

1

3,257,455

PREPARATION OF BORON HYDRIDES AND AMINE BORANES

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9 Claims. (Cl. 260—583)

This application is a division of co-pending application Serial No. 832,145, filed August 7, 1959, now abandoned.

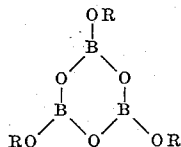
This invention relates to and has at its chief objective the provision of a chemical process for the preparation of hydrides of boron.

According to this invention, there is provided a process for the preparation of hydrides of boron characterized by the step of reacting (1) a fully esterified ester of an oxyacid of boron in which (a) the boron is bonded solely to oxygen atoms and (b) all of the esterifying groups are hydrocarbyl groups, with (2) a light metal aluminum hydride in which the metal is a light metal of atomic number 3 through 56, the reaction being conducted in admixture with a substance selected from the group consisting of (A) an inert liquid hydrocarbon, (B) an inert liquid ether, (C) a hydrocarbyl compound of a Group VA element of atomic number 7 through 33, said compound being further characterized in that it contains 3 monovalent radicals directly affixed to the Group VA element, from 1 to 3 of said radicals being hydrocarbyl radicals with the balance, if any, being hydrogen, and (D) mixtures of these substances. As a result of this novel and highly important process, high yields of various hydrides of boron are achieved.

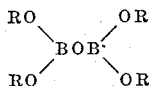
The above described hydrocarbyl esters of oxyacids of boron comprise a well recognized group of borate esters. Thus, one type is the hydrocarbyl orthoborates having the formula



where R is a hydrocarbyl group. Another type is the hydrocarbyl metaborates of the formula



R again being a hydrocarbyl group. Another type is composed of the hydrocarbyl pyroborates. These have the formula



where R is a hydrocarbyl radical. In the foregoing formulas the hydrocarbyl groups preferably contain not more than about 18 carbon atoms each. They can be the same or different hydrocarbyl groups. In other words, they can be alkyl, aralkyl, cycloalkyl, alkenyl, aryl, alkaryl, and related univalent hydrocarbyl radicals.

Aryl (and alkaryl) orthoborates, metaborates and pyroborates are preferred for use in the process of this invention because they provide the fastest reaction rates and give the greatest yields of desired product. Especially preferred from the foregoing standpoints are the aryl (and alkaryl) orthoborates.

2

Typical examples of the above borate esters include trimethyl orthoborate, triethyl metaborate, tridodecyl orthoborate, trioctadecyl metaborate, tetracyclohexyl pyroborate, triallyl orthoborate, tetramethyl pyroborate, and the like. Typical examples of the preferred borate esters include triphenyl orthoborate, triphenyl metaborate, tetraphenyl pyroborate, the tritoly ortho and metaborates, the tetraxylyl pyroborates, tri- α -naphthyl orthoborate, cumenyl diphenyl orthoborate, tri-(p-dodecylphenyl) metaborate, and the like.

The above defined light metal aluminum hydrides contain a light metal of atomic number 3 through 56. It is well recognized in the art, as exemplified by the Periodic Chart of the Elements as reprinted in Lange's Handbook of Chemistry, Handbook Publishers, Inc., Sandusky, Ohio, 1946 (6th edition), pp. 58-59, that these light metals are composed solely of the metals of Groups IA and IIA of the Periodic Table. Hence, these metals consist of lithium, sodium, potassium, rubidium, cesium, beryllium, magnesium, calcium, strontium and barium. Therefore, typical examples of the aluminum hydride reactant include lithium aluminum hydride, sodium aluminum hydride, potassium aluminum hydride, magnesium aluminum hydride, and the like. Of these compounds the alkali metal aluminum hydrides, especially lithium aluminum hydride and potassium aluminum hydride, and most especially sodium aluminum hydride, are preferred because of the very substantial cost-effectiveness they exhibit in the practice of this invention.

