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Auner et al.(10) **Pub. No.: US 2013/0043429 A1**(43) **Pub. Date: Feb. 21, 2013**(54) **CHLORINATED OLIGOGERMANES AND
METHOD FOR THE PRODUCTION
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(52) **U.S. Cl.** **252/182.33**; 423/494(57) **ABSTRACT**

A chlorinated oligogermane as a pure compound or mixture of compounds which each have at least one direct Ge—Ge bond, substituents of which include chlorine or chlorine and hydrogen and atom ratio for substituent:germanium is at least 2:1 in the composition thereof, wherein a) the mixture has on average a Ge:Cl ratio of 1:1 to 1:3, or the pure compound has a Ge:Cl ratio of 1:2 to 1:2.67, and b) the mixture has an average number of germanium atoms of 2 to 8.

CHLORINATED OLIGOGERMANES AND METHOD FOR THE PRODUCTION THEREOF

RELATED APPLICATIONS

[0001] This is a §371 of International Application No. PCT/EP2010/068986, with an international filing date of Dec. 6, 2010, which is based on German Patent Application No. 10 2009 056 731.3, filed Dec. 4, 2009, the subject matter of which is incorporated by reference.

TECHNICAL FIELD

[0002] This disclosure relates to chlorinated oligogermanes and mixtures of chlorinated oligogermanes which have a molar germanium:chlorine ratio of 1:2 to 1:3 and also to a method for producing such chlorinated oligogermanes and oligogermane mixtures.

BACKGROUND

[0003] Germanium dichloride can more particularly be produced thermally from trichlorogermane (HGeCl_3) (cf. Holleman Wiberg, *Lehrbuch der Anorganischen Chemie*, Walter De Gruyter Verlag, 102nd edition, p. 1013 or C. E. Rick, T. D. McKinley, J. N. Tully (PB No. 96945 [1944] 1/10)).

[0004] WO 08/110386 A1 discloses a method and apparatus for production of halogenated polygermanes from halogermanes in a plasma-chemical way.

[0005] Halogenated oligogermanes are little known apart from hexachlorodigermane, which is described in the literature.

[0006] Lastly, a reaction of chloropolygermanes with chlorine gas is described; the chloropolygermanes become degraded to purely GeCl_4 .

[0007] It could therefore be helpful to provide chlorinated oligogermanes and mixtures of chlorinated oligogermanes as well as a method for production thereof.

SUMMARY

[0008] We provide a chlorinated oligogermane as a pure compound or mixture of compounds which each have at least one direct Ge—Ge bond, substituents of which include chlorine or chlorine and hydrogen and atom ratio for substituent: germanium is at least 2:1 in the composition thereof, wherein a) the mixture has on average a Ge:Cl ratio of 1:1 to 1:3, or the pure compound has a Ge:Cl ratio of 1:2 to 1:2.67, and b) the mixture has an average number of germanium atoms of 2 to 8.

[0009] We also provide a method for producing a halogenated oligogermane, including A) providing a chlorinated polygermane, and B) chlorinating the chlorinated polygermane with chlorine, a chlorine-releasing compound and/or a chlorine-containing gas.

[0010] The chlorinated oligogermanes (as pure compound) and the mixture of such chlorinated oligogermanes have at least one direct germanium-germanium bond, the substituents of which comprise either chlorine or chlorine and hydrogen, or at least one direct germanium-germanium bond, the substituents of which consist of chlorine or of chlorine and hydrogen. The atom ratio therein for substituent:germanium (where substituent here more particularly represents chlorine and hydrogen) is at least 2:1. The chlorinated oligogermanes as pure compound have a germanium:chlorine ratio of 1:2 to 1:2.67. The mixtures of chlorinated oligogermanes further

have a germanium:chlorine ratio of 1:1 to 1:3 and more particularly 1:2 to 1:3 and also an average number of germanium atoms per molecule of 2 to not more than 8.

[0011] The mixture of chlorinated oligogermanes is more particularly to be understood as meaning that only some of the compounds present therein need have at least one direct germanium-germanium bond with the abovementioned substituents. The general case is that at least two such compounds having a direct germanium-germanium bond will be present in the mixture, but frequently three or more. In the general case, moreover, it is exclusively compounds having such a defined germanium-germanium bond which will be present in such a mixture with or without any tetrachlorogermane.

