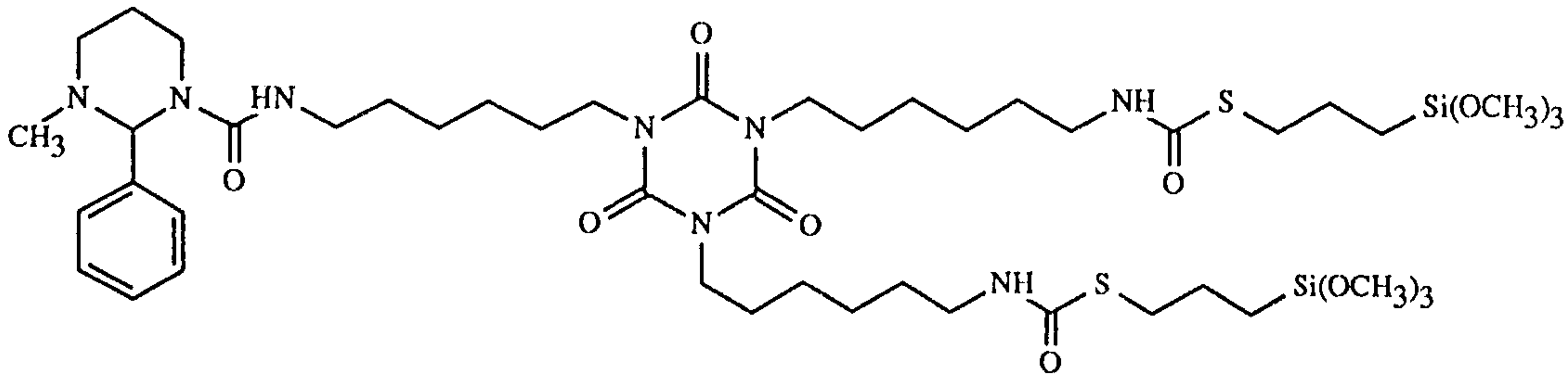


The procedure of Example A is repeated, using 1 mol of p-anisaldehyde instead of the terephthalaldehyde.
Yield : 78 %
Boiling point : 97°C/0.04 mbar

Elemental analysis:	calculated:	C 69.87 %; H 8.80 %; N 13.58 %
	found:	C 69.55 %; H 8.81 %; N 13.59 %

II. Synthesis of the adhesion promoters

Example 1:



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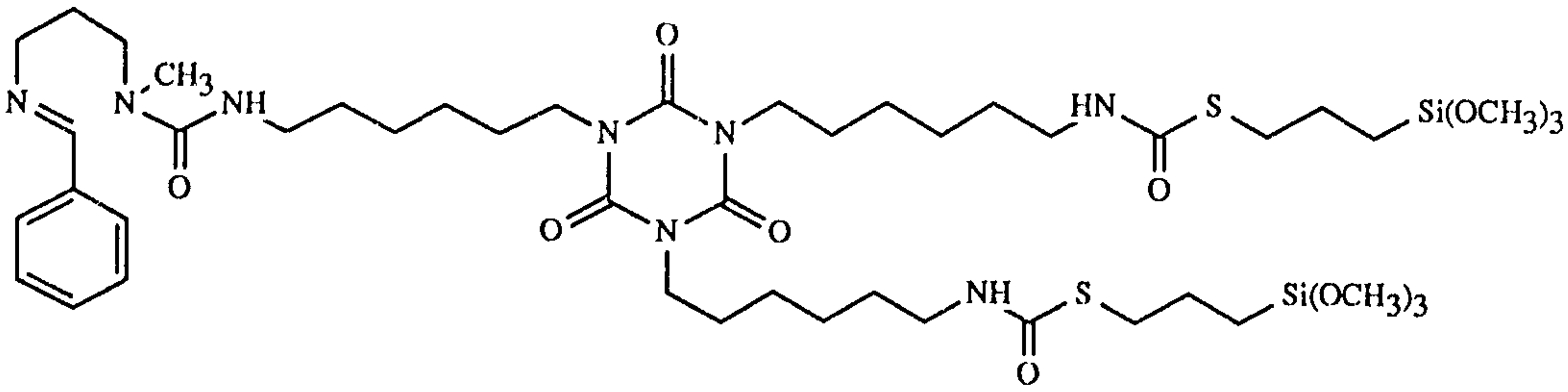


In a 100 ml sulfonating flask, 20 g (0.1032 mol of -NCO) of partially trimerised hexamethylene diisocyanate having an isocyanate content of 21.6 % (Desmodur® N 3200 from Bayer AG) are dissolved in 20 g of xylene, and the solution is heated to 80°C. 13.51 g (0.0688 mol) of 3-mercaptopropyltrimethoxysilane are then added dropwise under nitrogen using a dropping funnel, and stirring of the mixture is then continued at 80°C for 1.5 hours and then at 130°C for 2.5 hours. After cooling to room temperature, 0.03411 mol of the aminal according to Example B is added dropwise at such a rate that the temperature always remains below 30°C. Stirring at room temperature is then continued for another 4 hours, and the free NCO content is then checked by titration.

Viscosity (according to Epprecht): η = 76 800 mPa·s

Average molecular weight (GPC, polystyrene-calibrated):