As brought out above, the process of this invention is conducted in the presence of an inert liquid hydrocarbon, an inert liquid ether, a hydrocarbyl compound of a Group VA element, or a mixture of two or more of these materials. Exemplary of such inert liquid hydrocarbons are hexane, heptane, octane, decane, benzene, toluene, xylene, gasoline fractions, kerosene, naphtha, petroleum ethers, and in general hydrocarbons which are liquid at temperatures within the range of about -80° to about 100° C. Exemplary of such inert ethers are tetrahydrofuran, dimethyl carbitol, dibutyl ether, dixylyl ether, trimethylol propane, diethyl ether, tetrahydropyran, and the like.

The hydrocarbyl compound of a Group VA element can be represented by the formula



where Z is nitrogen, phosphorus or arsenic, R_1 is a hydrocarbyl group; and R_2 and R_3 are hydrocarbyl groups or hydrogen atoms. Each such hydrocarbyl group can contain up to about 36 carbon atoms. In other words, these hydrocarbyl compounds are primary, secondary or tertiary amines, phosphines and arsines. The hydrocarbyl radicals of these compounds can be alkyl, cycloalkyl, aralkyl, alkenyl, aryl, alkaryl, and related univalent hydrocarbon groups. Generally speaking, the stronger the basicity of the hydrocarbyl compounds the better are the yield of desired product and the rate of reaction. Accordingly, it is desirable to use compounds having an ionization constant characteristic of a base of at least 10^{-12} as measured in aqueous solution at 25° C. A preferred embodiment of this invention involves the use of primary, secondary and tertiary alkyl amines; secondary and tertiary alkyl phosphines; and secondary and tertiary arsines, especially those compounds in which each alkyl group contains from 1 to about 8 carbon atoms. Triethyl amine, dipropyl amine, butyl amine, methyl ethyl amine, triethyl phosphine, trihexyl arsine, dioctyl phosphine, di-

3

isoamyl arsine, and the like, serve as examples of these preferred compounds.

From the viewpoints of cost and desirability of end products the use of amines as the hydrocarbyl compound is preferred.

The temperature at which the process of this invention takes place varies, depending upon the nature of the materials used. In general, however, reaction is caused to take place by bringing the borate ester and the light metal aluminum hydride in contact with each other in admixture with the above hydrocarbon, ether or hydrocarbyl compound. Generally speaking, the reaction is highly exothermic and, therefore, it is ordinarily unnecessary to supply heat to the reaction vessel. Instead, the reactants can be admixed at room temperature (or below) and as soon as reaction starts the temperature increases. In most cases, temperatures ranging from about -80 to 150°C . are efficacious with temperatures ranging from about -40° to 25°C . being especially preferred. In this latter temperature range, exceedingly good reaction rates are achieved without the necessity of providing external heat to the reaction system.

The present process can be conducted at atmospheric pressure when the several components are not vaporized under the temperatures used. However, under most instances it is desirable to conduct the reaction in a closed system (such as in an autoclave) and, therefore, take advantage of autogenous pressure. Under these circumstances a positive pressure can be initially imposed upon the system if desired. For example, the reaction vessel can be charged with an inert gas blanket (nitrogen, argon, neon, krypton, etc.) to a pressure of as high as about 5,000 p.s.i.g. and then the reaction caused to take place. These latter techniques are advantageous when using the more volatile starting materials.

In conducting the process of this invention good results are achieved when using from about 0.5 to about 5 moles of the borate per mole of the aluminum hydride compound. While departures from this ratio can be effected, there is no particular advantage in doing so. The other component—viz. the inert liquid hydrocarbon, inert liquid ether, hydrocarbyl compound of a Group VA element of atomic numbers 7 through 33, or mixture of two or more of these—should be present in amount such that there is at least one mole thereof per mole of the borate. A considerable excess of this third component can be used. For example up to about 20 moles of this component per mole of the borate can be successfully used. If desired, a still greater amount of the third component can be used, the precise amount being determined largely by matters of convenience.

An outstanding feature of this invention is the fact that a wide variety of desirable end products—hydrides of boron—are formed, depending upon the nature of the third component used in the process. Thus, when inert liquid hydrocarbons, inert liquid ethers, or both are used, the product is diborane. When amines are used as the third component, the resultant product is a hydride of boron which contains nitrogen in the molecule. By the same token, when phosphines or arsines are used, the resultant hydrides of boron contain phosphorus or arsenic, respectively.

