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(54) Title: PROCESS FOR PREPARING TRIMETHYLSILYLOXY FUNCTIONALIZED ALKYL LITHIUM COMPOUNDS		
(57) Abstract		
<p>A process for producing compounds of the formula $(CH_3)_3SiORLi$, wherein R is selected from alkyl groups containing 2 to 10 carbon atoms and aryl groups containing 6 to 10 carbon atoms, by reacting, optionally in the presence of a catalyst, in an inert atmosphere, a haloalcohol of the formula HORX, wherein R is selected from alkyl groups containing 2 to 10 carbon atoms and aryl groups containing 6 to 10 carbon atoms and X is selected from chlorine or bromine, is reacted with neat hexamethyldisilazane at a temperature between 20 °C and 200 °C, optionally in the presence of a catalyst, after which the resulting product, a trimethylsilyloxyalkylhalide compound, is reacted at a temperature between 50 °C and 160 °C, with powdered lithium metal, in an inert hydrocarbon medium, to produce the $(CH_3)_3SiORLi$ compound.</p>		

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PROCESS FOR PREPARING TRIMETHYLSILYLOXY FUNCTIONALIZED ALKYLLITHIUM COMPOUNDS

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This application is a continuation in part of U.S. Application Number 08/279,721 filed July 25, 1994, now U.S. Patent Number 5,403,946.

The present invention concerns an improved process for preparing functionalized alkyllithium compounds of the formula $(\text{CH}_3)_3\text{SiORLi}$, novel
10 trimethylsilyloxy alkyllithium compounds and novel intermediates used in the process.

Functionalized organolithium compounds have been used in organic synthesis reactions for some time and more recently have been used as initiators in the anionic polymerization of olefinic monomers. United
15 Kingdom published patent application 2,241,239 discloses a process for producing initiators of the formula $\text{R}^1\text{R}^2\text{R}^3\text{SiOALi}$ wherein R^1 , R^2 and R^3 are aliphatic and aromatic radicals and A is a hydrocarbon bridging group. This patent recommended using a 1.5 to 6 stoichiometric excess of lithium, an excess of 6 was used in the examples, to get high yields. Reaction
20 temperatures below 50 °C were employed because above 40 °C undesired by-products were observed.

U.S. Patent 5,321,148, issued June 14, 1994 discloses a process for preparing functionalized alkyllithium compounds by reacting a fine particle size lithium metal of not more than 300 microns average particle size with
25 an organosilyloxyalkyl halide of the formula $\text{R}^1\text{R}^2\text{R}^3\text{SiORX}$ wherein R^1 , R^2 and R^3 are independently selected from alkyl groups containing 1 to 10 carbon atoms and aryl groups containing 6 to 10 carbon atoms, R is selected from alkyl groups containing 1 to 8 carbon atoms either straight chain or substituted by alkyl or aryl groups, X is selected from chlorine or
30 bromine, the reaction temperature is above 50 °C, the reaction medium is a hydrocarbon solvent and the reaction is conducted in an inert atmosphere. The precursor, $\text{R}^1\text{R}^2\text{R}^3\text{SiORX}$, is prepared by reaction of an omega-halo alcohol HORX with $\text{R}^1\text{R}^2\text{R}^3\text{SiCl}$ and an acid acceptor, in a hydrocarbon solvent. Compounds of the formula $\text{R}^1\text{R}^2\text{R}^3\text{SiORX}$, when R^1 , R^2 and R^3
35 are methyl, prepared according to the disclosed process, have been found

to not uniformly lithiate, thus requiring more halide feed and resulting in slow filtration rates and lower than expected yields.

The present invention provides a process for producing compounds of the formula $(\text{CH}_3)_3\text{SiORLi}$ wherein R is selected from alkyl groups containing 2 to 10 carbon atoms and aryl groups containing 6 to 10 carbon atoms, by first reacting a haloalcohol of the formula HORX, wherein R has the meaning ascribed above and X is chlorine or bromine with hexamethyldisilazane, without solvent (neat). The resulting product, a trimethylsilyloxy-alkylhalide compound, is then reacted, in a second process step, with powdered lithium metal suspended in an inert liquid hydrocarbon solvent to produce the desired trimethylsilyloxyalkyllithium compound. The first step of the reaction can be done at temperatures from about 20 °C to 200 °C; the second step of the reaction is done at a temperature that is between 50 ° and 160 °C. Both the first and second step of the process are conducted in an inert atmosphere. The first reaction can be catalyzed by a number of catalysts, for example hydrogen chloride, trimethylsilyl chloride, succinimide, saccharin, and barbituric acid.

