The present invention relates to a polyorganoborosilane ceramic precursor polymer comprising a plurality of repeating units of the formula:

\[
\begin{align*}
&\left[\left(\text{R}_1\right)\left(\text{R}_2\right)\left(\text{R}_3\right)\right]_n \\
&\quad \left(\left(\text{R}_2\right)\left(\text{R}_3\right)\text{Si}(\text{X}_2)\right)_q
\end{align*}
\]

with the segments being linked together by second units of the formula: \([-\left(\text{R}_2\right)\left(\text{R}_3\right)\text{Si}(\text{X}_2)\]_q, where \(\text{R}_1\) is lower alkyl, cycloalkyl, phenyl, or...
FIGURE 1  FTIR of POLYMER I

FIGURE 2  FTIR of POLYMER II
FIGURE 3 FTIR of POLYMER III

FIGURE 4 TGA of POLYMER II
POLYMERS AND CERAMIC MATERIALS THEREOF

BACKGROUND OF THE INVENTION

Origin of the Invention

The invention disclosed herein was made in the performance of work under a NASA Contract and is subject to Public Law 96-517 (35 U.S.C. §200 et seq.). The contractor has not elected to retain title in this invention.

This is a division of application Ser. No. 06/890,577, filed July 30, 1986, U.S. Pat. No. 4,767,728.

Field of the Invention

The present invention relates to organic silicon-boron polymers which upon pyrolysis produce high-temperature ceramic materials. More particularly, it relates to the polyorganoborosilanes containing -Si-B- bonds which generate high-temperature ceramic materials (e.g., SiC, SiB4, SiB6, BaC) upon thermal degradation. The processes for preparing these organic silicon-boron polymer precursors are also a part of this invention.

Description of the Prior Art

Silicon carbide, silicon nitride, silicon-boron-oxide and mixtures thereof have generated considerable interest as ceramic materials. They have high thermal and oxidation stability and, are among the hardest materials that can be made. Other advantageous properties include low electrical conductivity, low co-efficient of thermal expansion, thermal shock resistance, creep resistance, high strength at elevated temperatures, and corrosion resistance. A few references which are of general interest follow:

D. Seyferth et al. disclose in the Communications of the American Ceramic Society, July 1984, pp. C-132 to C-133, the high-yield synthesis of Si3N4/SiC/C ceramic materials by the pyrolysis of a polyorganosilazane. The polyorganosilazane is prepared by the reaction of dichlorosilane, H2SiCl2, with gaseous ammonia. The amonolysis product is pyrolyzed in nitrogen atmosphere to give a 70 percent yield of Si3N4.

In a similar manner, D. Seyferth et al. disclose in U.S. Pat. No. 4,482,669 the preparation of pre-ceramic polymers having repeating units of -(NH-SiR)n- and R-(CBioHloC)-(CH2)a-Si(X)z-R.

None of the above references disclose or suggest the polymer precursors the polyorganoborosilanes or silicon-boron ceramic polymers of the present invention. It is highly desirable to have polymer precursors for -Si-B- ceramic materials that are formed from readily available and relatively inexpensive starting materials and in high yield. Additional desirable properties include stability at room temperature for prolonged periods of time, relatively stable to hydrolysis at atmospheric moisture levels, and high yield of ceramic material upon pyrolysis.

SUMMARY OF THE INVENTION

The present invention relates to a polyorganoborosilane ceramic precursor polymer comprising a plurality of repeating units of the formula: R-[(CH3)2Si]-[(CH2)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH! 2 Si)]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2S

where R is hydrogen or one of a variety of alkyl, aryl, alkyllsiline, or alkylaminogroups. Upon pyrolysis, these polymers are useful to produce varieties of silicon nitride or silicon nitride-silicon carbide. Silicon-boron polymers are not disclosed or suggested.

In U.S. Pat. No. 3,514,520, J. A. DuPont et al. disclose the preparation of monomeric high-energy boron-containing compounds of the formula: X-CH2C-

H2-Si(A)(B) where X is -B4H4 or -B10H12, A is chloro or bromo and R is -CH3 or -CH2CH3.

In U.S. Pat. No. 3,431,234, M. M. Fein et al. disclose novel polymeric products of a carboranylsilane prepared by reacting a compound of the formula:

R-[(CH3)2Si]-[(CH2)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2Si]-[(CH3)2Si]-[(CH2)2S

with water to form a polysiloxane (—Si—O—) polymer.

