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BORON-CONTAINING COMPOUNDS

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10 Claims. (Cl. 260—308)

The present invention relates to novel compounds containing both boron and nitrogen and to methods for making the same.

In recent years, there has been considerable interest in boron-containing compounds because the high heat of combustion of these compounds renders them desirable for use as rocket fuels or components of rocket fuels. According to the present invention, boron compounds have been prepared, which compounds are useful as explosives as well as high-energy fuels and as fuel additives. The solid products of this invention, either per se or after incorporation into a polymer, can be used in solid propellants for rocket power plants and other jet-propelled devices when mixed with suitable oxidizers such as ammonium, potassium, or sodium perchlorates, ammonium nitrate, etc. Such propellant mixtures may be compounded by a number of techniques known to the art. For example, the mixtures may comprise from 5 to 35 parts by weight of boron-containing materials and from 65 to 95 parts by weight of solid oxidizing agents mixed therewith. In some cases the propellant may also be made by combining the boron compounds and oxidizers with a curable polymer, for example, of the polysulfide, polyurethane, polyester or polyether types.

Other products of the invention may be used as additives in high energy liquid fuels by mixing the products with combustible liquids such as compatible hydrocarbon fuels.

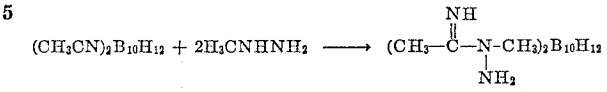
The compounds of the instant invention are particularly advantageous because they contain high percentages of such light elements as hydrogen and nitrogen in addition to the boron. Compounds comprising such elements tend to produce a relatively large quantity of gas, per unit weight of compound, on combustion. Such compounds are especially important where large quantities of gas are to be generated at high altitudes as in rocketry applications. The weight of the propellant necessary to produce a given quantity of propulsion gas becomes highly important because the weight of the payload of military or scientific apparatus may be increased in proportion to the weight saving allowed by lighter fuels.

The compounds of the instant invention may be utilized not only in the fuel-burning process associated with rocketry but also in the relatively rapid decomposition associated with explosives. Thus, properly fuzed and detonated as is known to the art, the compounds of the invention can be valuable explosives for use in mining, construction, and other such industrial operations.

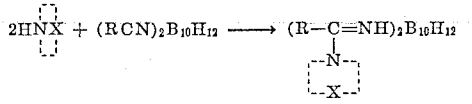
Therefore it is an object of the invention to provide novel compounds comprising elements which provide large quantities of gas on combustion. It is another object of the invention to provide compounds which detonate releasing large quantities of energy. Another object of the invention is to provide boron-containing compounds useful in solid fuel compositions. It is also an object of the invention to provide processes by which these novel compounds may be conveniently manufactured.

The compounds of the present invention are those formed by reaction of a nitrilo decaborane with nitrogen-containing compounds wherein an active hydrogen removed from a nitrogen atom of the nitrogen-containing

compound bonds to the nitrilo nitrogen of the decaboranyl compound, and the nitrogen atom from which said active hydrogen is removed attaches to the nitrilo carbon as indicated by the following illustrative reaction:

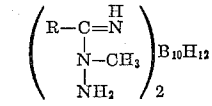


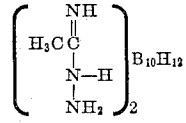
A more generalized representation of the reaction by which the products of the present invention are formed is

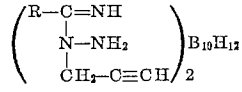


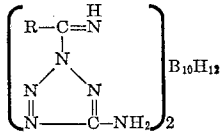
wherein R represents a hydrocarbon radical of a nitrilo compound and X represents a residue of the nitrogen-containing compound. The broken line is used to indicate that the nitrogen having the active hydrogen involved in the reaction need not be terminal, i.e., at the end of a molecule, but may be elsewhere in the molecule. For example, it may be a member of a ring structure or be an internal member of a linear molecule. X, therefore, may be a divalent radical forming a cyclic structure with the indicated nitrogen or may represent two distinct monovalent radicals.