Advantages of conducting the first step with no solvent include:

- No solvent expense.
- Faster reaction kinetics.
- No need to strip solvent.
- No waste solvent stream generated.
- Product can be used directly in the subsequent reaction.
- Extensive purification of the precursor eliminated.
- Greater throughput per batch.

The haloalcohol is of the formula HORX, wherein R is selected from alkyl groups of 2 to 10 carbon atoms, straight chain or substituted by alkyl or aryl groups and aryl groups containing 6 to 10 carbon atoms and X is chloro or bromo. The trimethylsilyloxyalkylhalide compounds are produced by reaction of the haloalcohol with hexamethyldisilazane, with no solvent. Trimethylsilyloxyalkylhalides useful in the practice of this invention include but are not limited to 3-(trimethylsilyloxy)-1-propyl halide, 3-(trimethylsilyloxy)-2-methyl-1-propyl halide, 3-(trimethylsilyloxy)-2,2-dimethyl-1-propyl halide, 4-(trimethylsilyloxy)-1-butyl halide, 5-(trimethylsilyloxy)-1-pentyl halide, 6-(trimethylsilyloxy)-1-hexyl halide, 8-(trimethylsilyloxy)-1-octyl halide, and the like.

The lithium metal is used in particulate or powder form of not greater than 300 micron average particle size and preferably 10 to 300 microns. The lithium typically contains 0.4 to 0.76 weight percent sodium and is used in at least stoichiometric amounts, preferably in excess of stoichiometric of
5 1 to 100% and preferably 20 to 40% excess. The lithium dispersion is prepared for use by washing several times with pentane or some other hydrocarbon solvent of choice, to remove the dispersing fluid, and preferably subjected to high speed agitation at elevated temperatures to condition the lithium for the reaction.

10 The second process step, the lithiation reaction, utilizes a temperature that is from at least 50 °C up to just below the decomposition temperature of the product, and preferably from 50 °C up to the boiling point of the solvent with reflux temperatures being most preferred. The optimal temperature for running the reaction can be exceeded by using only
15 a high boiling solvent such as decane (BP-174 °C). The useful temperature range for operating the process is between about 50 °C and about 160 °C. Reduced or elevated temperature can be employed if desired but are not required. The reactants and the products are not highly corrosive so many materials of construction can be used for the reactor and related process
20 equipment.

The reaction solvent is an inert, liquid, non-polar hydrocarbon solvent selected from aliphatic, cycloaliphatic and aromatic hydrocarbons or mixtures thereof. Preferred solvents are aliphatic, cycloaliphatic and aromatic hydrocarbons, especially alkanes having 3 to 12 carbon atoms,
25 cycloalkanes having 4 to 8 carbon atoms and aromatic hydrocarbons having 6 to 10 carbon atoms and mixtures thereof. The inert hydrocarbon medium includes but is not limited to pentane, hexane, cyclopentane, cyclohexane, methylcyclopentane, methylcyclohexane, heptane, methylcycloheptane, octane, decane, toluene, ethylbenzene, p-xylene, m-
30 xylene, o-xylene, n-propylbenzene, 2-propylbenzene, n-butylbenzene, and t-butylbenzene, and mixtures thereof.

According to the process of the present invention, the precursor triorganosiloxyalkyl halide was prepared neat from the corresponding omega halo-alcohol, and hexamethyldisilazane. The lithium metal
35 dispersion, when prepared in mineral oil, is washed free of mineral oil with a liquid hydrocarbon solvent, dried in a stream of argon and transferred to the

