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PROCESS FOR PREPARING DIBORANE

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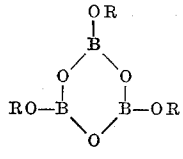
This invention relates to and has as its chief objective the provision of a chemical process for the preparation of hydrides of boron. This application is a continuation in part of copending application, Serial Number 832,145, filed August 7, 1959.

According to this invention, there is provided a process for the preparation of hydrides of boron, said process being characterized by adding (1) a light metal aluminum hydride in which said metal is a light metal of atomic number 3 through 56, to (2) 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, the reaction being conducted in admixture with a substance selected from the group consisting of (A) inert liquid hydrocarbons and (B) inert liquid ethers. As a result of this novel and highly important process, high yields of various hydrides or boron, such as diborane, are achieved.

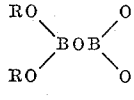
The above described hydrocarbyl esters of oxyacids of boron comprise a well recognized group of borate esters. Thus, one type is the hydrocarbyl orthoborates having the formula

$$(RO)_3B$$

where R is a hydrcoarbyl 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.

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 tritolyl ortho and metaborates, the tetraxylyl pyroborates, tri-a-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 light 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 or an inert liquid ether. 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 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 light metal aluminum hydride in contact with the borate ester 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, or mixture of both—should be present in an 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.

In conducting the process of this invention it is advantageous to employ a mode of addition wherein the light metal aluminum hydride is added to the reaction mixture containing the boron ester. Less undesirable side reactions occur where this technique is employed. When the reverse mode of addition is employed, undesirable side reactions occur, producing by-products and mixtures of by-products other than the desired boron hydrides.

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

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 II

To 7.14 parts of phenyl borate in 80 parts by volume of the dimethyl ether of diethylene glycol was added 5.37 parts of sodium aluminum hydride and 135 parts by volume of the dimethyl ether of diethylene glycol. The reaction was exothermic and gas was liberated. The product obtained was diborane.

Example III

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 boron hydrides are formed.

Example IV

2.59 parts of magnesium aluminum hydride (in 100 parts by volume of benzene) is charged to a reaction vessel containing 32.16 parts of tritolyl 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.

Example V

To a reaction vessel containing 13.08 parts of ethyl borate and 100 parts by volume of tetrahydrofuran, is added at room temperature, 3.06 parts of calcium aluminum hydride in 100 parts of tetrahydrofuran. The system is then heated to 100° C. for two hours. The products formed are hydrides of boron.

Example VI

Potassium aluminum hydride (1.75) and 100 parts by volume of dimethyl ether of diethylene glycol is charged into a reactor containing 19.5 parts of trioctyl metaborate in 100 parts by volume of dimethyl ether of diethylene glycol. Reaction is heated to a temperature of 80° C. for two hours and the products obtained are hydrides of boron.

Example VII

Into a reaction vessel containing 7 parts of triphenyl borate and 60 parts by volume of xylene, is charged 1.3 parts of lithium aluminum hydride in admixture with 100 parts by volume of xylene. Reaction is conducted at 95° C. for 5 hours and the product recovered is diborane. Similar excellent results are obtained when cyclohexane, kerosene, decane, benzene, toluene, and the like are employed in place of xylene as the solvent.

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 metaborates 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 aluinum hydride, strontium aluminum hydride and barium aluminum hydride.

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 made 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 international 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 diborane characterized by adding (1) a metal aluminum hydride in which said metal is a light metal of atomic number 3 through 56, to (2) 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, the addition being conducted in admixture with a substance selected from the group consisting of (A) inert liquid hydrocarbons and (B) inert liquid ethers, and recovering the diborane so produced.

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

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

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

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

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

7. A process for the preparation of diborane characterized by adding sodium aluminum hydride to an orthoborate ester, the addition being conducted in admixture

with an inert liquid ether, and recovering the diborane so produced.

8. A process for the preparation of diborane characterized by adding lithium aluminum hydride to triphenyl orthoborate, the addition being conducted in admixture with diethyl ether, and recovering the diborane so produced.

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