M_n = 1 680 g/mol

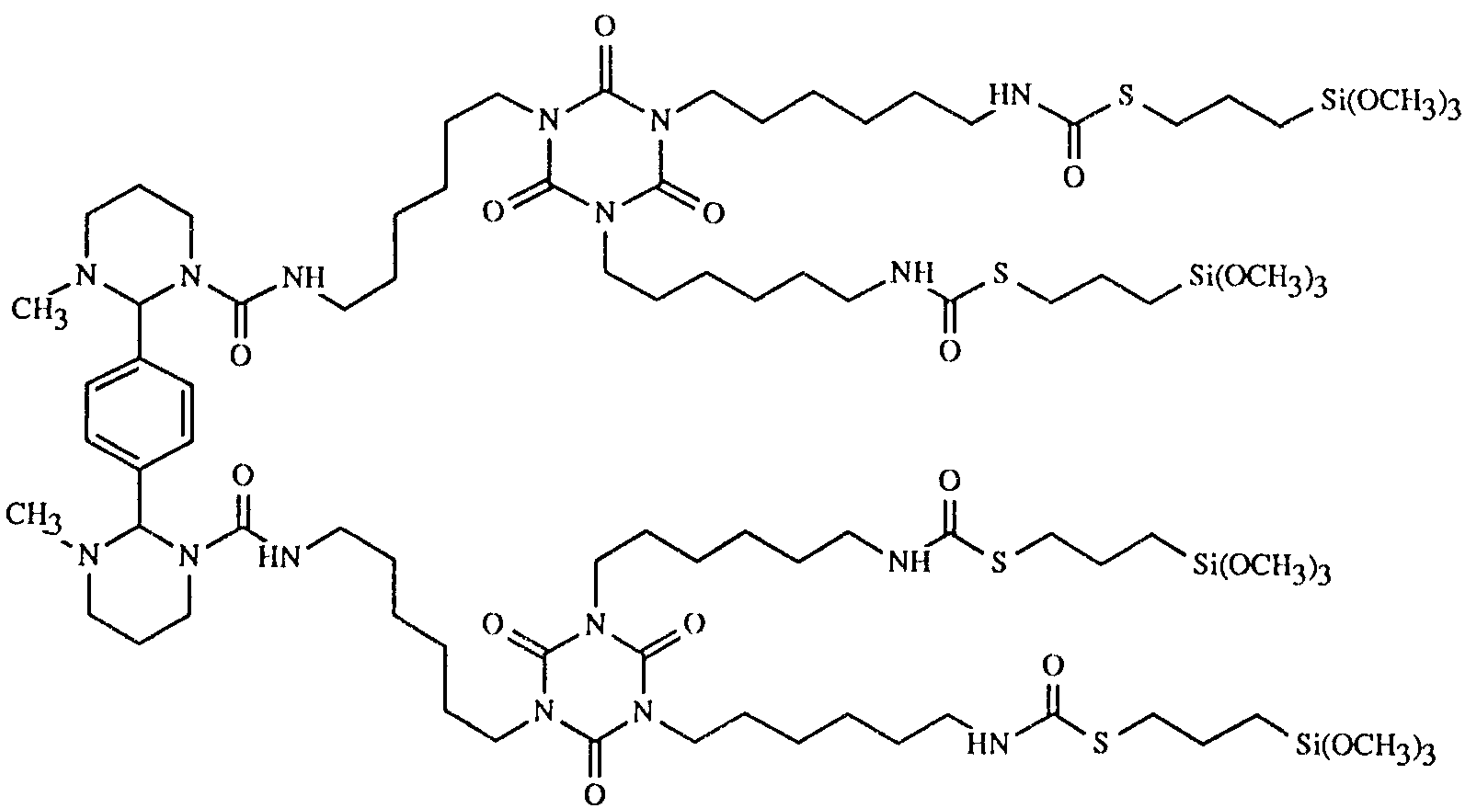
M_w = 2 640 g/mol

Elemental analysis: found: C 56.40 %; H 8.34 %; N 10.26 %

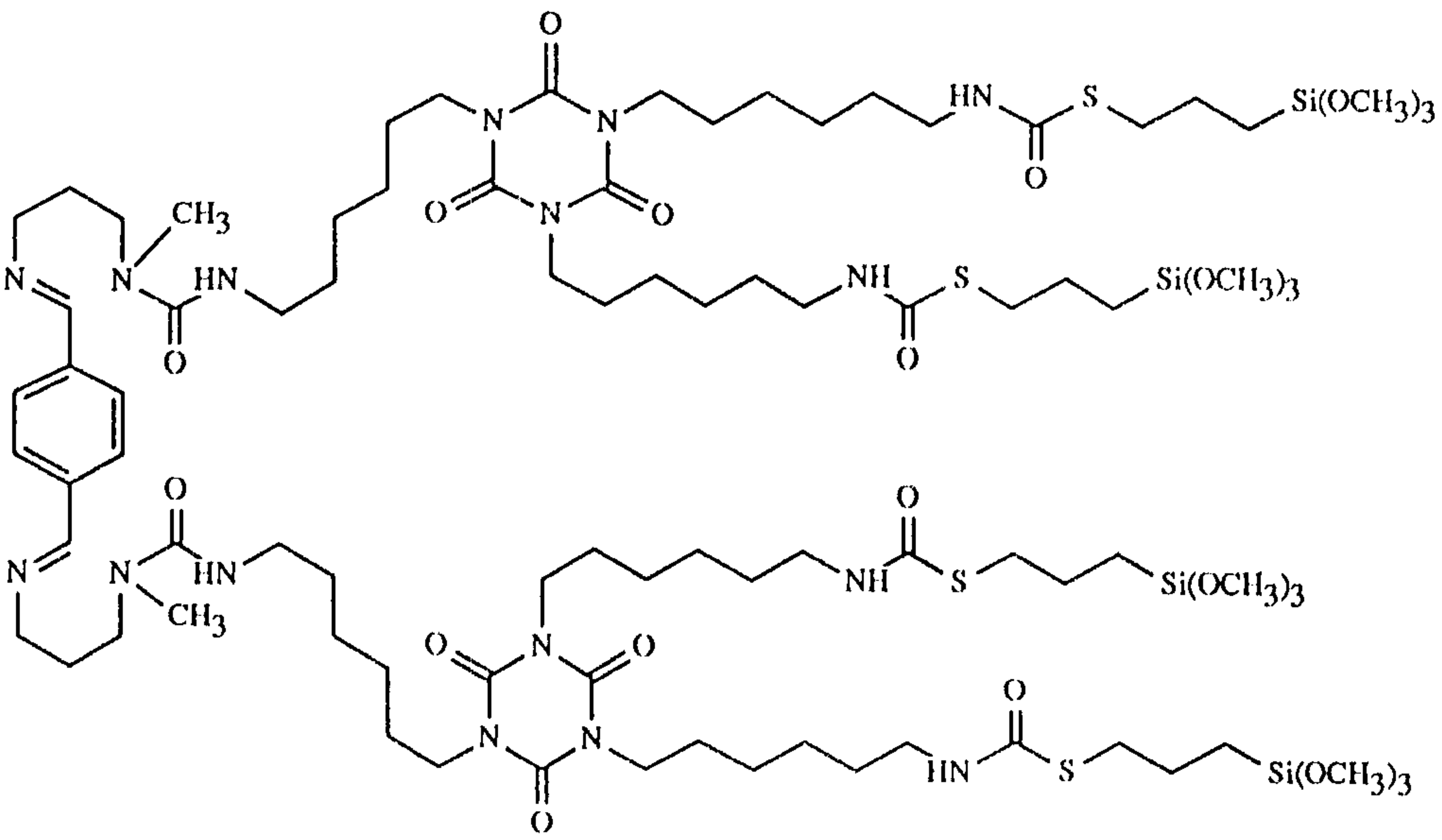
Imine/aminal ratio (%, ^{1}H NMR analysis [N-CH_3]): 61/39

Isocyanate group content: < 0.1 %

Example 2:



and



The procedure of Example 1 is repeated, using the aminal from Example A instead of the aminal from Example B.

Viscosity (according to Epprecht): η > 100 000 mPa·s

Average molecular weight (GPC, polystyrene-calibrated):

$M_n = 1\ 780$ g/mol

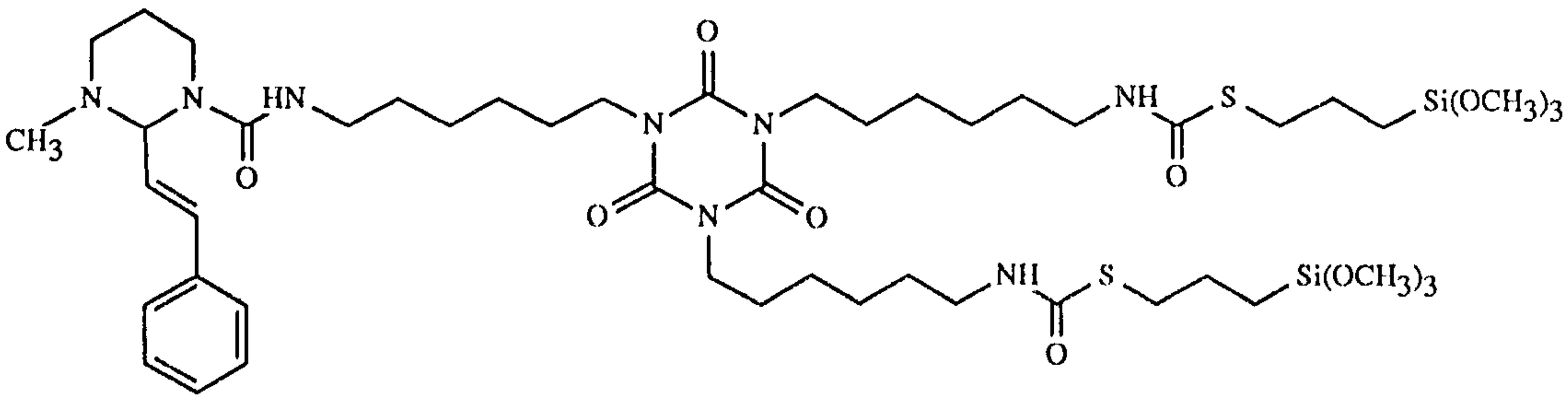
$M_w = 4\ 640$ g/mol

Elemental analysis: found: C 53.33 %; H 7.93 %; N 7.42 %

Imine/aminal ratio (%, ^{1}H NMR analysis [N-CH_3]): 69/31

Isocyanate group content: < 0.1 %

Example 3:



