Our Ref: 466504

P/00/001
Section 29

AUSTRALIA

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659005

PATENT REQUEST : STANDARD PATENT

I/We, being the person/s identified below as the Applicant, request the grant of a patent to the person/s indicated below as the Nominated Person/s, for an invention described in the accompanying standard complete specification.

Full application details follow.

[71] [70] Applicant/s and Nominated Person/s:
Witco GmbH,
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[54] Invention Title:
Method of preparing trialkyl-tin hydrides

[72] Name/s of actual inventor/s: (optional)

[74] Address for service in Australia:
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BASIC CONVENTION APPLICATION/S DETAILS:

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Witco GmbH
By Patent Attorneys
DAVIES COLLISON CAVE

Peter Stearne

Dr. PETER STEARNE, FIPAA

Fee: $ 197.00

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NOTICE OF ENTITLEMENT

We, **WITCO GMBH** the applicant in respect of Australian Patent Application **No. 39818/93** state the following:

1. Witco GmbH is the Nominated Person in respect of the application.

2. The actual inventors of the invention, the subject of the application, are Ralf-Jürgen BECKER, Ulrich STEWEN and Udo WEINBERG.

3, The Nominated Person, Witco GmbH is entitled to the grant of the patent in respect of the application because the Nominated Person derived title to the invention from the said inventors by way of assignment.

4. The Nominated Person is entitled to claim priority from the basic application listed in the patent application form because (i) the Nominated Person is the applicant in respect of the basic application and (ii) the basic application was the first application made in a convention country in respect of the invention, the subject of the application.

DATED this 21st February, 1995.

Peter Stearne

DR PETER A STEARNE

A member of the firm of
DAVIES COLLISON CAVE
for and on behalf of the applicant.

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(12) PATENT ABRIDGMENT (11) Document No. AU-B-39818/93
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(54) Title
METHOD OF PREPARING TRIALKYL-TIN HYDRIDES

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(57) Claim

1. Method of preparing trialkyl-tin hydrides of the general formula $R_1R_2R_3SnH$, wherein R_1, R_2, and R_3 can be identical or different branched and/or unbranched and/or substituted alkyl groups, characterized by the stages

a) converting bis-[trialkyl-tin] oxide with a stabilized aqueous solution of sodium borohydride in the presence of an inert solvent that mixes only to some extent if at all with water,

b) maintaining the reaction temperature between approximately 0 and 140 °C and preferably between 20 and 60 °C,

c) allowing the batch to stand 0 to 3 hours subsequent to reaction,

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d) separating the organic from the aqueous phase, and

e) obtaining the product by distilling the solvent off.

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Regulation 3:2

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ORIGINAL
COMPLETE SPECIFICATION
STANDARD PATENT

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Invention Title: Method of preparing trialkyl-tin hydrides

The following statement is a full description of this invention, including the best method of performing it known to me:-

METHOD OF PREPARING TRIALKYL-TIN HYDRIDES

The present invention concerns an improved method of preparing trialkyl-tin hydrides of the general formula $R_1R_2R_3SnH$. The particular process involved ensures that they will remain stable when stored for a long time. Organo-tin hydrides, especially tri-n-butyl-tin hydride, are valuable organic-synthesis reagents with an extraordinarily wide range of applications. This value has been demonstrated in a number of publications. Detailed information can be obtained from such reviews as W.P. Neumann, Synthesis 1987, 655; B. Giese, Radicals in Organic Synthesis: Formation of Carbon Bonds, Oxford, Pergamon Press, 1986; M. Pereyre, J.P. Quintard, & A. Rahm, Tin in Organic Synthesis, London, Butterworth, 1987; D.P. Curran, Synthesis 1988, 417 & 489; I. Omar, Organotin Chemistry, Amsterdam, Elsevier, 1989; and P.G. Harrison, Chemistry of Tin, Glasgow & London, Blackie, 1989.

Industrial-scale use as so far been restricted by the limited stability of the organo-tin hydrides, a direct result of unsatisfactory preparation and purification.

