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3,836,558

PROCESS FOR THE PRODUCTION OF TRIS-(TRIMETHYLSILOXY)-PHENYLSILANE

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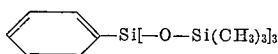
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7 Claims

ABSTRACT OF THE DISCLOSURE

The method of producing tris-(trimethylsiloxy)-phenylsilane by hydrolytic reaction of trimethylchlorosilane, phenyltrichlorosilane and water is improved to give significant rise of yield by carrying out the reaction, according to the invention, in the presence of hexamethyldisiloxane in a proportion of 0.2 to 12 mols per mol of phenyltrichlorosilane, applying a molar ratio of trimethylchlorosilane to phenyltrichlorosilane of between 3.3:1 and 4:1, and adding the water gradually, in excess, until the hydrolysis is complete. This process is further improved by admixing the additionally employed hexamethyldisiloxane some time before the addition of any other ingredient with an acid equilibration catalyst, preferably followed by heating.

The present invention relates to the production of tris-(trimethylsiloxy)-phenylsilane of the formula



It is known in the art, for example from U.S. Patent Specification 3,012,052, to produce this tetrasiloxane by hydrolyzing a mixture of trimethylmonochlorosilane and monophenyltrichlorosilane in the molar ratio of 3:1 by gradual stirring in of water in the molar ratio of 3 H₂O:4 Si. However, the siloxane condensation which thereupon takes place spontaneously only gives a yield of 27% of tetrasiloxane, relative to the amounts of chlorosilane employed; the remaining phenyl compounds contain more than one phenylsiloxane unit. Since these by-products are only used to a limited extent, the economy of the process is unsatisfactory.

Obvious modifications of this process in our own experiments did not give any improvement. Thus, doubling the amount of water only increased the yield to 34%; while tripling the amount of (CH₃)₃SiCl resulted in 83% of the amount of C₆H₅SiCl₃ employed being turned to account, the utilization of the amount of (CH₃)₃SiCl employed was at the same time of course only 25%, so that the proportion by weight of undesired by-products, here essentially hexamethyldisiloxane, was, similarly to the case of the known process, approximately twice as great as the proportion by weight of the tris-(trimethylsiloxy)-phenylsilane.

Another obvious attempt, to convert the higher polymers, left after distillative removal of the main product, to the tetramer by the known equilibration method by means of sulphuric acid in the presence of a large excess of hexamethyldisiloxane, was not successful to an economically significant extent.

As has now been found, however, the phenyltrichlorosilane can be converted to the extent of more than 90% into the desired tetrasiloxane, by a new combination of several process steps, without the simultaneously freshly formed amount of hexamethyldisiloxane exceeding a tol-

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erable level. According to the invention, tris-(trimethylsiloxy)-phenylsilane is produced by carrying out the hydrolytic reaction of trimethylchlorosilane, phenyltrichlorosilane and water in the presence of an amount of hexamethyldisiloxane which is 0.2 to 12 mols, preferably 2 to 6 mols, per mol of phenyltrichlorosilane, using a molar ratio of trimethylchlorosilane to phenyltrichlorosilane of between 3.3:1 and 4:1 and adding the water gradually, in excess, until the hydrolysis is complete. Depending on the molar ratio of the chlorosilanes, yields of up to 74% result. By "yield" there is to be understood here, and in all the following text, the ratio of the number of mols of tris-(trimethylsiloxy)-phenylsilane produced to the number of mols of phenyltrichlorosilane employed.