[0012] Chlorinated oligogermanes are more particularly compounds of the formula $\text{Ge}_n\text{X}_{2n+2}$ where n is not more than 8, or mixtures of chlorinated oligogermanes having an average n of not more than 8, where X is more particularly chlorine or else chlorine and hydrogen. In the individual case, single chlorine atoms can be replaced by bromine atoms, but generally there will be no bromine. Chlorinated polygermanes are accordingly more particularly compounds of the formula $\text{Ge}_n\text{X}_{2n+2}$ where n > 8.

[0013] The chlorine content of the pure compounds, or the average chlorine content of a mixture, is determined herein by completely digesting the sample and then titrating the chloride by the Mohr method.

[0014] The hydrogen content is determined by integration of ^1H NMR spectrum using an internal standard and comparing the integrals obtained at known mixing ratio.

[0015] The molar masses of halogenated oligogermanes and the average molar masses of mixtures thereof are determined via freezing point depression.

[0016] The recited parameters of chlorine content, molar mass and, if appropriate, hydrogen content can be used to determine the chlorine:germanium ratio and also the average number of germanium atoms per molecule directly.

[0017] The chlorinated oligogermanes are obtainable in one example by chlorinating chlorinated polygermanes. Chlorinated oligogermanes thus obtained then generally have a heightened kinetic stability, more particularly with regard to the further chlorination of the oligochlorogermanes since the most reactive molecules in the chlorinated polygermane mixture will have already reacted.

[0018] Accordingly, the chlorinated oligogermanes are more particularly suitable for applications where the chlorinated germanes are further processed under oxidizing conditions. An example is the application of layers of the chlorinated oligogermanes onto substrates in oxidizing atmospheres such as atmospheres containing chlorine gas, for example.

[0019] In one example, the oligogermanes are obtained by splitting chlorinated polygermanes (PCGs) using an oxidizing agent. Chlorine and/or HCl are more particularly useful here as oxidizing agent, in which case the splitting can also be performed such that either an excess of the oxidizing agent is present or that the oxidizing agent is always present at low concentration only.

[0020] The chlorinated polygermanes used as starting material are more particularly obtainable thermally as per Holleman Wiberg, *Lehrbuch der Anorganischen Chemie*, Walter De Gruyter Verlag, 102nd edition, p. 1013 or C. E. Rick, T. D. McKinley, J. N. Tully (PB No. 96945 [1944] 1/10). In effect, trichlorogermane (HGeCl_3) is distilled at about 75° C. and splits into GeCl_2 and HCl in the process.

[0021] Plasma-chemically obtained chlorinated polygermanes can also be used as an alternative or additional starting material, more particularly chlorinated polygermanes as described in WO 2008/110386 A1, the subject matter of which is incorporated herein by reference. In general, however, the chlorinated polygermanes can also be plasma-chemically produced similarly to chlorinated polysilanes, methods for production of which are described, for example, in WO 2006/125425 A1 and WO 2009/143823 A2. Instead of the silicon halides used there, the corresponding germanium compounds are then used as starting material, while the concrete plasma-chemical production is essentially identical to that of the corresponding silanes except that the power density of the irradiation should be lower than for the corresponding silanes. More particularly, the power density should correspond to about 50 to 67% of the power density (in watts per cm^3) which is described in the two above-mentioned publications. With regard to further details of the method, structure and spectroscopic parameters of the polymers obtained, the subject matter of WO 2006/125425 A1 and WO 2009/143823 A2 is incorporated herein by reference.

[0022] In a further example, the mixture of oligogermanes has a higher solubility in inert solvents than at least one and typically two or more of the respective individual components of the mixture insofar as these individual components have more than 3 germanium atoms. Individual components are more particularly all the components that are present in the mixture at not less than 1 wt %. Individual components further more particularly include the respective perchlorinated compounds n-tetragermane, isotetragermane, n-pentagermane, isopentagermane and/or neopentagermane. The solubility of the mixture of oligogermanes is heightened compared with at least one of these compounds, usually compared with three or more than three of the recited compounds and frequently also compared with all recited compounds.