Instability is in particular provoked by traces of contaminants that remain in the product in consequence of production and directly catalyze decomposition. Traces of such Lewis acids as aluminum, boron, and organo-aluminum and organo-tin halogenides for example will trigger immediate

decomposition.

Methods of subsequently stabilizing organo-tin hydrides have been published (e.g. German 1 167 345 & German 1 468 709). Purification by additional extraction with alcohols or basic solutions is inefficient and results in unacceptably low yields.

Methods of preparing organo-tin hydrides have been described. They involve the aforesaid drawbacks or result in low yields of the tin hydrides or both.

US Patent 4 282 166 describes a method of preparing trialkyl-tin hydrides from trialkyl-tin chloride and sodium bis-(2-alkoxyethoxy)aluminum dihydride.

Canadian 90: 204 205 p describes reducing trialkyl-tin chloride with sodium borohydride ($NaBH_4$) in mixtures of ether and water that yields 65 to 80 %.

US A 3 439 010 describes obtaining yields of approximately 80 % trialkyl-tin hydrides by thermally decomposing trialkyl-tin formiates.

The preparation of organo-tin hydrides from sodium hydride and alkyl-tin chlorides are protected in US A 3 401 183.

Alkyl-tin oxides and chlorides can be converted into tin hydrides with siloxanes and silanes as points of departure (K. Hayashi et al, J. Organomet. Chem. 10, 1, 81-94; Japanese Patent 43 010 134 [Canadian 69: 106 880 b]; Japanese Patent 43 010 133 [Canadian 69: 106 879 h]; Japanese Patent 43 012 132 (Canadian 70: 37 922 y]; and German Patent 3 119 643).

Using aluminum lithium hydride (AlH_4Li) yields 66 to at most 89 % trialkyl-tin hydrides (H.J. Albert, T.N. Mitchell, and W.P. Neumann in H. Zimmer, ed., Methodicum Chimicum Vol. 7, Part A, New York, Academic Press, 1977, 361-62).

Satisfactory yields of trialkyl-tin chlorides can be obtained with sodium borohydride, although the reaction and preparation are complicated and difficult (J. Organomet. Chem. 9, 2, 379-82 [1967]).

Hungarian Patent A-41-412 describes a method of preparing tri-n-butyl-tin hydride from bis-[tri-n-butyl-tin] oxide. The process is characterized by dissolving the oxide in an aliphatic alcohol and reacting it at 10 to 30 °C with an alcoholic and/or aqueous solution of sodium borohydride for 10 to 60 minutes. Yields of 64 to 84 % tri-n-butyl-tin hydride are isolated subsequent to a complicated series of purifications.

It has, surprisingly, been discovered, however, that trialkyl-tin hydrides of the general formula $R_1R_2R_3SnH$ can be prepared in a simple and reliable reaction that comprises the stages

a) converting bis-[trialkyl-tin] oxide with a stabilized aqueous solution of sodium borohydride in the presence of an inert solvent that mixes only to some extent if at all with water,

b) maintaining the reaction temperature between approximately 0 and 100 °C and preferably between 20 and 60 °C,

c) allowing the batch to stand 0 to 3 hours subsequent to reaction, and

d) obtaining the product by separating the organic from the aqueous phase.

The method results in high yields of high-purity organo-tin hydrides from inexpensive and easily obtained starting compounds. The product is, apparently due to the method's extraction-and-neutralization effect, free from decomposition initiators and promoters.

It is of advantage to the method in accordance with the invention to employ an inert solvent that reacts with neither organo-tin hydrides nor sodium borohydride. Diethylether, dioxan, acetonitrile, and hydrocarbons, preferably tetrahydrofuran, are examples. The starting compounds are preferably introduced stoichiometrically or almost stoichiometrically at ratios of 0.5 to 1.5 moles of sodium borohydride to 1 mole of bis-[trialkyl-tin] oxide.

The procedure can be facilitated to advantage by using a stabilized aqueous solution of sodium borohydride. Such bases as sodium hydroxide are particularly appropriate.