Among the preferred products of the invention are those of the formulae

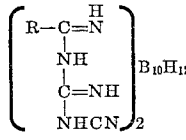






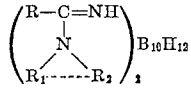


and



wherein R is a lower alkyl group such as those having 1 to 4 carbon atoms.

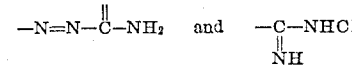
A formula representative of such compounds is



wherein R is an alkyl group, R_1 is selected from the group consisting of hydrogen, amino, and —N=, R_2 is selected from the group consisting of —CH_3,

—CH_2—C≡CH

amino



and wherein the dotted line represents the joining of R_1 and R_2 when necessary to satisfy valences of the two radicals.

Especially advantageous, as decaborane addition product is the coordination compound of decaborane with acetonitrile, bis(acetonitrilo) decaborane, which may be prepared by reacting decaborane with acetonitrile at reflux in an inert solvent such as toluene as disclosed in commonly owned and copending application Serial No. 269,848 filed March 28, 1963 by Fein et al.

Primary alkylamines, secondary alkylamines, and alkyl hydrazines are advantageous as the nitrogen-containing compounds useful as starting materials in the process of the present invention. Especially useful are the lower alkyl compounds wherein the alkyl group has up to about 4 carbon atoms. Among such useful compounds are included methylhydrazine, propargyl hydrazine, dipropargyl hydrazine, 5-aminotetrazole, and cyanoguanidine. Hydrazine may also be used.

The decaborane compound and the nitrogen compound are preferably reacted in an inert solvent medium such as ether, benzene, toluene or other such aliphatic and aromatic compounds or mixtures thereof. The formation of the decaborane addition product with acetonitrile may be carried out in the same reactor as the novel process of the instant invention and an excess of acetonitrile charged to the reactor is an acceptable solvent in which the novel reaction may suitably proceed.

The reaction is suitably carried out at temperautres from 25° to 100° C., but may be carried out at lower or higher temperatures according to the convenience of the situation. For example, while it is usually most convenient to operate at least at room temperature, the use of an extremely hazardous nitrogen compound may suggest the synthesis be carried out below room temperature to assure no local heating above the decomposition point of such a hazardous compound. Furthermore, in order to accelerate the reaction, temperatures above 100° C. may be used when care is taken to assure that the higher temperature does not cause decomposition of the reactants or products.

In order to point out more fully the nature of the present invention, the following specific examples are given as illustrative embodiments of the present process and products produced thereby.

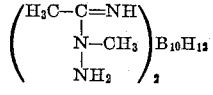
Example 1

Ten grams (0.05 mole) of bis(acetonitrilo) decaborane was suspended in 100 ml. of dry benzene in a glass reaction vessel. To this suspension was added 25 ml. of methyl hydrazine hydrate. An exothermic reaction resulted. After the addition of this alkyl hydrazine compound was complete, the contents of the vessel were heated at reflux for three hours. No gas evolved during this three-hour period. The contents of the vessel were then cooled and filtered. A white solid was recovered which was dissolved in acetonitrile and recrystallized. The resulting material had a melting point of 218°–219° C. The yield, eight grams, represented 54% of the yield theoretically possible.

A chemical analysis of the material indicated the following chemical composition:

Percent found: B, 36.73; N, 26.02. Percent calculated for product: B, 36.93; N, 28.52.

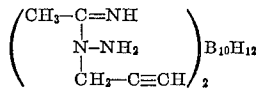
An infra-red analysis of the chemical structure confirmed that the product was of the formula



Example 2

To a glass reaction vessel containing a suspension of 3 grams (0.003 mole) of bis(acetonitrilo) decaborane in 60 ml. of dry benzene was added a mixture containing 0.3 gram (0.003 mole) of dipropargyl hydrazine hydrate and 0.7 gram (0.010 mole) of propargyl hydrazine hydrate.

