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## (54) PREPARATION OF SILICON-NITROGEN COMPOUNDS


(71) We, DYNAMIT NOBEL AKTIENGESELLSCHAFT, a German company, of 521 Troisdorf, near Cologne, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-


This invention relates to the preparation of silicon-nitrogen compounds.

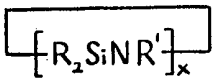
According to the invention, there is provided a process for the preparation of a silicon-nitrogen compound having the general formula:

$$(R_3Si)_nNR'_{3-n}$$

or

$$R_2Si(NR'_2)_2$$

or



wherein $n$ is 1 or 2, the radicals R′ are the same or different when two or more thereof are present in the compound and each is a hydrogen atom or a hydrocarbyl group, the radicals R are the same or different when two or more thereof are present in the compound and each is a hydrocarbyl group, and $x$ is 3 or 4, which process comprises reacting a silane having the general formula:

$$R_{3-y}SiH_{y+1}$$

wherein $y$ is 0 or 1 and R is as defined above, with a compound having the general formula:

$$NR'_{3-n}H_n$$

wherein R′ and $n$ are as defined above, in the presence of a catalyst.

The silicon-nitrogen compounds (i.e. silazanes) prepared according to the present invention have acquired technical importance, for example as synthesis agents and protective group reactants in the synthesis of semisynthetic penicillins or cephalosporins and other substances (see U.S. Patent Specification No. 3,994,545).

The compounds have hitherto been prepared by reaction of chlorosilanes with amines, but an excess quantity of amine must be used to react with resulting chloride to form a hydrochloride. The formation of amine hydrochlorides causes considerable disadvantages. The process must be carried out in dilute solutions in order to keep the reaction mixture in a state where it is still able to be stirred and transported. The reaction mixture must be filtered or centrifuged from salt and subsequently washed with solvents, which must them be separated off by distillation. In spite of washing, considerable losses in yield occur as a result of adsorption on the salt, and the separated salt wastes must be removed. These difficulties are eliminated in simple manner by the process of the invention.

The process of the invention is preferably effected at elevated temperature. Preferred catalysts are the elements of Group VIII of the Periodic Table and their salts and compounds.

The radicals R and R′ may be aryl groups, branched or unbranched alkyl groups (which alkyl groups preferably contain from 1 to 8 carbon atoms, more preferably from 1 to 4 carbon atoms), or mono- or poly-olefinically unsaturated aliphatic groups. R and R′ may also be alkyl-substituted cycloalkyl groups, e.g. cyclohexyl groups. Examples of suitable aryl groups are nuclear alkyl substituted aryl, aralkyl and alkaryl groups, preferably mononuclear groups. The side chains (i.e. the alkyl substituents) may be branched or unbranched as well as, if desired, mono- or poly-olefinically unsaturated. The alkyl substituents are preferably those with 1 to 4 carbon atoms.

The amine or ammonia and the hydrogen silane are mixed in any desired ratio, but preferably in a stochiometric ratio. The mixture is reacted in the liquid or gaseous state, preferably in the gaseous state, if desired at elevated temperature. The mixture may be contained with the catalyst arranged in a solid bed, the silicon-nitrogen compound being formed according to, for example, the following equation:

$$2\ R_3SiH + NH_3 \rightarrow (R_3Si)_2NH + 2\ H_2.$$

Usually, the yields are nearly 100%. If a stoichiometric ratio of the starting materials is used, the product is usually obtained in a purity such that it can be used without purification. If one reactant is used in excess, then purification is effected if desired, for example by distillation.

Examples of suitable catalysts are iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium and platinum in metallic form or in the form of salt-like compounds or complex compounds. Examples of suitable salt-like compounds or complex compounds are the salts of the oxyacids of sulphur and phosphorus, halides, carbonates, acetylacetonates, and salts of organic acids.

The catalyst may be supported on a carrier, for example activated carbon, aluminium oxide or silicon dioxide, preferably having a high specific surface area, for example a specific surface area of from 50 to 1000 $m^2/g$. Porous moulded parts, such as described in for example German Patent Specification No. 1,249,147, are also suitable as carriers.

The catalysts may also be used without a carrier, for example in compact metallic form, for example in the form of fillings, pellets and fillers. The catalyst metals can also be used as the material for the reactor itself.

The preparation of the supported catalysts is effected in a known manner by impregnating the carrier with a solution of salt-like compound or complex salt of the catalyst metal, with subsequent drying and if necessary reduction to the metallic form, for example by means of formaldehyde or hydrogen.