[0023] Inert solvents here and hereinbelow are more particularly non-nucleophilic aprotic solvents, of which in turn the solvents toluene, benzene and cyclohexane must be mentioned more particularly. The above-mentioned mixture of oligogermanes preferably has a higher solubility than the individual components having more than 3 germanium atoms in one or more of the recited preferred solvents at least.

[0024] Any reference herein to a higher or better solubility in inert solvents is to be understood as meaning that the specific solvent is capable of dissolving at room temperature a larger amount of chemical compound or of the mixture of chemical compounds before saturation is reached, while not more than 5 wt % of the amount used may remain as solid material. The determinative amount here is not for instance the molar amount, but the amount used (in g) of the still just soluble oligogermane/polygermane as individual compound or as mixture.

[0025] We realized that the mixture of oligogermanes has particularly good solubility because the various components appear to act as reciprocal solubilizers. Hence, the mixture of oligogermanes is also superior to the pure individual compounds since it is not just the case that the higher kinetic stability is advantageous, but it is generally also the case that when operating in solution more solvent is required for a specific further use.

[0026] In a further example, the chlorinated oligogermane mixtures have a higher solubility in inert solvents than the known thermally produced chlorinated polygermanes as described in Holleman Wiberg, *Lehrbuch der Anorganischen*

Chemie, Walter De Gruyter Verlag, 102nd edition, p. 1013 or C. E. Rick, T. D. McKinley, J. N. Tully (PB No. 96945 [1944] 1/10).

[0027] This holds more particularly again for the inert solvents toluene, benzene and cyclohexane in that our chlorinated oligogermanes have better solubility in one of these solvents at least, but usually in two or all of the solvents mentioned.

[0028] We realized that it is more particularly the short-chain components which act as solubilizers in our chlorinated oligogermanes.

[0029] A particularly interesting fraction of chlorinated oligogermane mixtures is the fraction with essentially no germanium tetrachloride, no Ge_2Cl_6 and no Ge_3Cl_8 left. This fraction can be isolated via fractional distillation from an as-obtained crude mixture of our chlorinated oligogermanes, and is hereinafter referred to as "fraction of compounds having more than three germanium atoms". Germanium tetrachloride, Ge_2Cl_6 and Ge_3Cl_8 can be removed, for example, by distillation at 0.01 to 0.1 hPa (i.e., in an oil pump vacuum for example) and room temperature so that the fraction of compounds having more than three germanium atoms may be separated off.

[0030] The fraction of compounds having more than three germanium atoms is obtained by distillation, as mentioned, or else by crystallization and, hence, has essentially no germanium tetrachloride, hexachlorodigermane and octachlorotrigermane left. Essentially it is to be understood as meaning that the compounds mentioned are present at not more than 10 wt % in that the proportion of these three compounds is typically less than 5 wt % and usually even less than 2 wt %. Ultrahigh-vacuum distillation can be used to effect a concrete determination of the remaining level of these compounds.

[0031] The fraction of compounds having more than three germanium atoms generally has a heightened degree of branching (as can be evidenced using IR or Raman spectroscopy) and correspondingly has a particularly good kinetic stability. Branching occurs with germanium atoms having bonds leading to three further germanium atoms (that is, they are tertiary germanium atoms) and with germanium atoms having bonds leading to four further germanium atoms (that is, they are quaternary germanium atoms). There are further certain applications (for example, the deposition of germanium layers) where the preference is for such branched chlorinated oligogermanes having a reduced chlorine content, or a higher germanium content, compared with GeCl_4 , Ge_2Cl_6 and Ge_3Cl_8 , since the former have heightened reactivity compared with the latter.

[0032] It is believed that the heightened proportion of branching in the fraction mentioned is attributable to the fact that bonds leading to tertiary or quaternary germanium atoms are less readily splittable by the oxidizing agent, thus preserving the original branching present while the molecular size continually diminishes as a result of the chlorination.

[0033] In one example, the fraction of compounds having more than three germanium atoms has a more than 8 atom % fraction and more particularly more than 11 atom % fraction of branching sites. In other words, at least 8% and more particularly more than 11% of the germanium atoms in the mixture are tertiary or quaternary germanium atoms. The degree of branching here can be determined via Raman spectra from the significant bands for vibrations of germanium-germanium bonds involving tertiary or quaternary germanium atoms.