The mixture of the above-identified chemicals was heated at reflux for four hours during which time the liquid and solid phases in the vessel turned red. The contents of the vessels were then cooled and filtered. 3.6 grams of a solid were obtained which had a melting point above 250° C. An infra-red analysis confirmed that the solid was a bis(acetonitrilo) decaborane-substituted hydrazine adduct of the formula



Example 3

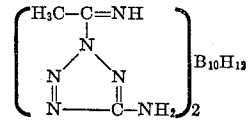
Into a glass reaction vessel containing 100 ml. of acetonitrile were placed 2.5 grams (0.012 mole) of bis-(acetonitrilo) decaborane and 2.0 grams (0.024 mole) of 5-aminotetrazole. The contents of the vessel were then heated to reflux for four hours during which time the contents turned orange.

The contents of the vessel were then cooled and filtered. The filtrate was evaporated leaving 3.3 grams of a solid product which melted above 300° C.

A chemical analysis of the solid material indicated the following chemical composition.

Percent found: C, 18.56; N, 6.86; B, 30.78. Percent calculated for product: C, 19.34; N, 6.49; B, 29.04.

An infra-red analysis of the chemical structure confirmed that the solid product was of the formula

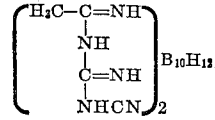


Example 4

120 ml. of acetonitrile was placed in a glass reaction vessel and 2.02 grams (0.01 mole) of bis(acetonitrilo) decaborane and 1.68 grams (0.02 mole) of cyanoguanidine were added to the acetonitrile. The contents of the vessel were reacted under reflux for two hours after which the contents were cooled and filtered. About 2.2 grams of a brown solid was obtained which did not melt below 300° C. Chemical analysis and elemental analysis confirmed that an addition product of bis(acetonitrilo) decaborane and cyanoguanidine had been formed:

Percent found: C, 19.52; H, 6.22; N, 35.14; B, 26.78. Percent calculated for product: C, 25.93; H, 7.07; N, 37.96; B, 29.20.

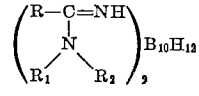
The compound had a structural formula believed to be



It is of course to be understood that the foregoing examples are intended to be illustrative and that numerous changes can be made in the reactants, proportions, and conditions set forth therein without departing from the spirit of the invention as defined in the appended claims.

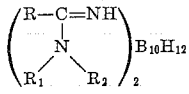
We claim:

1. A compound of the formula

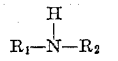


wherein R is a hydrocarbon radical, R_1, taken alone, is hydrogen or amino, R_2, taken alone, is amino, methyl, propargyl, or cyanoguanidinyl, but R_1 and R_2 are not both amino, and R_1 and R_2, taken together with the nitrogen atom to which they are attached, form a 5-amino-2-tetrazolyl group.

2. A process for preparing a compound of the formula

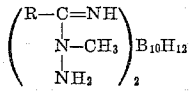


wherein R is a hydrocarbon radical, R_1, taken alone, is hydrogen or amino, R_2, taken alone, is amino, methyl, propargyl, or cyanoguanidinyl, but R_1 and R_2 are not both amino, and R_1 and R_2, taken together with the nitrogen atom to which they are attached, form 5-amino-2-tetrazolyl group, which process comprises reacting a bis(R-nitrilo)-decaborane with a compound of the formula



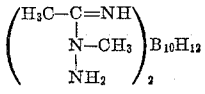
wherein R, R_1 and R_2 have the meanings given earlier herein.

3. A compound of the formula

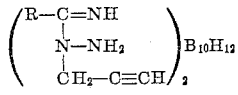


wherein R is a lower alkyl group.

4. A compound of the formula

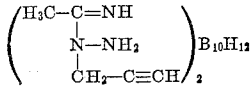


5. A compound of the formula

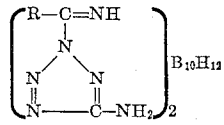


wherein R is a lower alkyl group.

6. A compound of the formula

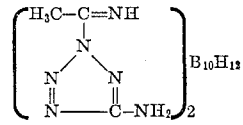


7. A compound of the formula

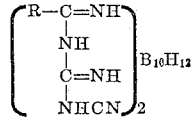


wherein R is a lower alkyl group.

8. A compound of the formula

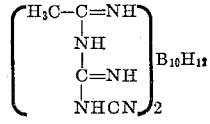


9. A compound of the formula



wherein R is a lower alkyl group.

10. A compound of the formula



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