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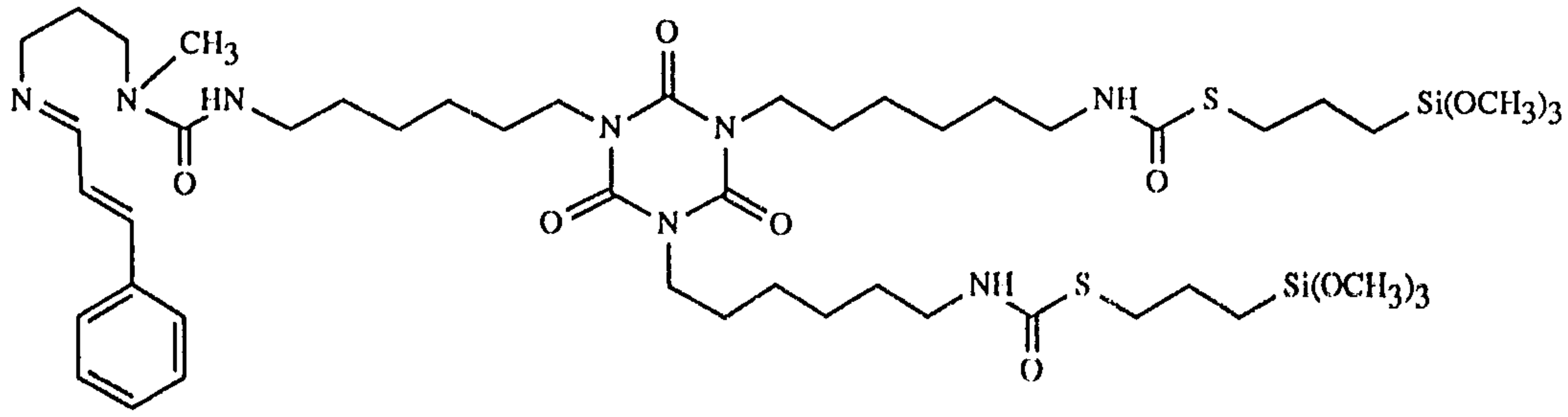


The procedure of Example 1 is repeated, using the aminal from Example E instead of the aminal from Example B.

Viscosity (according to Epprecht): $\eta = 12\ 000$ mPa·s

Average molecular weight (GPC, polystyrene-calibrated):

$M_n = 1\ 480$ g/mol

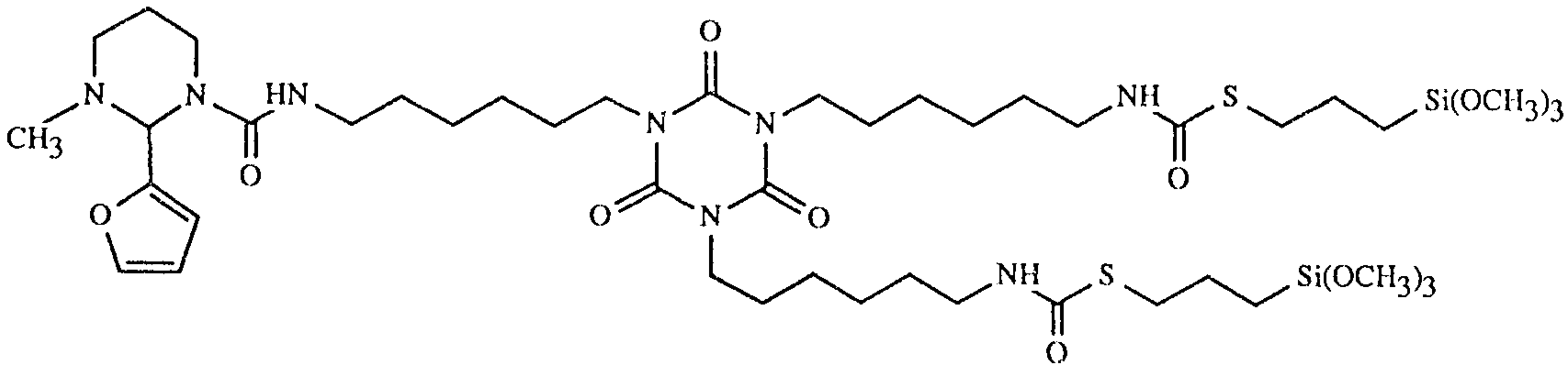
$M_w = 2\ 320$ g/mol

Elemental analysis: found: C 61.80 %; H 8.44 %; N 8.62 %

Imine/aminal ratio (%, ^{1}H NMR analysis [N-CH_3]): 61/39

Isocyanate group content: < 0.1 %

Example 4:



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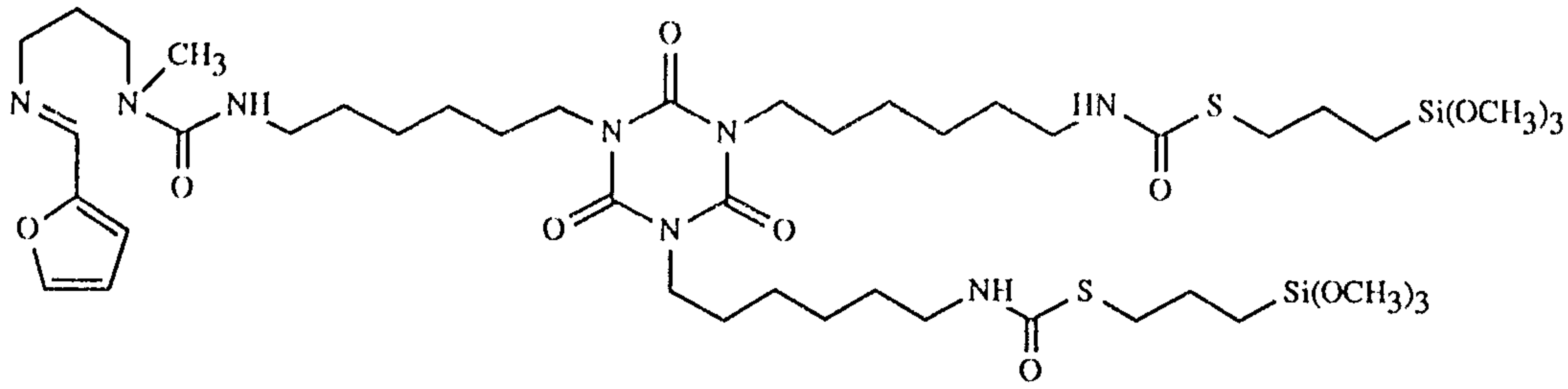


The procedure of Example 1 is repeated, using the aminal from Example F instead of the aminal from Example B.

Viscosity (according to Epprecht): η = 9 600 mPa·s

Average molecular weight (GPC, polystyrene-calibrated):

M_n = 1 650 g/mol

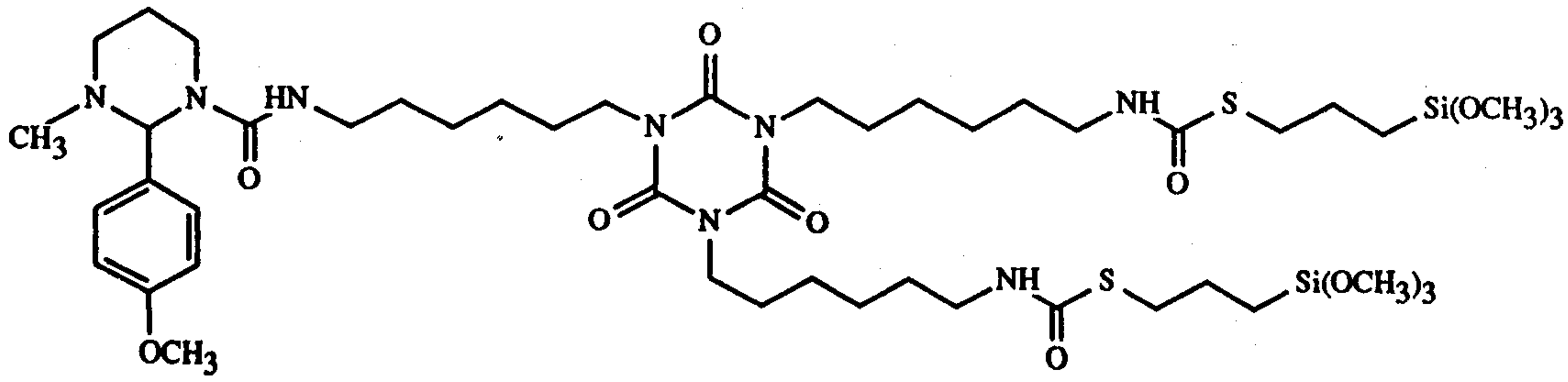
M_w = 2 970 g/mol

Elemental analysis: found: C 59.25 %; H 8.27 %; N 8.50 %

Imine/aminal ratio (%, ^{1}H NMR analysis [N-CH_3]): 68/32

Isocyanate group content: < 0.1 %

Example 5:



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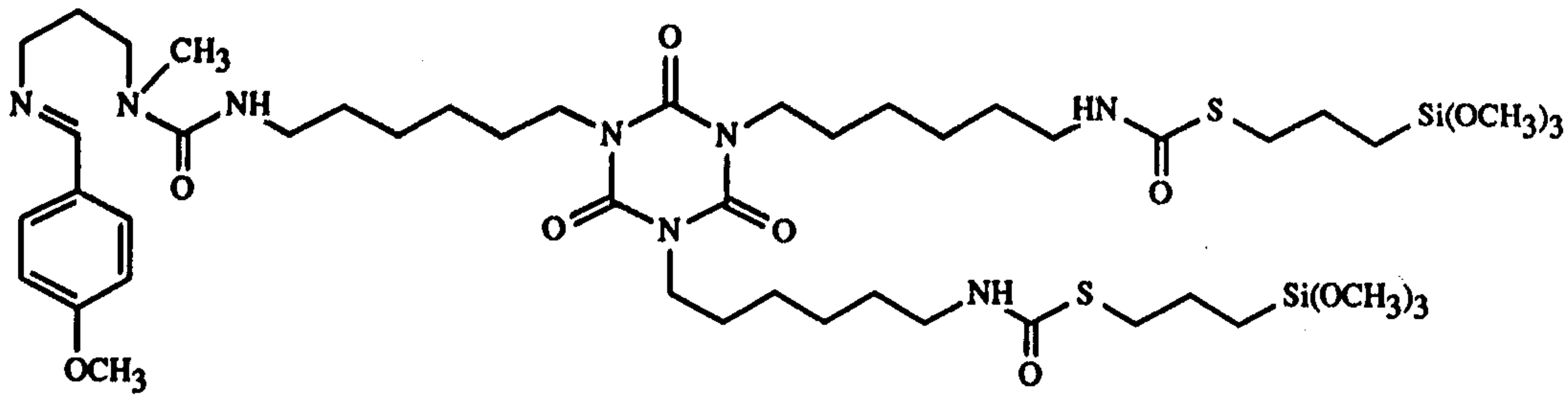


The procedure of Example 1 is repeated, using the aminal from Example G instead of the aminal from Example B.

Viscosity (according to Epprecht): η = 4 800 mPa·s

Average molecular weight (GPC, polystyrene-calibrated):

M_n = 2 120 g/mol

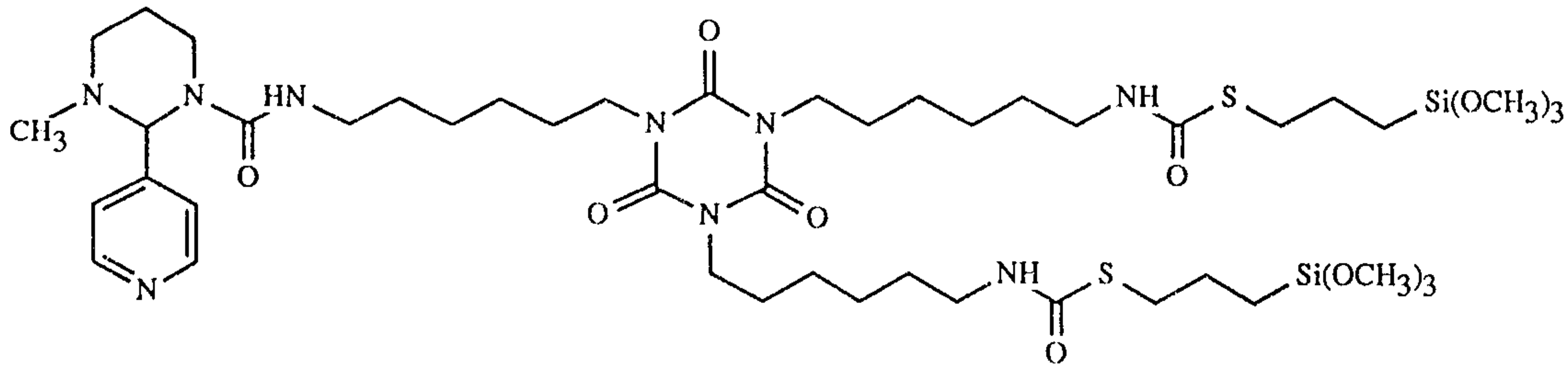
M_w = 4 970 g/mol

Elemental analysis: found: C 59.60 %; H 7.92 %; N 6.59 %

Imine/aminal ratio (%, ^{1}H NMR analysis [N-CH_3]): 68/32

Isocyanate group content: < 0.1 %

Example 6:



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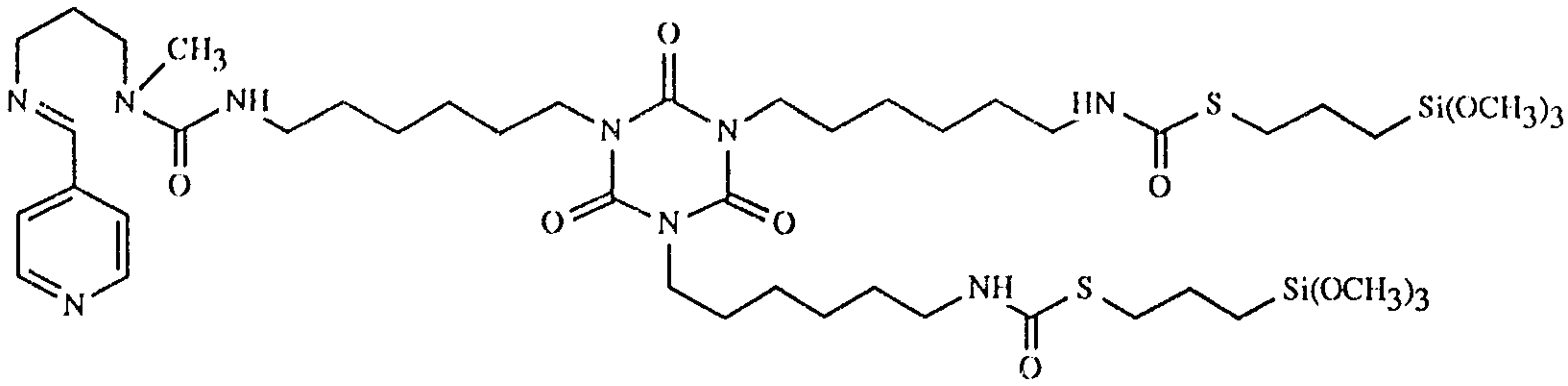


The procedure of Example 1 is repeated, using the aminal from Example D instead of the aminal from Example B.