The type of amine, phosphine or arsine used likewise exerts a profound influence upon the type of end product formed. For example, when tertiary amines are used the product is a tertiary amine borane—i.e. a hydride of boron having the formula

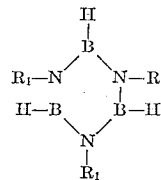


where R_1 , R_2 and R_3 are as defined above. When a secondary amine is used, the product is an N,N-dihydrocarbyl borazene of the formula



4

in which R_1 and R_2 are as defined above. When primary amines are used the resultant product is an N,N',N''-tri-hydrocarbyl borazole of the formula



where R_1 is as defined above.

The same type of products are formed when primary, secondary and tertiary phosphines and arsines are used except that, of course, the nitrogen atoms shown in the preceding 3 formulas are replaced with phosphorus or arsenic atoms. It is seen, therefore, that the present process provides the art with a highly efficient method for the preparation of a wide variety of important chemical products.

This invention can be further understood by reference to the following specific examples in which all parts and percentages are by weight unless otherwise specified.

Example I

Into a reaction vessel containing 28.5 parts of triphenyl orthoborate dissolved in 100 parts (by volume) of triethyl amine was introduced 3.2 parts of lithium aluminum hydride dissolved in 100 parts (by volume) of diethyl ether. The reaction was exothermic and was completed in 30 minutes. Triethyl amine borane was formed in 60 percent yield.

Example II

Lithium aluminum hydride (3.5 parts) in 125 parts (by volume) of diethyl ether was added at room temperature to 31.6 parts of triphenyl orthoborate dissolved in 100 parts (by volume) of diethyl ether. A rapid exothermic reaction occurred giving diborane in 47 percent yield.

Example III

Lithium aluminum hydride (5.7 parts) in 125 parts (by volume) of diethyl ether was added at room temperature to 20.8 parts of trimethyl orthoborate in 80 parts (by volume) of triethyl amine. The reaction was exothermic and completed in 30 minutes. A 60 percent yield of triethyl amine borane resulted.

Example IV

Sodium aluminum hydride (1.62 parts) in 80 parts (by volume) of hexane is added at room temperature to 12.0 parts of tributyl metaborate dissolved in 100 parts (by volume) of hexane. The reaction commences at room temperature and is exothermic. The system is then refluxed for 3 hours whereby diborane is formed in excellent yield.

Example V

To a reaction vessel containing 13.08 parts of tetraethyl pyroborate dissolved in 100 parts (by volume) of N,N-dimethyl aniline is added at room temperature 3.06 parts of calcium aluminum hydride in 100 parts (by volume) of diethyl ether. The system is then heated to 100°C . for 2 hours. Formed is N,N-dimethyl N-phenyl amine borane.

Example VI

Potassium aluminum hydride (2.1 parts) in 100 parts (by volume) of diethyl ether is added to 12.32 parts of tricyclohexyl orthoborate in 100 parts (by volume) of diethyl ether. The reaction is caused to take place in admixture with 4.72 parts of triethyl phosphine. The temperature ranges from 25° to 60°C . for 2 hours. The resultant product is triethyl phosphine borane.

5

Example VII

Sodium aluminum hydride (1.62 parts) in 100 parts (by volume) of dimethyl Carbitol is added to 18.72 parts of trioctyl metaborate in 100 parts (by volume) of dimethyl Carbitol. The reaction is caused to take place in admixture with 9.84 parts of tributyl arsine. The reaction is run at 25° to 80° C. for 2 hours. The product is tributyl arsine borane.

Example VIII

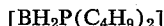
To a reaction vessel containing 14.8 parts of dihexyl amine are added 24.6 parts of tetraphenyl pyroborate in 100 parts (by volume) of benzene and 2.59 parts of magnesium aluminum hydride in 100 parts (by volume) of benzene. The reaction is caused to take place at about 100° C. for 3 hours whereby N,N-dihexyl borazene is formed.