reaction vessel with the hydrocarbon solvent. The mixture of clean metal and liquid hydrocarbon solvent was heated to the reaction temperature and the functionalized triorganosiloxyalkyl halide was added slowly to the heated lithium metal-hydrocarbon solvent mixture. An exotherm developed after 5 - 5 30% of the halide was added. The reaction temperature was controlled by external cooling of the reaction mixture. At the end of the halide feed, the reaction temperature rapidly declined to room temperature. The reaction mixture was stirred several hours at room temperature. At the end of the lithiation reaction, the reaction mixture was transferred to a sintered glass 10 filter through which the solution was filtered rapidly with 3 psi (20.68×10^3 Pa) argon pressure. After the insolubles were removed by filtration, the filtrate was an essentially pure solution of the trimethylsiloxyalkyllithium compound. The resultant non-turbid solution was analyzed for total base, active carbon-lithium (modified Watson-Estham titration) and inorganic 15 halide.

The following examples further illustrate the invention.

PREPARATION OF HALOORGANOSILYLOXYALKANE MATERIALS

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1. Preparation of 3-Chloro-2,2-dimethyl-1-trimethylsilyloxy-propane at 150 °C, Lot 9277

A 500 milliliter, three-necked flask was fitted with a large magnetic 25 stir bar, a reflux condenser, a thermocouple attached to a THERM-O-WATCH®, a 125 ml. pressure-equalizing addition funnel, and an argon inlet. This apparatus was dried in an oven overnight at 125 °C, assembled hot, and allowed to cool to room temperature in a stream of argon. The flask was charged with 122.58 grams (1.00 mole, 1.00 equivalent) of 3-chloro- 30 2,2-dimethyl-1-propanol. Hexamethyldisilazane, 83.24 grams (0.516 mole, 0.516 equivalent), was then added rapidly dropwise via the addition funnel. Trimethylsilylchloride catalyst, one ml., was added via a syringe. An immediate exotherm of 21.7 °C was observed. A white precipitate also formed when the catalyst was added. The reaction mixture was heated to 35 150 °C with a heating mantle, controlled by the THERM-O-WATCH®. After ninety minutes at this temperature, all the solids had dissolved. The heat

source was removed. The reaction mixture was analyzed by Gas Chromatography (GC), thirty meter X 0.53 mm AT-1 column. All the starting 3-chloro-2,2-dimethyl-1-propanol had been consumed, with the formation of a single, higher-boiling component. After the reaction mixture had cooled to room temperature, it was transferred to a medium porosity sintered glass filter. The filtrate was collected in a dry 250 ml. bottle. This afforded a clear, very pale yellow solution, yield = 188.84 grams (97.0 % yield).

GC assay = 97.5 % desired product, and 2.5 % unknowns.

10

2. Preparation of 3-Chloro-2,2-dimethyl-1-trimethylsilyloxy-propane at 100 °C, Lot 9279

15 A 500 milliliter, three-necked flask was fitted with a large magnetic stir bar, a reflux condenser, a thermocouple attached to a THERM-O-WATCH®, a 125 ml. pressure-equalizing addition funnel, and an argon inlet. This apparatus was dried in an oven overnight at 125 °C, assembled hot, and allowed to cool to room temperature in a stream of argon. The flask was charged with 122.68 grams (1.00 mole, 1.00 equivalent) of 3-chloro-2,2-dimethyl-1-propanol. Hexamethyldisilazane, 83.35 grams (0.516 mole, 0.516 equivalent), was then added dropwise via the addition funnel. Trimethylsilylchloride catalyst, one ml., was added via a syringe. An immediate exotherm of 23.4 °C was observed. A white precipitate also formed when the catalyst was added. The reaction mixture was heated to 100 °C with a heating mantle, controlled by the THERM-O-WATCH®. Periodically, an aliquot was removed, filtered through a 0.45 micron syringe filter, and analyzed by Gas Chromatography (GC), thirty meter X 0.53 mm AT-1 column. After twenty-four hours at 100 °C, both of the starting materials were still present. Therefore, an additional 0.5 ml. of trimethylsilylchloride was added. After forty-eight hours at 100 °C, both of the starting materials were still present. Therefore, an additional 0.5 ml. of trimethylsilylchloride was added. After a total of seventy-two hours at 100 °C, all the starting 3-chloro-2,2-dimethyl-1-propanol had been consumed, with the formation of a single, higher-boiling component. The heat source was removed. After the reaction mixture had cooled to room

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temperature, it was transferred to a medium porosity sintered glass filter. The filtrate was collected in a dry 250 ml. bottle. This afforded a clear, very pale yellow solution, yield = 178.37 grams (91.65 % yield).