Examples of silicon-nitrogen compounds which can be prepared by the process of the invention are hexamethyldisilazane; N-methylhexamethyldisilazane; N-ethylhexamethyldisilazane; N,N-dimethyltrimethylsilylamine; N,N-diethyltrimethylsilylamine; N-phenyltrimethylsilylamine; hexaethyldisilazane; hexamethylcyclotrisilazane; nonamethylcyclotrisilazane; oxtamethylcyclotetrasilazane; bis(dimethylamino)dimethylsilane; bis(phenylamino)dimethylsilane; Si, Si′, Si″-trivinyltrimethylcyclotrisilazane; bis(dimethylamino)vinylmethylsilane; Si, Si′, Si″-triphenyltrimethylcyclotrisilazane; and bis(methylamino)diphenylsilane.

According to the process of the invention, these products are usually obtained in a pure or easily purified form without the simultaneous occurrence of waste products.

Hydrogen silanes and amines can be used as starting materials. The hydrogen silanes can be obtained in a known manner from suitable organochlorosilanes by hydrogenation in a chemical or electrochemical manner. Examples of the silanes are trimethylsilane, dimethylsilane, triethylsilane, diethylsilane, methylvinylsilane, methylphenylsilane and diphenylsilane.

Amines which can be used in the invention are for example primary and secondary amines, for example methylamine, dimethylamine, ethylamine, diethylamine, allylamine, aniline and N-methylaniline.

In a preferred method, the reactants are brought into contact with catalyst particles or moulded bodies in the form of a solid bed without using a solvent, the reaction preferably being effected in the gas phase. However, the reaction may also be effected in an inert solvent. Preferably, there should be used as the inert solvent a solvent which dissolves both the starting materials and the end products. Saturated hydrocarbons, for example benzine, are examples of suitable solvents.

An example of a suitable reactor is a heatable double-jacketted tube, consisting of for example glass, ceramic, steel, nickel, or if desired another catalyst metal, in which the

catalyst is disposed, preferably in the form of a solid bed. An equimolar mixture of silane and amine or ammonia, or a non-equimolar mixture thereof, is brought into contact with the solid bed, adjusted to reaction temperature, preferably continuously and preferably in a descending direction. A silicon-nitrogen compound is formed thereby in accordance with the invention, hydrogen also being generated. Even with very brief residence times, for example up to 180 seconds (calculated on the empty reactor tube), noticeable conversion takes place. High conversion rates to the extent of quantitative conversion and yield are usually obtained when the residence time is from 3 to 30 minutes. Obviously, high to quantitative conversions and yields are also obtained with longer residence times.

The reaction temperature is preferably from 0°C to about 280°C, more preferably above 100°C. The higher the reaction temperature, the shorter is the residence time required.

Differences in the reactivity of the various silanes, amines and catalysts are also of some importance. For example, advantageous reaction conditions for the substantially quantitative reaction of ammonia and trimethylsilane in the presence of nickel filings to form hexamethyldisilazane are a catalyst temperature of about 168°C and a residence time of about 10 to 15 minutes. On the other hand, for the reaction of aniline and diphenylsilane, these values are about 230°C and 22 to 26 minutes, respectively.

The reaction is preferably effected in the presence of atmospheric oxygen and with moisture substantially excluded.

The isolation of the silicon-nitrogen compounds is effected in a known manner, for example by condensation in a cooler or quenching device.

The following Examples illustrate the process of the invention.

*Example 1*

A double-jacketted glass tube, 900 mm in length and 40 mm in diameter, filled with turnings of pure nickel of about 0.4 mm in diameter and heated by means of a thermostat in the double jacket to 168°C, was rinsed free from air with argon. A mixture of trimethylsilane (boiling point 6.7°C) and ammonia in a ratio of 2:1 was passed through the tube from above, the residence time being varied. The gas issuing from the lower end of the reaction tube was passed to a water cooler in which the resultant hexamethyldisilazane is condensed. The hydrogen, cooled to −62°C by means of which about 2% of liquid product separated out, was drawn off for further use.

The following table shows the yields of hexamethyldisilazane obtained at 168°C with different residence times.

| Residence time, related to the empty reaction tube, at 168°C on the catalyst | Yield of hexamethyldisilazane | Conversion |
|---|---|---|
| 2 minutes 10 seconds | 98.8% | 84.2% |
| 6 minutes 35 seconds | 99.2% | 92.1% |
| 12 minutes | 99.3% | 95.4% |
| 15 minutes | 99.2% | 96.8% |
| 15 minutes | 99.0% | 98.9% |
| 40 minutes | 99.2% | 98.7% |

According to this Example, 627 g of hexamethyldisilazane of boiling point 127°C were produced. The small quantities of trimethylsilane and ammonia occurring in the distillation for purification were recycled to the reactor. The raw product obtained, however, is of such a high degree of purity that it can be used even without distillation.

*Example 2*

The process was carried out as described in Examples 1, using a temperature of 144°C.