Though it has proved to be impossible to cause the mixture of the siloxanes issuing from the reaction, after addition of acid, to undergo an equilibration with renewed formation of tetrasiloxane, a further improvement in the yield can be achieved, contrary to expectations, by adding to the additionally employed hexamethyldisiloxane, before the start of the reaction, an acid equilibration catalyst, especially 1 to 20 percent of the weight of disiloxane of concentrated sulphuric acid (or, less effectively, hydrochloric acid) and stirring either for 12 to 24 hours at room temperature or for a shorter time at an elevated temperature which does not reach the boiling point. The yields are then 76 to 91%. The amount of sulphuric acid can be kept low, for the same high yield, if initially the mixture of hexamethyldisiloxane and sulphuric acid is warmed to 50° C. for about 30 minutes, the phenyltrichlorosilane is gradually added thereto, the trimethylchlorosilane is then added at 30° C. and the water is finally stirred in at room temperature, spread over a prolonged period of time. An elevated temperature during the hydrolysis reaction leads to a substantially reduced yield, for example, at 50° C., to 46% instead of 76%.

The hexamethyldisiloxane can also be produced *in situ* from excess trimethylchlorosilane; and an appropriate amount of sulphuric acid can be mixed with the water used for the hydrolysis; while the yield then only remains moderate (for example 58%), it is nevertheless considerably higher than according to the known process mentioned initially.

EXAMPLE 1

A mixture of 974 g. (6 mols) of hexamethyldisiloxane and 29 g. (3% of the weight of the siloxane) of concentrated sulphuric acid is first heated to 50° C. for 30 minutes with continuous stirring, and 212 g. (1 mol) of phenyltrichlorosilane is added dropwise thereto over the course of a further 15 minutes; the mixture is then allowed to cool. When the temperature has reached 30° C., 435 g. (4 mols) of trimethylchlorosilane are added over the course of 15 minutes, followed by 180 g. (10 mols) of water added dropwise distributed over 6 hours; thereafter, stirring is continued for a further hour. After settling out, and separating off the aqueous phase, the oil thus obtained is washed with aqueous sodium chloride solution until it reacts neutral and is distilled. Hexamethyldisiloxane is first obtained, followed at 0.07 mm. Hg and 65° C. by 340 g. (=91% of the theoretical amount) of pure tris-(trimethylsiloxy)-phenylsilane.

EXAMPLE 2

If a procedure analogous to Example 1 is followed with the modification that 1949 g. (12 mols) of hexamethyldisiloxane, 45 g. (2.3% of the weight of the siloxane) of concentrated sulphuric acid and 270 g. (15 mols) of water are employed, 91% yield is again obtained.

EXAMPLE 3

If a procedure analogous to Example 1 is followed with the modification that 487 g. (3 mols) of hexamethyldisiloxane, 15 g. (3% of the weight of the siloxane) of concentrated sulphuric acid and 72 g. (4 mols) of water are employed, distillation first yields 550 of hexamethyldisiloxane and thereafter, at 0.07 mm. Hg and 65° C., 321 g. (=86% of the theoretical amount) of pure tris-(trimethylsiloxy)-phenylsilane.

EXAMPLE 4

If a procedure analogous to Example 3 is followed with the modification that instead of 4 mols only 3.3 mols of trimethylchlorosilane are used, and 3.5 mols of water are used, a 76% yield of tris-(trimethylsiloxy)-phenylsilane is still obtained.

If, however, the temperature is kept at 50° C. until hydrolysis is complete, the yield only attains 46%.

EXAMPLE 5

A mixture of 487 g. (3 mols) of hexamethyldisiloxane and 97 g. (20% of the weight of the siloxane) of concentrated sulphuric acid is initially stirred for 17 hours at room temperature. 212 g. (1 mol) of phenyltrichlorosilane is then added dropwise thereto over the course of 15 minutes, 435 g. (4 mols) of trimethylchlorosilane are added over the course of a further 15 minutes and subsequently 72 g. (4 mols) of water are added dropwise distributed over 6 hours; stirring is then continued for one hour. In other respects the procedure described in Example 1 is followed and finally 303 g. (=81% of the theoretical amount) of pure tris-(trimethylsiloxy)-phenylsilane are obtained.

EXAMPLE 6

108 g. (6 mols) of water are added dropwise over the course of 3 hours to a mixture of 487 g. (3 mols) of hexamethyldisiloxane, 212 g. (1 mol) of phenyltrichlorosilane and 435 g. (4 mols) of trimethylchlorosilane at room temperature, while stirring, and the further procedure followed is as described in Example 1. The yield is 74%.