- 5 GC assay = 96.8 % desired product, 0.1 % hexamethyldisilazane, and 3.1 % unknowns.

10 B. PREPARATION OF TRIMETHYLSILYLOXYALKYLLITHIUM
COMPOUNDS

1. Preparation of 2,2-Dimethyl-3-trimethylsilyloxy-1-propyllithium
Lot 9291

15 A 500 ml., three-necked flask was equipped with a mechanical stirrer, a 125 ml. pressure-equalizing addition funnel, and a Claisen adapter fitted with a dry ice condenser, a thermocouple, and an argon inlet. This apparatus was dried in an oven overnight at 125 °C, assembled hot, and allowed to cool to room temperature in a stream of argon. Lithium
20 dispersion was washed free of mineral oil with hexane (2 X 70 ml.), and pentane (1 X 70 ml.), then dried in a stream of argon. The dry lithium powder, 6.80 grams (0.980 mole, 2.80 equivalents) was transferred to the reaction flask with 280 ml. cyclohexane. This slurry was stirred at 450
25 RPMs, and heated to 64.7 °C with a heating mantle. The heat source was removed. 3-Chloro-2,2-dimethyl-1-trimethylsilyloxy-propane, 68.10 grams (Lot 9277, 0.350 mole, 1.00 equivalent) was then added dropwise to the reaction mixture. An exotherm was noted after 12.3% of the feed had been added. A dry ice/hexane cooling bath was employed to maintain the
30 reaction temperature at 60-65 °C. The total halide feed time was eighty-five minutes. The reaction temperature rapidly fell off at the end of the halide feed. The reaction mixture was stirred at room temperature for seventy minutes, then transferred to a small, sintered glass filter. The product filtered rapidly with 2 psi argon. The muds were reslurried with cyclohexane
35 (2 X 60 ml.). This afforded a pale yellow solution, yield = 450 ml., 352.05 grams.

Total base = 15.6 wt. %.

Active C-Li = 15.3 wt. %.

5 Soluble chloride = 182 ppm.

Yield based on active C-Li = 92.6%.

10 2. Preparation of 2,2-Dimethyl-3-trimethylsilyloxy-1-propyllithium
Lot 9295

A 500 ml., three-necked flask was equipped with a mechanical stirrer, a 125 ml. pressure-equalizing addition funnel, and a Claisen adapter
15 fitted with a dry ice condenser, a thermocouple, and an argon inlet. This apparatus was dried in an oven overnight at 125 °C, assembled hot, and allowed to cool to room temperature in a stream of argon. Lithium dispersion was washed free of mineral oil with hexane (2 X 70 ml.), and pentane (1 X 70 ml.), then dried in a stream of argon. The dry lithium
20 powder, 6.50 grams (0.936 mole, 2.80 equivalents) was transferred to the reaction flask with 280 ml. cyclohexane. This slurry was stirred at 450 RPMs, and heated to 64.7 °C with a heating mantle. The heat source was removed. 3-Chloro-2,2-dimethyl-1-trimethylsilyloxy-propane, 65.09 grams (Lot 9277, 0.334 mole, 1.00 equivalent) was then added dropwise to the
25 reaction mixture. An exotherm was noted after 9.6 % of the feed had been added. A dry ice/hexane cooling bath was employed to maintain the reaction temperature at 60-65 °C. The total halide feed time was ninety-one minutes. The reaction temperature rapidly fell off at the end of the halide feed. The reaction mixture was stirred at room temperature for
30 ninety minutes, then transferred to a small, sintered glass filter. The product filtered rapidly with 2 psi argon. The muds were reslurried with cyclohexane (2 X 50 ml.). This afforded a pale yellow solution, yield = 430 ml., 335.10 grams.

35 Total base = 15.5 wt. %.

Active C-Li = 15.3 wt. %.

Yield based on active C-Li = 92.4 %.