Reduction can be accelerated to advantage by adding 0.1 to 10 % by weight of such hydrogen-acid compounds as thiosalicylic acid, lactic acid, dodecanethiol, and preferably thioglycolic acid.

Also of advantage is the addition of 0 to 10 % by weight of antioxidants. Such typical radical traps as butylated hydroxytoluene (BHT), 3-tert-butyl-4-hydroxyanisole, pyrogallol, and such typical metal-ion deactivators as triphenylphosphine, 4,4-thio-bis-(2-tert-butyl-5-methylphenol), ethelenediamine N,N,N',N'-tetra-2-propyl alcohol, and N',N'-diphenyl-1,4-phenylenediamine can be employed.

The reaction recited in the following claims is simpler and more reliable than previously published methods, and its starting materials are cheap and cost-effective.

The reaction of bis-[trialkyl-tin] oxides with a stabilized aqueous solution of sodium borohydride is simple to regulate by adding controlled quantities of the reductant. The reaction can be reversed, to recover the sodium-borohydride solution, without decreasing the yield.

The reaction can be conducted both continuously and discontinuously.

Two phases occur while the materials are being added. The upper, organic, phase contains the trialkyl-tin hydride and, until the batch is complete, the as yet unconverted bis-[trialkyl-tin] oxide as well. The lower, aqueous phase, contains the reductant, sodium borohydride, and its oxidation products.

Since the reaction is liquid in liquid, any contaminants that enter with the starting materials will be constantly extracted from the organic phase. Any traces for example of Lewis acids, which catalyze the decomposition of organo-tin hydrides, will be neutralized by the basic sodium-borohydride solution and will enter the aqueous phase.

Such auxiliaries as hydrogen-acid compounds or antioxidants that tend to accelerate the reaction for example will also be eliminated from the organic phase and will not contaminate the trialkyl-tin hydride.

Yields are almost quantitative because the impoverishment in disruptive contaminants begins simultaneously with reduction.

The termination of reduction is followed by separation of the lower, aqueous phase, which, once more sodium borohydride is added, can be re-employed. The solvent is distilled from the upper, organic phase, which contains the organo-tin hydride. It is unnecessary to further purify the product.

The particular advantage of the method is that the extraction and neutralization performed by the basic aqueous phase makes it possible to prepare trialkyl-tin hydrides of high purity and in almost quantitative yields. The hydrides will be free of decomposition initiators or catalysts without additional purification and are accordingly extremely stable.

Examples

Example 1

810 g of bis-[tributyl-tin] oxide are accelerated with 2.5 % by weight of thioglycolic acid and dissolved in 600 g of tetrahydrofuran. A solution of 51.5 g of sodium borohydride in 130 g of water is stabilized with 12 g of sodium hydroxide

(NaOH) is added at 60 °C within 30 minutes. The tetrahydrofuran is distilled off, the aqueous phase separated, and 770 g (97 %) of product isolated.

Example 2

1 to 5 % by weight of such antioxidants as butylated hydroxytoluene, hydroquinone, or pyrogallol is of advantage when reduction occurs without a protective atmosphere.

The conversion is similar to the conversion described with reference to Example 1, although 3 % of butylated hydroxytoluene is added. bis-[Tributyl-tin] hydride is isolated almost quantitatively.

Example 3

135 g of bis-[tributyl-tin] oxide and 3.4 g of thioglycolic acid are added to 100 g of acetonitrile. 8.5 g of sodium borohydride, dissolved in 20 g of water and stabilized with 1.0 g of sodium hydroxide are added at 20 °C. The temperature rises to approximately 38 °C. The reaction is allowed to continue for 1 hour. The phases are separated and 123 g (93 %) of product isolated by fractionated distillation.

Example 4

Conversion as in Example 3 although with dioxan as a

solvent.

Example 5

51 g of sodium borohydride is dissolved in 150 mℓ of water. The batch is stabilized with 12 f of sodium hydroxide and 600 g of tetrahydrofuran. 810 g of bis-[tributyl-tin] oxide and 34.8 g of thiosalicylic acid are added. The organic phase is separated and employed for distillation. The yield of tri-n-butyl-tin hydride is 770 g (97 %).