In U.S. Pat. No. 4,152,509, S. Yajima et al. disclose the preparation of a number of polysiloxanes by treating at least one boric acid or phenylsilane. Polyborosiloxanes are not disclosed. In U.S. Pat. No. 4,283,376, S. Yajima et al. disclose a process for producing polycarbosilane partly containing siloxane bonds (—Si—O—) wherein a part of the polycarbosilane comprises polyborosiloxane and a structure composed of boron, silicon, and oxygen. The polycarbosilane is converted into silicon carbide fibers by first preparing a spinning dope, treating the dope to render it infusible under tension or under no tension and firing the treated dope in a vacuum or in an inert atmosphere.

In U.S. Pat. No. 4,298,559, R. H. Baney et al. disclose the preparation of polyorganosilanes having the average formula [(CH3)2Si][Si(CH3)2]. These polyorganosilanes are prepolymers which produce silicon carbide ceramic materials when pyrolyzed in an inert atmosphere.

In U.S. Pat. No. 4,572,902, Matano et al. disclose a method for producing ceramics having a closed-pore size from a sintered body of a Si3N4—SiC composition. The process includes heating the ceramic sintered article in a flowing gas mixture of chlorine and nitrogen at 500° C. to 1,500° C.

In U.S. Pat. No. 4,490,192, A. Gupta et al. disclose the preparation of finely divided particles of less than 1 micron in diameter having the composition of B6Si4, B6N6, P3Si6, P3N6, and the like. These particles are prepared in flowing argon with pyrolysis occurring using a laser.

Takamiza et al. in Japanese patent publications Nos. 80500/78 and 101099/78 disclose the preparation of polymers made from methylchlorosilanes, however, no mention is made of the yields of ceramic material generated by the decomposition of the polylaminates. More recently in Japanese Kokai Nos. 79/114460 and 79/83098 suggest that the preparation of silicon carbide precursor polymers having a silicon-carbon (Si—C—Si—) bond are prepared by heating organosilicon compounds including (CH3)3Si—Si(CH3)3Cl in the presence of B, Al, Si, Ge, Sn and Pb compounds or Hl and its salts at high temperatures.


None of the above references disclose or suggest the polymer precursors the polyorganoborosilanes or silicon-boron ceramic polymers of the present invention.
The present invention also relates to a process for preparing a polyorganoborosilane, which process includes:

(a) combining an organic borohalide of the formula: \[ R^2 \text{B}(X_2) \text{Si}(X_2) \] wherein \( R^2 \) and \( R^3 \) are each independently selected from lower alkyl, cycloalkyl, or phenyl; \( n \) is an integer between 1 and 100; \( p \) is an integer between 1 and 100; and \( q \) is an integer between 1 and 10.

(b) heating the reaction mixture for a time and at a temperature up to 160°C effective to produce a polyorganoborosilane; and

(c) recovering the polyorganoborosilane of step (b).

Another aspect of the present invention is the production of silicon-boron-carbon ceramic materials, useful in high temperature applications, by the pyrolysis of the polyorganoborosilane polymers of the present invention. Generally temperatures between about 600°C and 1300°C are used.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is the Fourier Transform Infrared (FTIR) spectrum of the polyorganoborosilane—POLYMER I.

FIG. 2 is the Fourier Transform Infrared (FTIR) spectrum of the polyorganoborosilane—POLYMER II.

FIG. 3 is the Fourier Transform Infrared (FTIR) spectrum of the polyorganoborosilane—POLYMER III.

FIG. 4 is the thermogravimetric analysis (TGA) of POLYMER II.
In a general reaction, about four to six equivalents of the alkali metal is freshly cut and added to the anhydrous aprotic solvent at ambient temperature, then heated to between about 100° and 135° C. The R₄–B–(X¹)₂ compound, such as methylborondibromide, phenylborondichloride, etc. and the R₂(R₃)Si(X²)₂, such as dimethylchlorosilane, in equimolar amounts are combined and slowly added dropwise. The reaction mixture is then refluxed at between about 120° C. and 160° C. for 16 to 24 hours. Methyl iodide or similar alkyl iodide is added and continued to reflux up to an additional 4 hours to remove excess alkali metal and to quench the reaction. After cooling, the alkali halide precipitate has a purple to purple-blue color, and the liquid portion is tan to brown in color. The reaction product is filtered and the solid is washed with additional aprotic solvent. The filtrate is evaporated using reduced pressure or that the reactants may be pressurized in the SUMMARY hereinabove).