5

C. COMPARATIVE EXAMPLE

1. Preparation of 3-Chloro-2,2-dimethyl-1-trimethylsilyloxy-propane in Cyclohexane Solution, Lot 9103

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A one liter, three-necked flask was fitted with a large magnetic stir bar, a reflux condenser, a teflon clad thermocouple, a 125 ml. pressure-equalizing addition funnel, and an argon inlet. This apparatus was dried in an oven overnight at 125 °C, assembled hot, and allowed to cool to room temperature in a stream of argon. The flask was charged with 122.60 grams (1.00 mole, 1.00 equivalent) of 3-chloro-2,2-dimethyl-1-propanol, and 250 ml. of cyclohexane. This afforded a homogenous solution. Hexamethyldisilazane, 85.54 grams (0.53 mole, 0.53 equivalent) was then added dropwise. There was an initial endotherm, then the temperature slowly elevated. Total feed time was seventy minutes. The catalyst, trimethylsilylchloride (0.5 ml.) was then added with a pipette. A white precipitate formed immediately. The reaction flask was swept with a slight positive flow of argon, above the level of the liquid. The reaction mixture was heated to reflux with a heating mantle. Ammonia fumes were detected exiting from the apparatus with pH paper before reflux was achieved. After three hours at reflux, the reaction mixture was clear and homogenous. After five and a half hours heating, the heat source was removed. After six hours, an aliquot was removed, and analyzed by Gas Chromatography (GC), thirty meter X 0.53 mm AT-1 column. The conversion to the desired product was 64.2 %. The reaction mixture was again heated to reflux, and held at reflux overnight. In the morning, the heat source was again removed, and the reaction was reanalyzed by GC. Very little change in composition was detected by GC. 3-Chloro-2,2-dimethyl-1-propanol and hexamethyldisilazane were both still present in the reaction mixture. Therefore, an additional 0.5 ml. of trimethylsilylchloride was added to the reaction flask. A white precipitate was again observed. The reaction

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mixture was heated to reflux for an additional six hours, then allowed to cool to room temperature. All the starting material had been consumed. The reaction mixture was transferred to a dry, 500 ml. single-necked flask. The product was purified by distillation through a six inch Vigreux column.

5

The desired product had a boiling point of 169.8 - 175.0 °C.

This afforded a clear, colorless oil, yield = 183.07 grams, 94.1 %.

- 10 GC analysis of this material indicated it was 98.9 % desired product, 0.6 % hexamethyldisilazane, and 0.5 % unknowns.

- 15 The comparison example shows the superiority of performing the trimethylsilation reaction without solvent. The neat reaction featured faster reaction rates, easier work-up, and no need for extensive product purification by distillation.

Claims:

1. A process for producing compounds of the formula $(\text{CH}_3)_3\text{SiORLi}$, characterized in that R is selected from alkyl groups containing 2 to 10 carbon atoms and aryl groups containing 6 to 10 carbon atoms, by reacting, first, in an inert atmosphere, a haloalcohol of the formula HORX, wherein R is selected from alkyl groups containing 2 to 10 carbon atoms and aryl groups containing 6 to 10 carbon atoms and X is selected from chlorine or bromine, is reacted with neat hexamethyldisilazane at a temperature between 20 °C and 200 °C, , after which the resulting product, a trimethylsilyloxyalkylhalide compound, is reacted in a second step, at a temperature between 50 °C and 160 °C, in an inert liquid hydrocarbon medium, with powdered lithium metal to produce the $(\text{CH}_3)_3\text{SiORLi}$ compound.
2. The process of claim 1 characterized in that the trimethylsilyloxyalkylhalide is 3-(trimethylsilyloxy)-1-propyl halide, 3-(trimethylsilyloxy)-2-methyl-1-propyl halide, 3-(trimethylsilyloxy)-2,2-dimethyl-1-propyl halide, 4-(trimethylsilyloxy)-1-butyl halide, 5-(trimethylsilyloxy)-1-pentyl halide, 6-(trimethylsilyloxy)-1-hexyl halide, or 8-(trimethylsilyloxy)-1-octyl halide.
3. The process of claim 2 characterized in that the halide is selected from bromine and chlorine.
4. The process of claim 1 characterized in that the omega-halo alcohol is reacted neat with hexamethyldisilazane at a temperature between 100 °C and 180 °C.
5. The process of claim 1 characterized in that the lithium is used in an excess amount of 1 to 100% excess over the stoichiometric amount.
6. The process of claim 5 wherein the lithium metal contains 0.2 to 0.8 weight percent sodium.
7. The process of claim 5 characterized in that the lithium metal contains 0.3 to 0.5 weight percent sodium.
8. The process of claim 1 characterized in that the reaction temperature of the lithiation reaction is between 50 °C and 110 °C.
9. The process of claim 1 characterized in that the inert hydrocarbon medium of the lithiation reaction is a liquid alkane containing five to ten carbon atoms, a cycloalkane containing five to ten carbon atoms, or an aromatic solvent containing six to ten carbon atoms.