Example 6

The reaction conditions are similar to those in Example 5 except that the accelerator is lactic acid instead of thiosalicylic acid.

Example 7

The reaction conditions are similar to those in Example 5 except that the accelerator is dodecanethiol instead of thiosalicylic acid.

Example 8

306 g of bis-[tributyl-tin] oxide and 257 g of tetrahydrofuran are stabilized with 0.025 % of butylated hydroxytoluene. A solution of 14.6 g of sodium borohydride in 50 mℓ of 1 n sodium hydroxide is added at 40 °C. The batch is left for 1 hour at 50 °C and treated as hereintofore described. 290 g (96 %) of tri-n-butyl-tin hydride are

isolated.

Example 9

306 g of bis-[trioctyl-tin] oxide and 257 g of tetrahydrofuran are stabilized with 0.64 g of butylated hydroxytoluene. A solution of 12.4 g of sodium borohydride in 50 mℓ of .1 n aqueous sodium-hydroxide solution is added at 40 °C. The batch is left for 2 hours at 50 °C and treated as hereintofore described. 300 g (100 %) of trioctyl-tin hydride are isolated.

Example 10

9.3 g of sodium borohydride in 25 g of water stabilized with 2.2 g of sodium hydroxide are treated with 150 g of tetrahydrofuran stabilized with 0.025 % of butylated hydroxytoluene. 189 g of bis-[trihexyl-tin] oxide and 3.7 g of thioglycolic acid are added at room temperature. The batch is left for 10 minutes at 65 °C and cooled. The organic phase is separated. Fractionation is followed by isolation of 170 g (92%) of trihexyl-tin oxide.

Example 11

Trineophyl-tin hydride is prepared by a method similar to that described in Example 10.

Example 12

Tri-isobutyl-tin hydride is prepared by a method similar to

that described in Example 10.

The claims defining the invention are as follows:

1. Method of preparing trialkyl-tin hydrides of the general formula $R_1R_2R_3SnH$, wherein R_1, R_2, and R_3 can be identical or different branched and/or unbranched and/or substituted alkyl groups, characterized by the stages

a) converting bis-[trialkyl-tin] oxide with a stabilized aqueous solution of sodium borohydride in the presence of an inert solvent that mixes only to some extent if at all with water,

b) maintaining the reaction temperature between approximately 0 and 140 °C and preferably between 20 and 60 °C,

c) allowing the batch to stand 0 to 3 hours subsequent to reaction,

d) separating the organic from the aqueous phase, and

e) obtaining the product by distilling the solvent off.

2. Method as in Claim 1, characterized in that the inert solvent is a solvent that reacts with neither organo-tin hydrides nor sodium borohydride.

3. Method as in Claims 1 and 2, characterized in that the molar ratio between the bis-[trialkyl-tin] oxide and the sodium borohydride is approximately 1:1.

4. Method as in Claims 1 through 3, characterized in that the aqueous solution of sodium borohydride is stabilized with a base, especially sodium hydroxide.

5. Method as in Claims 1 through 4, characterized in that the reduction is accelerated by adding 0.1 to 10% by weight of hydrogen-acid compounds.

6. Method as in Claims 1 through 5, characterized in that the reduction is carried out in the presence of 0.01 to 10% by weight of antioxidants.

7. A method of producing trialkyl-tin hydrides substantially as hereinbefore described with reference to the examples.

DATED this 21st day of February, 1995.

WITCO GMBH
By Its Patent Attorneys
DAVIES COLLISON CAVE

AUSTRALIA PATENT OFFICE

Abstract

The invention concerns a method of preparing trialkyl-tin hydrides by a process that ensures outstanding long-term stability.

bis-[Trialkyl-tin] oxides are dissolved in a solvent that mixes only to some extent if at all with water and converted with an aqueous solution of sodium borohydride stabilized with a base. The product is obtained by phase separation and optionally by distillation. The trialkyl-tin hydride is obtained almost quantitatively with a yield of more than 95 %.