EXAMPLE 7

A solution of 15 g. of concentrated sulphuric acid in 90 g. of water is added dropwise over the course of 6 hours to a mixture of 212 g. (1 mol) of phenyltrichlorosilane and 435 g. (4 mols) of trimethylchlorosilane at room temperature, while stirring, and the further procedure followed is as described in Example 1. The yield is 58%.

COMPARISON EXPERIMENTS

The following comparison experiment was carried out without admixture of hexamethyldisiloxane or sulphuric acid, but instead with a large excess of trimethylchlorosilane: 234 g. (13 mols) of water were added dropwise over the course of 7 hours to a mixture of 212 g. (1 mol) of phenyltrichlorosilane and 1086 g. (10 mols) of trimethylchlorosilane at room temperature, while stirring. Thereafter the reaction mixture was stirred for a further hour and was then left to stand for 15 hours. It was subsequently washed with aqueous sodium chloride solution until it reacted neutral, and the oil phase was dried with sodium sulphate and filtered. 866 g. of a water-clear filtrate were obtained, from which it was admittedly possible to isolate 309 g. (=83% of the theoretical amount)

of the desired tetrasiloxane, in addition to 33 g. of more highly condensed products, by fractional distillation, but from which additionally 518 g. (3.2 mols) of hexamethyldisiloxane were isolated, this being a by-product which is economically undesirable because, in contrast to the process according to the invention, it is not utilized in successive batches of this process and is insufficiently pure for other purposes.

In a further comparison experiment, a mixture of methylphenylhexasiloxanes and more highly condensed siloxanes, as obtained from the initially mentioned known process, was subjected to an equilibration reaction with concentrated sulphuric acid by stirring 732 g. of this mixture for 66 hours at room temperature with 1435 g. of hexamethyldisiloxane and 65 g. of sulphuric acid. Thereafter, the acid was eluted with aqueous sodium chloride solution. Fractional distillation of the siloxane mixture thus obtained gave, amongst phenyl compounds, only 12 g. of tris-(trimethylsiloxy)-phenylsilane, and additionally 512 g. of 1,1,3,3-tetrakis-(trimethylsiloxy)-1,3-diphenyldisiloxane and 156 g. of more highly condensed products.

What we claim is:

1. In a process for the production of tris-(trimethylsiloxy)-phenylsilane wherein a mixture of trimethylchlorosilane and phenyltrichlorosilane is hydrolyzed by addition of water, the improvement which comprises carrying out the hydrolysis in the presence of 0.2 to 12 mols of hexamethyldisiloxane, per mol of phenyltrichlorosilane, the molar ratio of trimethylchlorosilane to phenyltrichlorosilane being between 3.3:1 and 4:1 and adding the water gradually in excess until the hydrolysis is completed.

2. The process according to claim 1, in which said hexamethyldisiloxane is present in a proportion of 2 to 6 mols per mol of phenyltrichlorosilane.

3. The process according to claim 1, in which hexamethyldisiloxane is produced *in situ*.

4. The process according to claim 1, in which said hexamethyldisiloxane is admixed, before the addition of any of the aforesaid reactants, with an acid equilibration catalyst in an amount of 1 to 20 percent by weight of said disiloxane.

5. The process according to claim 4, in which said acid equilibration catalyst is sulphuric acid.

6. The process according to claim 4, in which the mixture of said hexamethyldisiloxane and said acid equilibration catalyst is stirred at an elevated temperature below its boiling point before the addition of any further reactant.

7. The process according to claim 6, which comprises warming to 50° C. for about 30 minutes a mixture of hexamethyldisiloxane and sulphuric acid, gradually adding phenyltrichlorosilane to said mixture, adding trimethylchlorosilane thereto at 30° C., and gradually adding the aforesaid excess of water thereto at room temperature.

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