Viscosity (according to Epprecht): η = 38 400 mPa·s

Average molecular weight (GPC, polystyrene-calibrated):

M_n = 1 140 g/mol

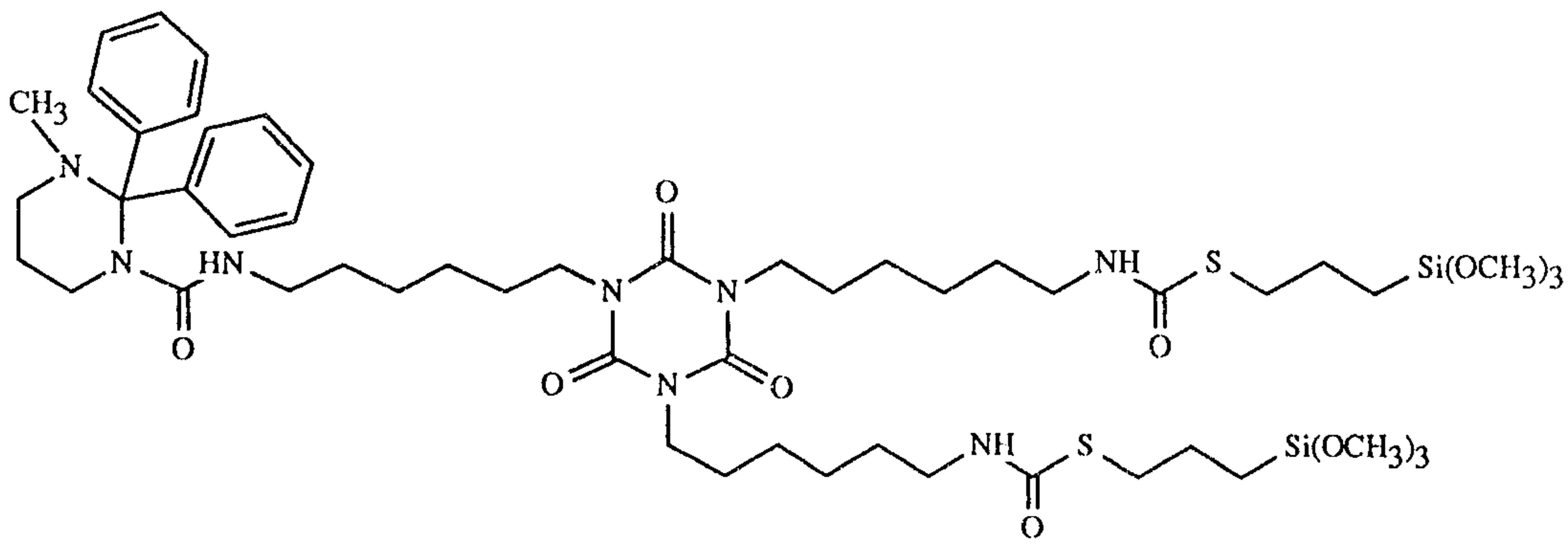
M_w = 1 660 g/mol

Elemental analysis: found: C 55.92 %; H 8.43 %; N 10.97 %

Imine/aminal ratio (%, ^{1}H NMR analysis [N-CH_3]): 57/43

Isocyanate group content: < 0.1 %

Example 7:



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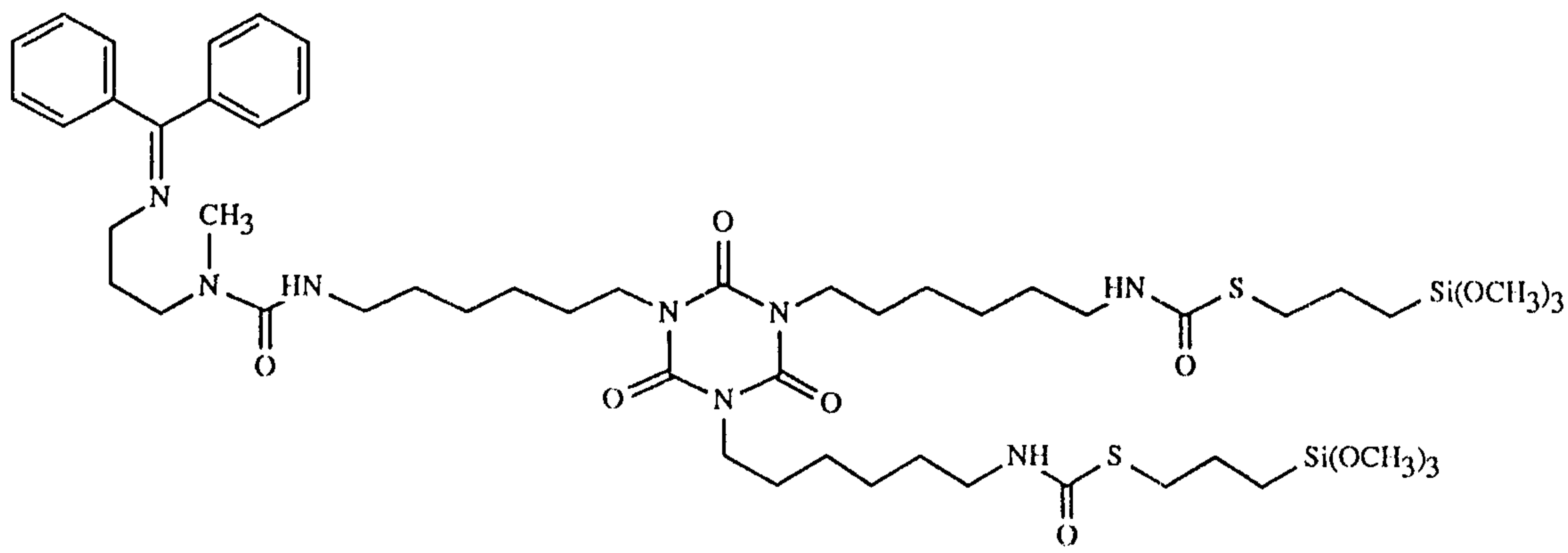


The procedure of Example 1 is repeated, using the aminal from Example C instead of the aminal from Example B.

Viscosity (according to Epprecht): η = 1 960 mPa·s

Average molecular weight (GPC, polystyrene-calibrated):

M_n = 1 080 g/mol

M_w = 2 460 g/mol

Elemental analysis: found: C 63.90 %; H 8.21 %; N 7.47 %

Imine/aminal ratio (%, ^1H NMR analysis [N-CH_3]): 61/39

Isocyanate group content: < 0.1 %

III. Adhesive formulations

Example 8: One-component system (moisture-curing)

8A) Synthesis of the prepolymer:
An isocyanate-terminated prepolymer is prepared by adding a mixture of 240 g of dry bishydroxy-terminated polypropylene glycol of molecular weight 2000 (Desmophen® 1900 U from Bayer AG) and 0.3 ml of dibutyltin dilaurate at 80°C to 50 g of methylenediphenyl diisocyanate (Isonate® M 125 from Upjohn) over a period of 1 hour. 1.0 g of trimethylolpropane is then added to the mixture obtained, which is stirred at 80°C for another 2 hours until an isocyanate-terminated prepolymer having an isocyanate content of 2.0 % has been formed.

8B) Formulation:
The adhesive formulation has the following composition:

55.1 % by weight of the prepolymer according to Example 8A
20 % by weight of ground lamp black
14.9 % by weight of dioctyl phthalate
5 % by weight of silica aerogel (thixotropic agent)
5 % by weight of the adhesion promoter according to Example 1

8C) Adhesion to various substrates:
The adhesive formulation obtained in 8B) is poured onto a substrate (according to the table below) such that a 5 mm thick polyurethane layer is formed. After storage in air for 2 weeks, these samples are stored for 2 weeks in water at room temperature. The results are summarised in Table 1, in which (--) means that the layer can be peeled off with ease and the substrate surface remains clean; (-) means that the layer can be peeled off with difficulty and the substrate surface remains clean; (+/-) means that the majority of the layer on the substrate surface can be removed by scratching using a knife; (+) means that the majority of the layer remains attached to the substrate surface despite scratching using a knife; (++) means that the entire layer remains attached to the substrate surface despite scratching using a knife.