[0034] In a further example, the perchlorinated neopentagermane within the fraction of compounds having more than three germanium atoms has a share of at least 10 atom %, more particularly more than 18 atom % and more particularly more than 25 atom %. Owing to the highly symmetrical structure of neopentagermane and the attendant relatively small full width at half maximum value of the signals obtained, the proportion of this compound can be quantified via the signal for the quaternary germanium atom in ^{73}Ge NMR. The content can be determined versus a known internal reference substance of known quantity (for example, an ampoule with tetramethylgermanium) by integration.

[0035] In a further example, the fraction of chlorinated oligogermane mixtures having more than 3 germanium atoms has a germanium:chlorine ratio of 1:2.2 to 1:2.5 and more particularly of 1:2.25 to 1:2.4.

[0036] In a still further example, appropriately chosen conditions of chlorination provide an oligochlorogermane mixture in which the Ge_2Cl_6 content after step B) is particularly high. The Ge_2Cl_6 content can then be at least 70 wt %, more particularly more than 85 wt % and preferably more than 95 wt %. When HCl is used as chlorinating agent, it is more particularly also possible for a significant $\text{Ge}_2\text{Cl}_5\text{H}$ content to also be present.

[0037] In yet a further example, the mixtures of chlorinated oligogermanes have an average number of germanium atoms per molecule in the range from 3 to 8.

[0038] In a further example, the chlorinated oligogermane, or the mixture thereof, has a hydrogen content of less than 2 atom % and more particularly less than 1 atom %. Frequently, the chlorinated oligogermane (mixture) will at most have a hydrogen content corresponding to the customary degrees of purity. The hydrogen substituents in the chlorinated oligogermane may more particularly come from the oxidation with HCl or be already present in the starting material since the chlorinated polygermanes can also have hydrogen substituents due to their method of production.

[0039] The general rule applicable to all compounds mentioned herein is that they have customary degrees of purity. That is, the purity of a compound consisting of particular varieties of atoms, or of a mixture which consists of two or more such individual compounds (which may also include GeCl_4), is at least 99.5% and frequently is at least 99.95%, and that the proportion of impurities is more particularly less than 10 ppm (% by weight is always meant). In the individual case, chlorine atoms may be partly replaced by bromine substituents. These then do not count as impurity in the above sense.

[0040] In another example, the chlorinated oligogermane when considered as individual compound includes more than 2 atom % and more particularly more than 2.8 atom % (in $\text{Ge}_{11}\text{Cl}_{23}\text{H}$ for example) and even more particularly more than 6 atom % of hydrogen (in $\text{Ge}_5\text{Cl}_{11}\text{H}$ for example). Even $\text{Si}_2\text{Cl}_5\text{H}$ is capable of being produced by reaction with HCl and of being obtained as pure substance by distillation.

[0041] The hydrogen contents recited herein can be determined as described above, via ^1H NMR spectroscopy. The signals observed therein are in the chemical shift range between 7.2 and 3.5 ppm and more particularly in the range between 5 and 3.8 ppm, and in the case of mixtures can be signals having very large full width at half maximum values.

[0042] In a further example, the chlorinated oligogermanes, and the mixtures thereof, have significant bands in the Raman spectrum at below 600 wavenumbers, more particu-

larly between 500 and 370 and even more particularly at <320 wavenumbers. A significant band here and hereinbelow is generally any band whose intensity is greater than 10% of the highest intensity band in the Raman spectrum.

[0043] The mixture of chlorinated oligogermanes may be more particularly colorless to slightly yellow or ivory white. The mixture is more particularly obtained as a mobile liquid or at least partly crystalline substance. When the chlorinated oligogermanes are mobile liquids, the viscosity of the liquid proportion at room temperature is less than 1000 mPa s and more preferably less than 400 mPa s. Crystallinity can be determined using X-ray powder diffractometry, since crystalline compounds generate significant signals which naturally cannot occur in the case of liquid or viscid compounds.