10. The process of claim 1 characterized in that the inert hydrocarbon medium is selected from pentane, hexane, cyclopentane, cyclohexane, methylcyclopentane, methylcyclohexane, heptane, methylcycloheptane, octane, decane, toluene, ethylbenzene, p-xylene, m-xylene, o-xylene, n-propylbenzene, 2-propylbenzene, n-butylbenzene, and t-butylbenzene, or mixtures thereof.

11. A process for producing compounds of the formula $(\text{CH}_3)_3\text{SiORX}$, characterized in that R is selected from the group consisting of alkyl groups containing 2 to 10 carbon atoms and aryl groups containing 6 to 10 carbon atoms, X is chlorine or bromine by reacting, first, in an inert atmosphere, a haloalcohol of the formula HORX, wherein R is selected from alkyl groups containing 2 to 10 carbon atoms and aryl groups containing 6 to 10 carbon atoms and X is chlorine or bromine, is reacted with neat hexamethyldisilazane at a temperature between 20 °C and 200 °C, in the presence of a catalytic amount of a catalyst which is hydrogen chloride, trimethylsilyl chloride, succinimide, saccharin, or barbituric acid.

12. The process of claim 11 further characterized by employing an effective amount of a catalyst in step 1 of the reaction.

13. The process of claim 12 characterized in that the catalyst is hydrogen chloride, trimethylsilyl chloride, succinimide, saccharin, or barbituric acid.

14. The process of claim 11 characterized in that the omega-halo alcohol is reacted neat with hexamethyldisilazane at a temperature between 100 °C and 180 °C.

15. 3-(Trimethylsilyloxy)-1-propyl halide.

16. The compound of claim 15 wherein the halide is chloride or bromide.

17. 3-(Trimethylsilyloxy)-2-methyl-1-propyl halide.

18. The compound of claim 17 wherein the halide is chloride or bromide.

19. 4-(Trimethylsilyloxy)-1-butyl halide.

20. The compound of claim 19 wherein the halide is chloride or bromide.

21. 5-(Trimethylsilyloxy)-1-pentyl halide.

22. The compound of claim 21 wherein the halide is chloride or bromide.

23. 6-(Trimethylsilyloxy)-1-hexyl halide.
24. The compound of claim 23 wherein the halide is chloride or
bromide.
25. 8-(Trimethylsilyloxy)-1-octyl chloride.
- 5 26. 3-(Trimethylsilyloxy)-1-propyllithium.
27. 3-(Trimethylsilyloxy)-2-methyl-1-propyllithium.
28. 4-(Trimethylsilyloxy)-1-butyllithium.
29. 5-(Trimethylsilyloxy)-1-pentyllithium.
30. 6-(Trimethylsilyloxy)-1-hexyllithium.
- 10 31. 8-(Trimethylsilyloxy)-1-octyllithium.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/09256

A. CLASSIFICATION OF SUBJECT MATTER
 IPC(6) :C07F 7/08, 7/18.
 US CL :556/466, 482, 486.
 According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
 Minimum documentation searched (classification system followed by classification symbols)
 U.S. : 556/466, 482, 486.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 3,511,865 (PETERSON) 12 MAY 1970, see entire document.	1-31
A	US, A, 5,082,961 (FUKUMOTO ET AL.) 21 JANUARY 1992, see entire document.	1-31
A	US, A, 5,231,205 (RIEKE) 27 JULY 1993, see entire document.	1-31
A	US, A, 5,321,148 (SCHWINDEMAN) 14 JUNE 1994, see entire document.	1-31

Further documents are listed in the continuation of Box C. See patent family annex.

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