Table 1

Substrate	without adhesion promoter	with adhesion promoter according to Example 1
Glass	-	+ +
SMC	-	+
PC	- -	+ -
RIM-PUR	-	+
PA	- -	+ -

SMC = Sheet Moulding Compound
PC = Polycarbonate
RIM-PUR = Reaction Injection Moulding - Polyurethane
PA = Polyamide

Example 9: Two-component system (heat-curing)

9A) Formulation:

The adhesive formulation has the following composition:

100 parts by weight of polyol mainly comprising branched polyether polyols and mineral fillers

20 parts by weight of isocyanate based on diphenylmethane diisocyanate

5 parts by weight of the adhesion promoter according to Example 1

9B) Mechanical properties

The tensile shear strengths of various samples were determined.

Test specimens:	Substrate thickness	3.0 mm
	Width	25.0 mm
	Overlapping	12.5 mm
	Thickness of the adhesive joint	0.2 mm

The specimens were cured at 80°C over a period of 1 hour. The results are summarised in Table 2.

Table 2

Substrate	without adhesion promoter		with adhesion promoter according to Example 1	
PA	2.3	C (40 %)	3.2	C (70 %)
PC	3.5	Ad	5.0	C (50 %)
PP	1.6	Ad	4.5	MB

PA = Polyamide

PC = Polycarbonate

PP = Polypropylene (flame-pretreated)

Ad = Adhesion break

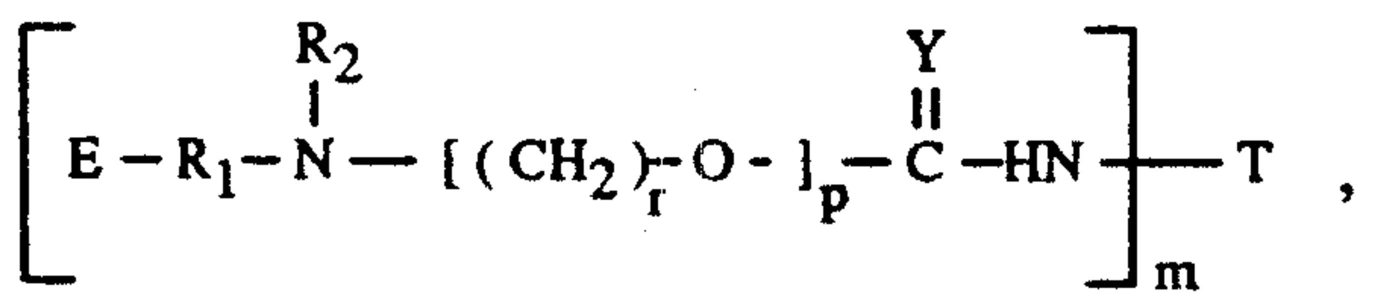
C = Cohesion break

MB = Material break, substrate break

The values obtained show that the use of the compounds according to the present invention as adhesion promoters substantially improves the tensile shear strength of these specimens.

CLAIMS:

1. A compound of the general formula I



(I)

in which

R_1 is C_2-C_3alkylene and

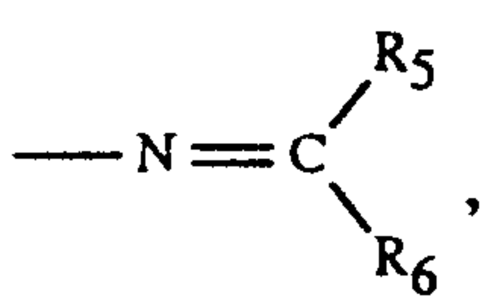
R_2 is hydrogen, C_1-C_6alkyl which is unsubstituted or substituted by -OH, -CN or $-Si(OR_3)_{3-q}(R_4)_q$ or is C_2-C_6alkenyl, in which

R_3 is C_1-C_4alkyl or two radicals R_3 together are C_1-C_4alkylene,

R_4 is C_1-C_4alkyl or phenyl and

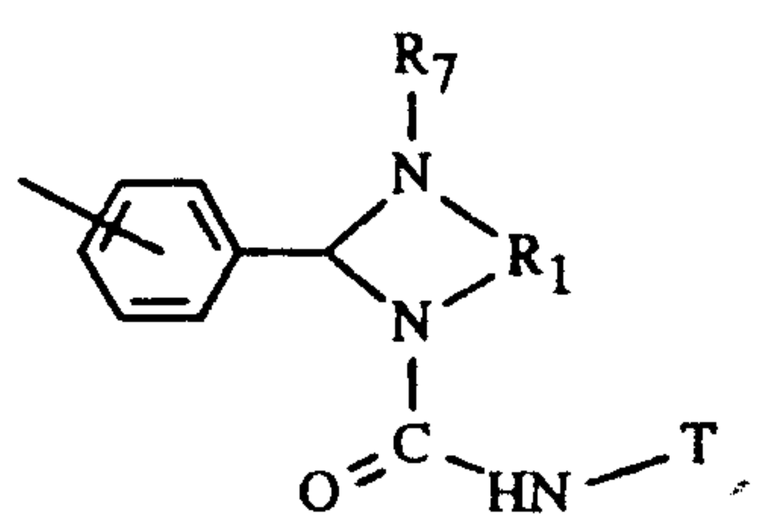
q can have values from 0 to 2, furthermore

E is a radical of the formula

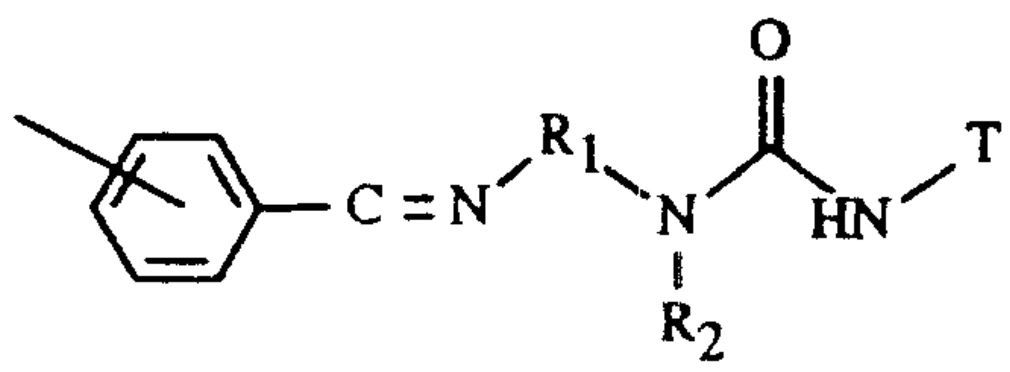


in which

R_5 and R_6, independently of one another, are hydrogen, C_1-C_4alkyl, aryl, ethenyl which is substituted by aryl, heteroaryl or radicals of the formulae IIa or IIb



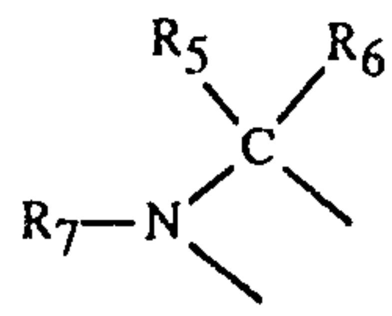
(IIa)



(IIb)

with the proviso that at least one of the radicals R_5 or R_6 is aryl, ethenyl which is substituted by aryl, heteroaryl or a radical of the formulae IIa or IIb or

E together with R_2 is a radical of the formula



in which R_7 is hydrogen, C_1-C_4alkyl or $-R_9-Si(OR_3)_{3-q}(R_4)_q$ and R_3,R_4 and q are as defined above, and

R_9 is C_1-C_8alkylene,

and

Y is oxygen or sulfur; furthermore,

T is a radical of the formulae $-R_9-Si(OR_3)_{3-q}(R_4)_q$ or

$$-Z\left[NH-\overset{\overset{Y}{\|}}{C}-X-R_9-Si(OR_3)_{3-q}(R_4)_q\right]_n$$

or, if R_7 is a radical of the formula $-R_9-Si(OR_3)_{3-q}(R_4)_q$ and m is greater than or equal to 2, is an m-valent radical Z in which R_3, R_4, R_9, Y and q are as defined above,

X is -S- or -NH- and

Z is an organic radical which is derived from a polyisocyanate or a polyisothiocyanate having at least 2 NCO or NCS groups, and

r is 1, 2 or 3 and

p is 0 or 1 and

m can have values of greater than or equal to 1 and

n can have values of greater than or equal to 1.