Example IX

Into a reaction vessel containing 2.92 parts of butyl amine are charged 1.14 parts of lithium aluminum hydride (in 100 parts by volume of tetrahydrofuran) and 6.96 parts of trimethyl metaborate (in 60 parts by volume of tetrahydrofuran). An adduct initially forms between the metaborate and the amine, but this is decomposed by the hydride. Consequently, reaction proceeds smoothly at 150° C. for 4 hours. The product is N,N',N''-tributyl borazole.

Example X

Charged to a reaction vessel are 1.62 parts of sodium aluminum hydride (in 100 parts by volume of diethyl ether), 7.52 parts of isopropyl orthoborate (in 100 parts by volume of diethyl ether) and 5.84 parts of dibutyl phosphine. The reaction is run at 100° to 150° C. for 3 hours. The product is dibutyl phosphenyl borane



Example XI

Charged to a reaction vessel are 2.59 parts of magnesium aluminum hydride (in 100 parts by volume of hexane), 38.56 parts of tridecyl orthoborate (in 100 parts by volume of hexane) and 10.72 parts of diethyl arsine. The reaction is run for 6 hours at 120° C. Formed is diethyl arsenyl borane $[\text{BH}_2\text{As}(\text{C}_2\text{H}_5)_2]$.

Example XII

Charged to a reaction vessel are 2.59 parts of magnesium aluminum hydride (in 100 parts by volume of benzene), and 32.16 parts of tritoyl metaborate (in 100 parts by volume of benzene). Reaction commences at room temperature and proceeds exothermically for 30 minutes. Then the mixture is refluxed for 2 hours. Diborane is formed in good yield.

It will be seen by reference to Example IX that adducts are formed between the amines and the metaborate esters. Generally speaking, these adducts are white crystalline solids which are insoluble in highly paraffinic solvents. On the other hand, they tend to remain in solution in highly aromatic solvents and the like. It will be seen, however, that the process of this invention is highly applicable to the formation of the present products using these metaborate-amine adducts as a starting material.

Conventional work-up procedures are readily adapted to the separation and recovery of the products of this invention from the reaction mixtures. Thus, such procedures as fractionation, decantation, centrifugation, solvent extraction, distillation at reduced pressure, etc. are advantageously used.

Methods are known to those skilled in the art and reported in the literature for the preparation of the several components used in the practice of this invention. For example, the orthoborates may be conveniently prepared by esterifying orthoboric acid with the appropriate alcoholic or phenolic compound. Temperatures of around 150° C. are quite satisfactory. The corresponding meta-

6

borates can be prepared by reacting the appropriate alcoholic or phenolic compound with orthoboric acid in proper molar ratio in the presence of a diluent which removes water azeotropically. Toluene, xylene, natural hydrocarbon fractions boiling in the range of 75° to 150° C., etc. are examples of such a diluent. The pyroborates are prepared in a manner similar to that used in the preparation of the metaborates. The chief differences are minor adjustments in the ratio of the alcoholic or phenolic compound and the orthoboric acid, and also the extent to which dehydration is effected.

A convenient method of preparing the light metal aluminum hydrides involves the reaction of a light metal hydride (e.g. sodium hydride, calcium hydride) with aluminum chloride. The mole ratio is 4 moles of light metal hydride per mole of aluminum chloride.

The light metal aluminum hydrides used in the practice of this invention are lithium aluminum hydride, sodium aluminum hydride, potassium aluminum hydride, rubidium aluminum hydride, cesium aluminum hydride, beryllium aluminum hydride, magnesium aluminum hydride, calcium aluminum hydride, strontium aluminum hydride and barium aluminum hydride.

Method of preparing the hydrocarbons, ethers, amines, phosphines, and arsines are likewise reported in the literature. Many of these substances, especially the hydrocarbons and ethers, are on the market. Many of the amines occur in and are readily recoverable from coal tar fractions, petroleum residues, and the like. Inasmuch as these amines, phosphines, and arsines are respectively derivatives of ammonia, phosphine and arsine, the art is well aware of procedures whereby these last-named materials can be converted into the corresponding hydrocarbyl compounds.