These three-dimension structures are very complex, and both larger and small ring structures are also possible.

In the preparation where the starting R⁴ is any alkyl or phenyl groups and X¹ is halogen, a number of different type of polymers are possible, when combined with (D), e.g.:

\[ \text{R}^2-\text{Si}-\text{R}^3 \]

(For the Group A and Group D designations are found in the SUMMARY hereinafter).

The solid separated from the reaction mixture is primarily alkali halide, e.g., sodium chloride, and also includes presently incompletely characterized high molecular weight solid organic product.

In the preparation where R⁴ is a halogen e.g. chloro and X¹ is halogen (Group A) and

\[ \text{D} - \text{A} - \text{A} - \text{D} - \text{D} - \text{D} - \text{D} - \text{D} - \text{E} ; \text{OR} \]

is for example dimethylsilyl (Group D) a number of two and three dimensional polymers [including Group (E)] are possible, e.g.:
EXAMPLE 1
Phenylborondichloride and Dimethyldichlorosilane to Produce Polymer I

(a) A mixture of phenylborondichloride (5 g, 0.03 mole) and dimethyldichlorosilane (3.9 g, 0.03 mole) in 10 ml of xylene is placed in a dropping funnel and added dropwise into a 3-neck round-bottom flask, containing xylene (30 ml) and sodium (2.8 g, 0.12 mole), equipped with a nitrogen gas inlet. The reaction is carried out at 130° C. to 140° C. (refluxing temperature of xylene) for 18 hrs. Upon cooling, a purple precipitate is filtered and washed with xylene or toluene. This precipitate is further treated with methanol and water. A small quantity of an insoluble, black solid is obtained, but not identified. The xylene filtrate is evaporated to dryness yielding a solid material, Polymer I, which has a molecular weight of 900–1,000. The FTIR spectrum as found in FIG. 1 shows phenyl and methyl peaks at 3000–3100 cm⁻¹ (peak 11) and 2850–2980 cm⁻¹ (peak 12) respectively. The NMR spectrum also shows phenyl and methyl peaks. Additional Polymer I is isolated from the methanol solution on evaporation of the solvent; the polymer is washed with methyl alcohol or toluene to remove any sodium methoxide. The ratio of Si–B for this polymer appears to be about 2 to 5. Total yield of Polymer I is 2 g (46%).

(b) Similarly, the reaction is repeated as is described in Subpart I(a) above except that a stoichiometrically equivalent amount of p-methylphenylborondichloride is used instead of phenylborondichloride and a stoichiometrically equivalent amount of dimethyldichlorosilane is used instead of dimethyldichlorosilane. A good yield of a polymer of the structure:

\[ \text{[C₆H₅CH₃]_p-B-[Si(C₂H₅₂)]_q} \]

where p and q are each integers between 1 and 12 is expected to be obtained.

EXAMPLE 2
Methylborondibromide and Dimethyldichlorosilane to Produce Polymer II

Sodium (13 g; 0.565 mole) and 100 ml of octane are placed in a 500-ml three-neck flask equipped with condenser, nitrogen inlet tube, magnetic stirrer, and dropping funnel. The flask is heated to the reflux temperature of the solvent. Dimethyldichlorosilane (17.4 g; 0.135 mole) and 25 g of methylborondibromide (0.135 mole) in 50 ml of octane are added dropwise to the reaction flask through the dropping funnel over a period of 30 min. The reaction mixture is refluxed for 20 hrs at 130° C. with stirring under a gentle flow of dry nitrogen gas. The solution in the dropping funnel is added to the flask over a period of 30 min. The reaction mixture is refluxed for 2 hrs. The DRY-ICE condenser is replaced with water condenser after the reaction is refluxed for 5 hrs. Methyl iodide (1 ml) is added to the reaction flask, and the reflux is continued for 3 hrs. After cooling, the mixture is filtered and the purple solid is washed with xylene. A brown solid (Polymer III; 4.2 g; 41% yield) is isolated from the xylene filtrate after evaporation of the solvent under reduced pressure. Polymer III has a melting point of about 100° C. and a molecular weight of about 1200.

The purple solid is washed with methanol and water to give a white-yellowish solid. Some white solid, isolated from the methanol solution after evaporation of the solvent, is washed with water. Both solids were considered to be high-molecular-weight forms of Polymer III.