[0044] In another example, the chlorinated oligogermane, or the mixture of chlorinated oligogermanes, is readily soluble in the inert solvent as defined above. Readily soluble here is to be understood as meaning that concentrations of at least 10 wt % can be put into solution. Preferably, our chlorinated oligogermanes and our chlorinated oligogermane mixtures have the solubility properties of this example in at least one of the solvents benzene, toluene and cyclohexane, frequently even in all three solvents. "Readily" soluble further refers to chlorinated oligogermane mixtures where a nonsoluble residue of not more than 5 wt % of the amount used remains (this means in the case of a solution with 10 wt % of dissolved chlorinated oligosilane that at most 0.5 wt % can remain as nondissolved solid material). Frequently, however, complete dissolution of the chlorinated oligogermane mixture will take place.

[0045] In a further example, at least 20 wt % of the above soluble fraction is distillable under reduced pressure, especially under a pressure in the range from 0.01 to 1 hPa, without decomposing. This stipulation is satisfied more particularly by compounds having up to 4 germanium atoms.

[0046] We further also provide a method for producing chlorinated oligogermanes or oligogermane mixtures according to any of the above-mentioned examples. The method comprises the following steps:

[0047] A) providing a chlorinated polygermane,

[0048] B) chlorinating the chlorinated polygermane with chlorine, a chlorine-releasing compound and/or a chlorine-containing gas. HCl is more particularly useful as chlorine-containing gas; chlorine is more particularly in the form of Cl_2 ; and nonmetal chlorides are more particularly useful as chlorine-releasing compounds. Particular preference is given to using either Cl_2 or HCl as a chlorinating agent.

[0049] Method step B) is generally subject to the following temperature conditions and/or pressure conditions, although in most cases not only the following pressure conditions, but also the following temperature conditions apply. It is accordingly more particularly the case that the temperature in method step B) is -60°C . to 200°C . and especially -30 to 40°C ., for example, -10 to 25°C . The pressure is more particularly 200 to 2000 hPa, for example, 800 to 1500 hPa.

[0050] We thus determined that the pressure and temperature parameters mentioned give particularly good results.

[0051] In one example of our method, the chlorination as per method step B) is followed by a fractional distillation to separate comparatively volatile chlorinated germanes from germanes having at least 4 germanium atoms in the molecule. It is thus more particularly the case that GeCl_4 , Ge_2Cl_6 and Ge_3Cl_8 are separated off in the fractional distillation. This fractional distillation can take place for example at a pressure

of 10^{-1} to 10^{-2} hPa and a temperature of up to 140°C ., preferably up to 100°C ., and will frequently be carried out at room temperature.

[0052] In a further example of the method, the chlorinated polygermanes provided in step A) are diluted before step B) and more particularly GeCl_4 , Ge_2Cl_6 and/or Ge_3Cl_8 can be used as diluent (hereinafter also referred to as solvent). Such a dilution can provide a more efficient chlorination in step B). As mentioned above, the diluents can subsequently also be distilled off again and optionally the distilled-off diluents can be reused afresh (i.e., recycled) as diluents.

[0053] In another example, the method can be carried out such that an excess of the chlorinating agent, more particularly an excess of HCl, is present during step B). Such an excess can be present when free HCl is constantly present in the reaction mixture, for example, such that the solution is saturated with HCl. To this end, further chlorinating agent can be constantly replenished in step B). In general, however, no saturated HCl solutions are used.

[0054] When other chlorinating agents are used (but optionally also in the case of HCl) there will frequently be a molar deficiency of chlorinating agent and then further chlorinating agent will be replenished as appropriate (so that it is permanently in molar deficiency). Especially when Cl_2 is used as chlorinating agent, Cl_2 will frequently be used in that manner in molar deficiency relative to the chloropolygermane. The reaction with the chloropolygermane may advantageously be controlled via the rate of chlorine addition to thereby try to suppress the formation of GeCl_4 .

[0055] To obtain a particularly high proportion of Ge_2Cl_6 in the product mix, the chlorination can be carried out by selecting a particularly long reaction time with Cl_2 which, as shown above, is always in molar deficiency. Should a significant proportion of $\text{Ge}_2\text{Cl}_6\text{H}$ be formed, HCl must be used as a chlorinating agent instead of Cl_2 (or some other chlorinating agent that does not contain hydrogen). When a particularly low proportion of Ge_2Cl_6 is desired, the reaction should be carried out at low temperatures and the Cl_2 should be added particularly carefully. In addition, the total molar quantity of chlorine added should be adjusted appropriately, for example, by choosing the added amount of chlorine in relation to the known chlorine:germanium ratio for the chloropolygermane used such that a certain chlorine:germanium ratio must automatically result for the chlorooligogermane mixture obtained.