2. A compound of the formula I according to claim 1, in which Y is oxygen.

3. A compound of the formula I according to claim 1, in which Z is derived from an aliphatic, cycloaliphatic, aliphatic/aromatic, aromatic or heterocyclic polyisocyanate or polyisothiocyanate in which the number of NCO or NCS groups is greater than or equal to 2, it being possible for the radical Z to contain, if desired, one or more ester, ether, urethane, thiourethane, isocyanurate, urea or biuret functions.

4. A compound of the formula I according to claim 3, in which Z is derived from an

aliphatic or mixed aliphatic/aromatic polyisocyanate in which the number of NCO groups is greater than or equal to 2, it being possible for this radical Z to contain, if desired, a total of one or two ester, ether, urethane, thiourethane, isocyanurate, urea or biuret functions.

5. A compound of the formula I according to claim 1, in which the radical Z has an average molecular weight M_n of less than 10 000.

6. A compound of the formula I according to claim 1, in which m and n, independently of one another, have values from 1 to 49.

7. A compound of the formula I according to claim 1, in which the sum of m + n is 2 to 50.

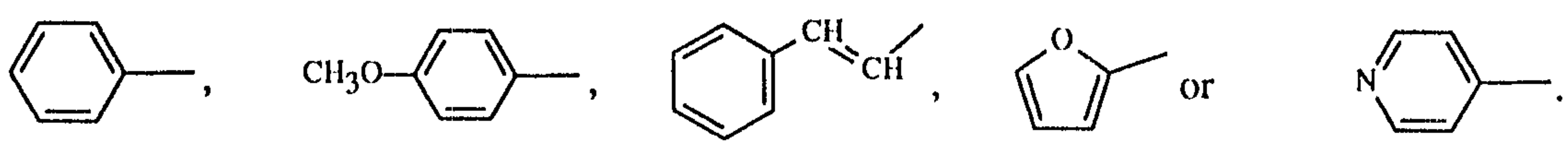
8. A compound of the formula I according to claim 1, in which n is 1, 2 or 3 and m is 3, 2 or 1.

9. A compound of the formula I according to claim 1, in which R_1 is propylene.

10. A compound of the formula I according to claim 1, in which p has the value 0.

11. A compound of the formula I according to claim 1, in which q has the value 0.

12. A compound of the formula I according to claim 1, in which at least one of the radicals R_5 or R_6 is a group of the formulae



13. A compound of the formula I according to claim 1, in which T is a radical of the formulae $-R_9-Si(OR_3)_{3-q}(R_4)_q$ or

$$-Z\left[NH-\overset{\overset{\displaystyle Y}{\|}}{C}-X-R_9-Si(OR_3)_{3-q}(R_4)_q\right]_n$$

in which, X, Y, Z, R_3, R_4, R_9, q and n are as defined in claim 1.

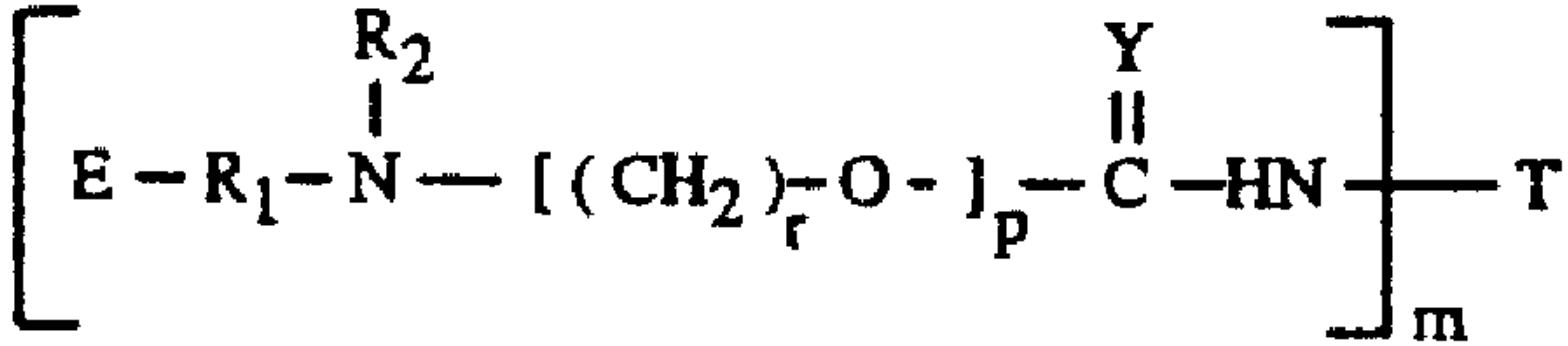
14. A compound of the formula I according to claim 13, in which at least one radical X is -S-.

15. A compound of the formula I according to claim 1, in which p and q are 0, m is 1 and n is 2, Y is oxygen, X is -S-, R_1 and R_9 are propylene, R_2 and R_3 are methyl, R_5 is phenyl and R_6 is hydrogen.

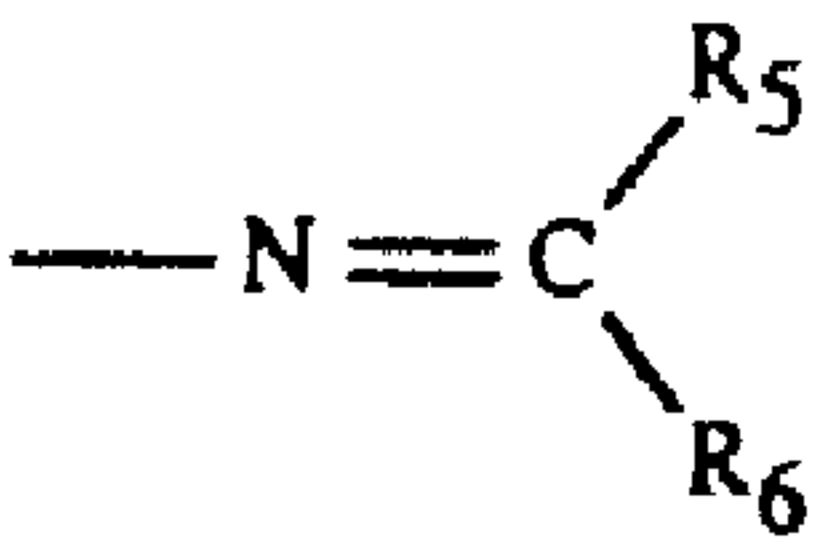
16. A polyurethane resin containing at least one compound of the formula I according to claim 1.