The following table shows the yields of hexamethyldisilazane obtained at 144°C with different residence times.

| Residence time, related to the empty reaction tube, at 144°C on the catalyst | Yield of hexamethyldisilazane | Conversion |
|---|---|---|
| 3 minutes 30 seconds | 99.0% | 76.4% |
| 10 minutes 10 seconds | 99.4% | 88.1% |
| 20 minutes | 99.8% | 92.1% |
| 30 minutes | 99.1% | 93.8% |

*Example 3*

The process was carried out as described in Example 1, using a temperature of 120°C. The following table shows the yields of hexamethyldisilazane obtained at 120°C with different residence times.

| Residence time, related to the empty reaction tube, at 120°C on the catalyst | Yield of hexamethyldisilazane | Conversion |
|---|---|---|
| 4 minutes 20 seconds | 98.0% | 69.5% |
| 17 minutes 30 seconds | 98.8% | 76.9% |
| 30 minutes 18 seconds | 99.0% | 80.4% |

*Example 4*

In the apparatus described in Example 1, N-phenyltrimethylsilylamine, having a boiling point of 206°C was obtained in a yield of 93.9%, by using a catalyst temperature of 210°C, water-free activated carbon containing 0.5% of metallic platinum (in the form of 4 mm pellets) as the catalyst, an equimolar mixture of trimethylsilane and aniline, and a residence time of 21 minutes.

*Example 5*

As described in Example 1, bis(allylamino)dimethylsilane having a boiling point 82°C at 20 Torr was obtained in a yield of 92.6% from a mixture of allylamine (boiling point 58°C) and dimethylsilane (boiling point - 20°C) in a molar ratio of 2:1, using a catalyst temperature of 176°C and a residence time of 11 minutes.

*Example 6*

As described in Example 1, but using a catalyst consisting of γ-aluminium oxide containing 1% of palladium (in the form of 4 mm pellets) and a residence time of 25 minutes, bis(dimethylamino)diphenylsilane having a boiling point 139°C at 1 Torr was obtained in a yield of 87.8% from a mixture of dimethylamine and diphenylsilane (boiling point 270°C) in a molar ratio of 2:1.

*Example 7*

As described in Example 1, but using steel turnings of about 0.3 mm diameter as the catalyst, a catalyst temperature of 190°C and residence time of 15 minutes, nonamethylcyclotrisilazane of boiling point 223°C (F. 33-34°C), and additionally some oligomers, was obtained in a yield of 82.6% from a mixture of methylamine and dimethylsilane in a molar ratio of 1:1.

*Example 8*

As described in Example 4, using a catalyst temperature of 180°C and a residence time of 12 minutes, N-ethylhexamethyldisilazane having a boiling point 162 to 163°C was obtained in a yield of 96.9% from a mixture of trimethylsilane and ethylamine in a molar ratio of 2:1.

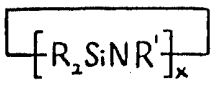
WHAT WE CLAIM IS:-

1. A process for the preparation of a silicon-nitrogen compound having the general formula:

$$(R_3Si)_nNR'_{3-n}$$

or $R_2Si(NR'_2)_2$

or



wherein *n* is 1 or 2, the radicals R′ are the same or different when two or more thereof are present in the compound and each is a hydrogen atom or a hydrocarbyl group, the radicals R are the same or different when two or more thereof are present in the compound and each is a hydrocarbyl group, and *x* is 3 or 4, which process comprises reacting a silane having the general formula:

$$R_{3-y}SiH_{y+1}$$

wherein $y$ is 0 or 1 and R is as defined above, with a compound having the general formula:

$$NR'_{3-n}H_n$$

wherein R′ and $n$ are as defined above, in the presence of a catalyst.

2. A process according to claim 1, wherein the or each radical R′ is an alkyl group containing from 1 to 8 carbon atoms or an aryl group.

3. A process according to claim 2, wherein the or each radical R′ is an alkyl group containing from 1 to 4 carbon atoms.

4. A process according to any of claims 1 to 3, wherein the or each radical R is an alkyl group containing from 1 to 20 carbon atoms or an aryl group.

5. A process according to claim 4, wherein the or each radical R is an alkyl group containing from 1 to 4 carbon atoms.

6. A process according to any of claims 1 to 5, wherein the reaction is effected at elevated temperature.

7. A process according to any of claims 1 to 6, wherein the catalyst is iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium or platinum, in elemental or conbined form.

8. A process according to any of claims 1 to 7, wherein the catalyst is supported on a carrier.

9. A process according to claim 8, wherein the carrier is activated carbon, aluminium oxide or silicon dioxide.

10. A process according to any of claims 1 to 9, wherein the reactants are contacted with the catalyst without the use of a solvent, the catalyst being in the form of a solid bed of catalyst particles or moulded bodies.

11. A process according to any of claims 1 to 10, wherein the reaction is effected in the gas phase.

12. A process for the preparation of a silicon-nitrogen compound as defined in claim 1, substantially as described in any of the foregoing Examples.

13. A silicon-nitrogen compound as defined in claim 1, whenever prepared by the process claimed in any of claims 1 to 12.

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