The NMR spectrum of POLYMER I has a broad peak at about 7 ppm (aromatic protons) to an internal reference (tetramethylsilane) and broad peaks at about 0.2 ppm (methyl groups). The NMR spectra of Polymer II and Polymer III showed only methyl protons about 0.2 ppm, as expected.

The Fourier Transform infrared (FTIR) spectrum of Polymer I (FIG. 1) showed both aromatic and aliphatic C–H absorption peaks at 3000–3100 (band 11) and 2850–2980 cm⁻¹ (band 12), respectively. The FTIR spectra of Polymer I, Polymer II and Polymer III also indicated the presence of the Si–B bond. Although small Si–H (2100 cm⁻¹, band 13, band 24 and band 34) and B–H (2500 cm⁻¹, band 14, band 25 and band 35) are present in the polymers, the major structure of the polymers are a polymer and/or a block copolymer as described herein.

EXAMPLE 3
Borontrichloride and Dimethyldichlorosilane to Produce Polymer III

(a) Sodium (13 g; 0.6 mole) and 75 ml of dry xylene are placed in a 250-ml three-neck round-bottom flask equipped with a magnetic stirrer, DRY-ICE condenser, nitrogen inlet tube, and a dropping funnel containing 75 ml of xylene, 0.1 mole of boron trichloride, and 19.3 g of dimethyldichlorosilane (0.15 mole). The flask is heated to about 130° C. with stirring under a gentle flow of dry nitrogen gas. The solution in the dropping funnel is added to the flask over a period of 30 min. The reaction mixture is refluxed for 22 hrs. The DRY-ICE condenser is replaced with water condenser after the mixture is refluxed for 5 hrs. Methyl iodide (1 ml) is added to the reaction flask, and the reflux is continued for 3 hrs. After cooling, the mixture is filtered and the purple solid is washed with xylene. A brown solid (Polymer III; 4.2 g; 41% yield) is isolated from the xylene filtrate after evaporation of the solvent under reduced pressure. Polymer III has a melting point of about 100° C. and a molecular weight of about 1200.

(b) Similarly when phenylborondibromide is replaced by a stoichiometrically equivalent amount of vinyl borondibromide or cyclobutylborondibromide the corresponding vinylboron or cyclobutylboron polymer having B–Si bonds is expected to be obtained in good yield.
The IR spectra obtained for these —B—Si— polymers described above show the presence of some B—H and Si—H groups in the polymeric material. The quantity of these B—H and Si—H groups, if present, is always very low, of the order of 1–5 percent. It is suggested that the Si—H and B—H bonds are observed because the very reactive Si and B groups during the reaction remove a hydrogen atom from the solvent medium and therefore terminate that Si—B unit as a further polymer addition group. It is, therefore, contemplated within the present invention that some small amount of R1, R2 and R3 groups in the organic polymer may be hydrogen.

EXAMPLE 4

Ceramic Products by Pyrolysis

(a) The boron-silicon polymers were pyrolyzed at 1300°C in flowing nitrogen for 1 hr. (Argon can also be used.) Table B shows the atom ratio in the resulting ceramic as measured by electron spectroscopy for chemical analysis (ESCA).

<table>
<thead>
<tr>
<th>Element</th>
<th>Polymer II</th>
<th>Polymer III</th>
<th>Ceramic Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>4.5 Carbide</td>
<td>5.5 Carbide</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>10 (2.8 SiC)</td>
<td>7.8 (3 SiC)</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>14</td>
<td>13</td>
<td></td>
</tr>
</tbody>
</table>

It is seen that in Polymer II carbon is present as 4.5 atom ratio as carbide. Of that carbide 2.8 atom ratio is present as silicon carbide. A portion of the remainder of the silicon is combined as borides, and the remainder of the carbide is combined as boron carbides.

Silicon, carbon, and boron were found in the ceramic products derived from the pyrolysis of the organoborosilicon polymer. The ratio of Si, C, and B indicate the presence of mixtures of SiC and SiB4 where X is between 2 and 6 or a combination. BaC may also be present in the ceramic product, but was not identified. X-Ray diffraction (X-RD) analysis confirmed the presence of SiC. Elemental analysis of the ceramic product from the pyrolysis of Polymer III showed a trace amount of carbon is present as free carbon.