17. A polyurethane resin according to claim 16, containing 0.1 to 20 % by weight of a compound of the formula I.

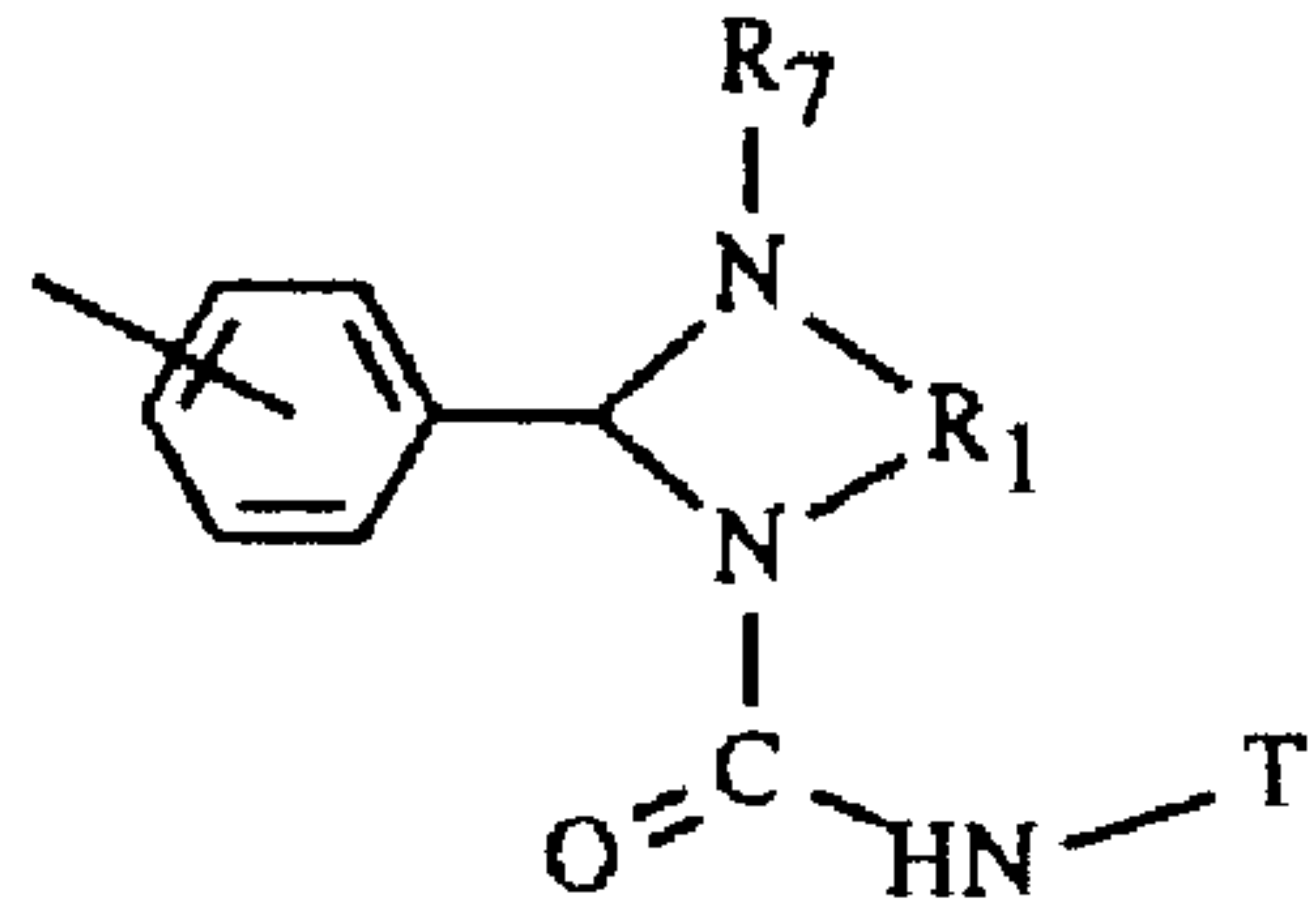
Fetherstonhaugh & Co.,
Ottawa, Canada
Patent Agents



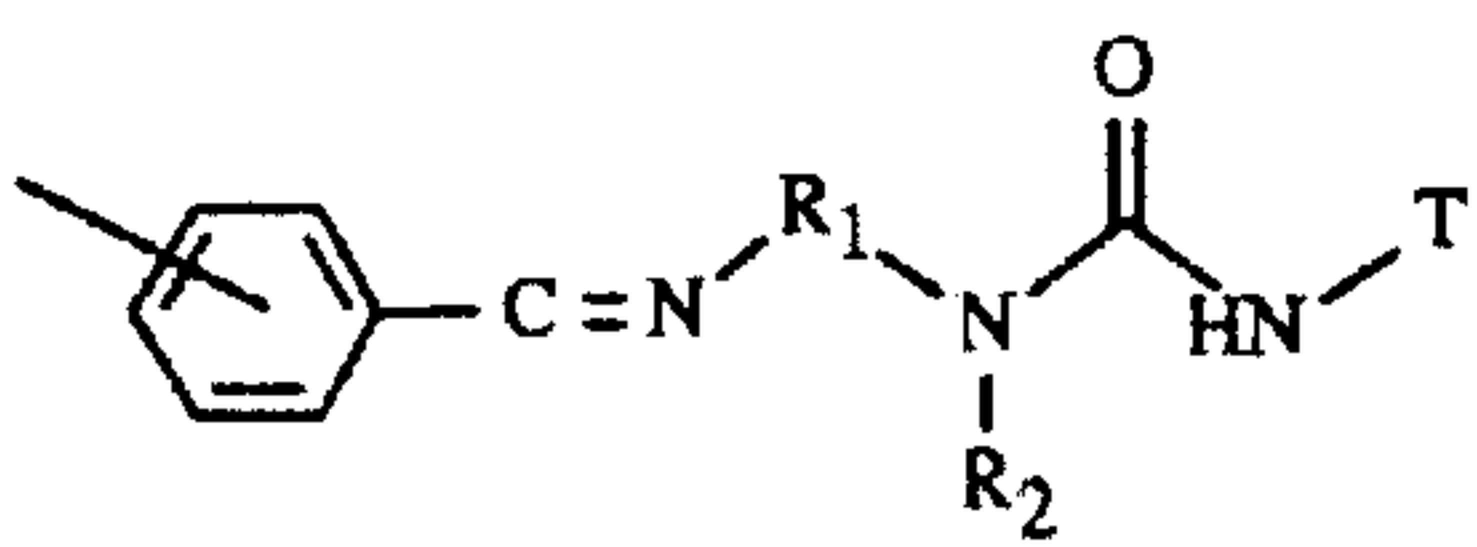
(I)



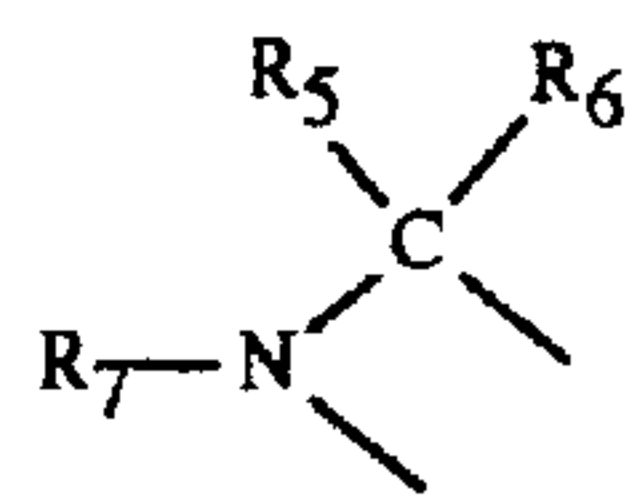
(II)



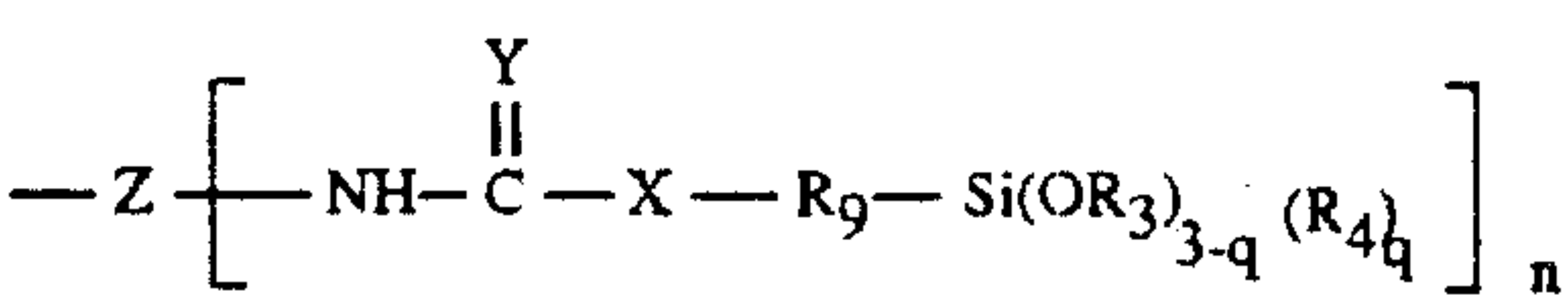
(IIa)



(IIb)



(III)



(IV)