Exemplary of the hydrocarbyl amines, phosphines and arsines are benzyl amine, allyl amine, diethylamine, di-n-propyl amine, dibenzyl amine, triethyl amine, aniline, o-toluidine, beta-naphthyl amine, 2,6-diethyl aniline, N-ethyl aniline, N,N-dimethyl aniline, N,N-diethyl aniline, pyridine, 2-picoline, 3-picoline, 2,6-lutidine, quinoline, quinaldine, morpholine, piperidine, n-hexyl amine, 2-ethyl-hexyl amine, di-n-butyl amine, dodecyl amine, dilauryl amine, tricicosyl amine, phenylmethylpropyl amine, 4-ethylcyclohexyl amine, triethyl phosphine, triisopropyl phosphine, tri-sec-amyl phosphine, tripentadecyl phosphine, triphenyl phosphine, tri-2,6-xylyl phosphine, tricumenyl phosphine, dimethyl phosphine, dicyclohexyl phosphine, diallyl phosphine, methylphenyl phosphine, alpha-naphthyl phosphine, n-hexyl phosphine, tridecyl phosphine, tripropyl arsine, tri-(1,1,3,3-tetramethylbutyl) arsine, tri-m-tolyl arsine, diphenylmethyl arsine, diethyl arsine, diheptyl arsine, diundecyl arsine, phenyl arsine, methyl arsine, octyl arsine, p-nonylphenyl arsine, and the like.

The products formed by the process of this invention are of considerable value in the chemical and allied arts. For example, the hydrides of boron are effective cetane improvers when dissolved in low concentrations in diesel fuels. Concentrations ranging from about 0.01 to about 5 weight percent are sufficient for this purpose. For further details reference should be had to U.S. Patent No. 2,860,167, issued November 11, 1958. These hydrides of boron are likewise useful as additives to gasoline and other fuels for spark ignition internal combustion engines; and to engine and industrial oils. In these media small concentrations of these hydrides of boron exert antioxidant and sludge inhibiting properties. Other uses for such compounds include use as chemical reducing agents, use as agricultural chemicals, and the like. Diborane itself is exceedingly useful as a chemical intermediate in the synthesis of other boron compounds.

What is claimed is:

1. A process for the preparation of hydrides of boron characterized by the step of reacting together (1) a fully esterified ester of an oxyacid of boron in which (a) the

7

boron is bonded solely to oxygen atoms and (b) all of the esterifying groups are hydrocarbyl groups, (2) a light metal aluminum hydride in which said metal is a light metal of atomic number 3 through 56, and (3) a hydrocarbyl compound of an element selected from the group consisting of nitrogen, phosphorus, and arsenic, said hydrocarbyl compound being further characterized by containing three monovalent radicals directly affixed to said element, from 1 to 3 of said radicals being hydrocarbyl radicals and from 0 to 2 of said radicals, being hydrogen.

2. The process of claim 1 further characterized in that it is conducted in admixture with a substance selected from the group consisting of (a) inert liquid hydrocarbons and (b) inert liquid ethers.

3. The process of claim 1 further characterized in that said light metal aluminum hydride is an alkali metal aluminum hydride.

4. The process of claim 1 further characterized in that said light metal aluminum hydride is sodium aluminum hydride.

8

5. The process of claim 1 further characterized in that said light metal aluminum hydride is lithium aluminum hydride.

6. The process of claim 1 further characterized in that said ester is an orthoborate.

7. The process of claim 1 further characterized in that said ester is triphenyl orthoborate.

8. The process of claim 1 further characterized in that said ester is trimethyl orthoborate.

9. A process for the preparation of triethyl amine borane characterized by the step of reacting lithium aluminum hydride, triphenyl o-borate, and triethyl amine, the reaction being conducted in admixture with diethyl ether.

References Cited by the Examiner

Schechter et al.: "Boron Hydrides and Related Compounds," pp. 20, 22 and 28, Jan. 8, 1951.

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