While a few embodiments of the present invention have been shown and described herein, it will be apparent to those skilled in the art that various modifications and changes can be made in the polyorganoborosilanes, the methods of preparation thereof, and the ceramic materials obtained on pyrolysis of the polyorganoborosilanes without departing from the scope and spirit of the present invention. All such modifications and changes coming within the scope of the appended claim are intended to be covered thereby.

We claim:

1. A polyorganoborosilane ceramic precursor polymer consisting essentially of a plurality of repeating units of the formula:

\[
\begin{align*}
&\text{(A)} \\
&\text{the polymer unit being linked together by second units of the formula:}
\end{align*}
\]

wherein R1 and R3 are each independently selected from halogen, lower alkyl, vinyl, cycloalkyl, or phenyl; and R2 is lower alkyl, vinyl, cycloalkyl, phenyl, or substituted aryl; and

X1 is between 1 and 100; p is an integer between 1 and 100; q is an integer between 1 and 100, wherein the precursor polymer has a linear block, linear alternating, linear random structure, or a random three dimensional structure.

2. The polyorganoborosilane of claim 1 wherein R1 is lower alkyl.

3. The polyorganoborosilane of claim 1 wherein R1 is methyl.

4. The polyorganoborosilane of claim 1 wherein R1 is phenyl.

5. The polyorganoborosilane of claim 1 wherein R2 and R3 are identical.

6. The polyorganoborosilane of claim 5 wherein R2 and R3 are each lower alkyl.

7. The polyorganoborosilane of claim 3 wherein R2 and R3 are each methyl.

8. The polyorganoborosilane of claim 4 wherein R2 and R3 are each methyl.

9. The polyorganoborosilane of claim 2 wherein R2 and R3 are each lower alkyl.

10. The polyorganoborosilane of claim 4 wherein R3 and R2 are each phenyl.

11. The polyorganoborosilane of claim 1 wherein R1 is

\[
\begin{align*}
\text{(B)} \\
&\text{the polymer unit being linked together by second units of the formula:}
\end{align*}
\]

wherein R1 and R2 are each independently selected from halogen, lower alkyl, vinyl, cycloalkyl, or phenyl; and X1 and X2 are each independently selected from chloro or bromo, in an anhydrous aprotic solvent having a boiling point at ambient pressure.
of not greater than 160° C., with at least four equivalents of a alkali metal; (b) heating the reaction mixture for a time and at a temperature up to about 160° C. effective to produce a polyorganoborosilane; and (c) recovering the polyorganoborosilane produced in step (b) which consists essentially of a plurality of repeating units of the formula:

\[
\begin{array}{c}
R^1 \\
\text{B} \\
p \\
\end{array}
\]

the polymer unit being linked together by second units of the formula:

\[
\begin{array}{c}
R^2 \\
\text{Si-B} \\
R^3 \\
q \\
\end{array}
\]

wherein \( R^1 \) is lower alkyl, vinyl, cycloalkyl, phenyl, or

\[
\begin{array}{c}
R^2 \\
\text{Si-B} \\
R^3 \\
q \\
\end{array}
\]

wherein \( R^2 \) and \( R^3 \) are each independently selected from halogen, lower alkyl, vinyl, cycloalkyl, or phenyl; \( n \) is an integer between 1 and 100; \( p \) is an integer between 1 and 100; and \( q \) is an integer between 1 and 100 wherein the polymer has a linear block, linear alternating, linear random structure or a random three dimensional structure.

14. The process of claim 13 wherein \( R^4 \) and \( X^1 \) are each chloro or bromo.

15. The process of claim 13 wherein \( R^4 \) is lower alkyl and \( X^1 \) is halogen.

16. The process of claim 13 wherein \( R^4 \) is phenyl and \( X^1 \) is chloro.

17. The process of claim 13 wherein \( R^2 \) and \( R^3 \) are each selected from lower alkyl or phenyl and \( X^2 \) is chloro.

18. The process of claim 15 wherein \( R^2 \) and \( R^3 \) are each methyl.

19. The process of claim 16 wherein \( R^2 \) and \( R^3 \) are each lower alkyl and \( X^2 \) is chloro.

20. The process of claim 17 wherein \( R^2 \) and \( R^3 \) are each lower alkyl and \( X^2 \) is chloro.

21. The process of claim 13 wherein the aprotic solvent is selected from hydrocarbons or aromatic hydrocarbons.

22. The process of claim 21 wherein the alkali metal is selected from sodium, potassium, or mixtures thereof.