1.-26. (canceled)

27. A chlorinated oligogermane as a pure compound or mixture of compounds which each have at least one direct Ge—Ge bond, substituents of which comprise chlorine or chlorine and hydrogen and atom ratio for substituent:germanium is at least 2:1 in the composition thereof, wherein

- a) the mixture has on average a Ge:Cl ratio of 1:1 to 1:3, or the pure compound has a Ge:Cl ratio of 1:2 to 1:2.67, and
- b) the mixture has an average number of germanium atoms of 2 to 8.

28. The oligogermane according to claim 27, obtained by splitting chlorinated polygermanes using an oxidizing agent comprising chlorine and/or HCl.

29. The oligogermane according to claim 27, a product fraction of the mixture having more than three germanium atoms in its skeleton has a more than 8% fraction of branching sites in the oligogermane.

30. The oligogermane according to claim 27, wherein the mixture has a higher solubility in inert solvents than its individual components having more than 3 germanium atoms.

31. The oligogermane according to claim 27, wherein the mixture has a higher solubility in inert solvents, than thermally produced chlorinated polygermanes.

32. The oligogermane according to claim 27, wherein a product fraction having more than three germanium atoms has a neo- $\text{Ge}_3\text{Cl}_{12}$ fraction of at least 10%.

33. The oligogermane according to claim 27, wherein the Ge:Cl ratio in a product fraction having more than three germanium atoms is 1:2.2 to 1:2.5.

34. The oligogermane according to claim 27, wherein an average number of germanium atoms per molecule in the mixture is 3 to 8.

35. The oligogermane according to claim 27, wherein the Ge_2Cl_6 fraction is at least 70 wt %.

36. The oligogermane according to claim 27, wherein hydrogen content is less than 2 atom %.

37. The oligogermane according to claim 27, wherein hydrogen content is greater than 2 atom %.

38. The oligogermane according to claim 27, having an ^1H NMR spectrum with signals in a chemical shift range of 7.2 to 3.5 ppm.

39. The oligogermane according to claim 27, having a Raman spectrum with significant bands at below 600 wavenumbers.

40. The oligogermane according to claim 27, having a Raman spectrum with at least three significant bands between 270 to 340 wavenumbers and at least two significant bands between 550 to 640 wavenumbers.

41. The oligogermane according to claim 27, which is a mobile liquid and/or at least partially solid at room temperature.

42. The oligogermane according to claim 27, wherein concentrations of 10 wt % of the oligogermane are soluble in at least one of the solvents benzene, toluene and cyclohexane.

43. The oligogermane mixture according to claim 27, wherein a soluble fraction is distillable under reduced pressure of 0.01 to 1 hPa, with a nondecomposition rate of 20%.

44. The oligogermane according to claim 27, obtained from thermally produced chlorinated polygermane.

45. The oligogermane according to claim 27, obtained from plasma-chemically produced chlorinated polygermane.

46. A method for producing a halogenated oligogermane according to claim 27, comprising:

- A) providing a chlorinated polygermane, and
- B) chlorinating the chlorinated polygermane with chlorine, a chlorine-releasing compound and/or a chlorine-containing gas.

47. The method according to claim 46, wherein temperature during a reaction in step B) is -60 to 200°C .

48. The method according to claim 46, wherein a pressure of 200 to 2000 hPa is present in step B).

49. The method according to claim 46, wherein chlorinating in step B) is effected using Cl_2 and/or HCl.

50. The method according to claim 46, wherein step B) is followed by a fractional distillation whereby chlorinated mono- and oligogermanes have up to 3 germanium atoms in the molecule are distilled off essentially completely.

51. The method according to claim 50, wherein Ge_2Cl_6 is obtained as pure product.

52. The method according to claim 46, wherein the chlorinated polygermane is diluted before step B) and GeCl_4 , Ge_2Cl_6 and/or Ge_3Cl_8 are used as a diluent.

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