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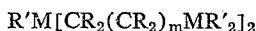
COMPOUNDS CONSISTING OF HYDROCARBON GROUPS AND ALUMINUM AND/OR BORON ATOMS

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This invention relates to new chemical compounds containing boron, or aluminum, or both, which are particularly useful as high energy fuels. It also relates to methods of preparing such compounds. More specifically, it relates to metal-hydrocarbon compounds containing at least three such metal atoms.

Alkyl boron and alkyl aluminum compounds have been found desirable for use as liquid fuels for propelling missiles, rockets, etc. In order to have a maximum energy content, the hydrocarbon portion of such compounds should represent as low a proportion as possible of the total weight. However, the presently known alkyl borons and alkyl aluminums having the desired high energy for such purposes are low boiling and have high volatility and toxicity. Attempts to decrease the boiling point and volatility by increasing the size or length of the alkyl groups attached to the metal result in a lower proportion of metal in the compounds, and, therefore, a lower energy content.

In accordance with the present invention, new metallo-hydrocarbon compounds containing a plurality of boron and/or aluminum atoms have been found which have higher boiling points and lower volatility, and thereby reduce the tendency to cause toxicity and eliminate the necessity for use under pressure. These new compounds have a high proportion of metal therein, and, therefore, have as high or even higher energy content that is utilisable for propellant purposes than the presently known alkyl boron or aluminum compounds. These compounds contain at least three atoms of metal therein and are represented by the formula



wherein M is boron or aluminum, R is preferably hydrogen but also can be a hydrocarbon group as defined for R' and said R can have on one of said hydrocarbon groups one or more other MR'_2 groups, preferably BR'_2; R' is a hydrocarbon group of no more than 8 carbon atoms, preferably no more than 3, and m is an integer having a value of at least 1 and no more than 8, preferably no more than 4. Generally the advantages of this invention are realized when the number of MR'_2 groups in a compound are no more than ten.

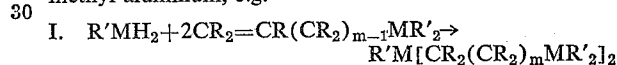
One advantage of boron compounds over aluminum compounds for use in rocket and missile fuels is the lower atomic weight of boron as compared to aluminum. The atomic weight of boron is approximately 11 and that for aluminum is approximately 27. Therefore, for corresponding types of compounds, a given weight of the boron compound will contain a greater number of boron atoms than the number of aluminum atoms contained in a corresponding weight of the aluminum compounds. Thus, in rockets and missiles where the amount of energy derived per unit weight of fuel is very critical and the fuel consists of compounds having high proportions of metal therein, the boron compounds have a decided advantage. In the compounds of this invention where at least three boron atoms are contained in each molecule, this advantage is even more emphasized. In those compounds in which there are one or more aluminum atoms, the higher atomic weight of the aluminum atom is offset

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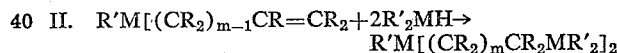
to some extent by the fact that there are a plurality of metal atoms per molecule, and the ratio of metal to hydrocarbon portions generally compensates for the higher atomic weight of aluminum.

- 5 A comparison of trimethyl boron with one of the simplest compounds of this invention, bis-(dimethyl-boro-ethyl) methyl borane, $CH_3B[CH_2CH_2B(CH_3)_2]_2$, can illustrate the advantage cited above. This latter compound has an empirical formula of $B_3C_9H_{23}$ and can be regarded as having $C_3H_{7.66}$ per boron atom. In comparison, trimethyl borane has an empirical formula of BC_3H_9 and whereas it has the same number of carbon atoms per boron atom, actually it has 1.33 hydrogen atoms more per boron atom than the new compound described above. However, trimethyl boron is a gas at room temperature, having a boiling point of $-20^\circ C.$, must be used as a liquefied compressed gas, and is very toxic. In contrast, the new compound described above has a much higher boiling point and relatively low volatility, therefore involving less danger with respect to toxicity, and can be used without pressure.

A simple preferred method for preparing the compounds of this invention is the addition of a boron or aluminum hydride having one hydrocarbon group per boron or aluminum atom to a boron or an aluminum compound having three hydrocarbon groups attached thereto, one of which hydrocarbon groups is an alkenyl group, for example vinyl dimethyl borane or vinyl dimethyl aluminum, e.g.



As an alternate synthesis, these compounds also can be prepared by reacting a boron or aluminum hydride having two hydrocarbon groups attached to the boron with a boron or aluminum compound having three hydrocarbon groups attached to the metal atom, two of which have ethylenic unsaturation, e.g.



These reactions are catalyzed by an ether compound, such as diethyl ether, tetrahydrofuran, diglyme, etc., as well as boron or aluminum compounds containing hydrocarbon and ether groups therein, such as, for example, (vinylloxy-ethyl)-dimethyl boron, (vinylloxy-ethyl)-diethyl boron, ethyl-bis-(ethoxy-ethyl)-boron, tris-(ethoxy-ethyl)-boron, (vinylloxy-ethyl)-dimethyl aluminum, (vinylloxy-ethyl)-diethyl aluminum, ethyl-bis-(ethoxy-ethyl)-aluminum, tris-(ethoxy-ethyl)-aluminum, etc.

Traces of the ether compounds are sufficient to catalyze reaction markedly. Therefore, the ether is used advantageously in minor amounts and, unless it is also to be used as a solvent or suspension medium, there is no need for more than 5 percent required for catalytic purposes. Also, as catalysts for the reaction of this invention, various compounds of the formulas $B(OR'')_3$ and $Al(OR'')_3$ can be used, in which R'' is hydrogen or a monovalent hydrocarbon group of the types indicated above, with at least one R'' in each compound being such a hydrocarbon group. Typical examples of such compounds include: trimethyl borate, dimethyl borate, methyl borate, tripropyl borate, dibutyl borate, mono-amy borate, dioctyl borate, monophenyl borate, dibenzyl borate, tricyclohexyl borate, triphenethyl borate, etc., and the corresponding aluminates, such as triethyl aluminate, propyl aluminate, benzyl aluminate, diphenethyl aluminate, cyclohexyl aluminate, etc.

As discussed more fully hereinafter, the reaction desirably is maintained at such a temperature that the hydride reacts only to the extent that there is hydrogen on

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the metal atom, and not high enough to replace any hydrocarbon groups thereon.

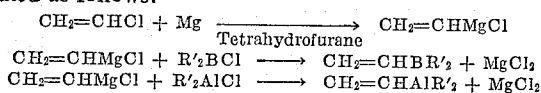
The addition reactions advantageously are conducted in the absence of moisture, or air, so as to prevent decomposition of the starting materials and products. Inert atmospheres and inert diluents advantageously are used. Nitrogen, argon, gaseous hydrocarbons, such as methane, ethane, etc., are used advantageously as inert atmospheres, and saturated hydrocarbons, such as pentanes, hexanes, heptanes, cyclohexanes, and even aromatic hydrocarbons, such as benzene, toluene, etc., are used advantageously as diluents.

Unsaturated compounds that can be used as intermediates in preparing the compounds of this invention by the first of the above reactions can be represented by the formula

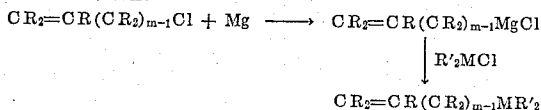


wherein R, R', M, and m are as defined above. Compounds having a terminal ethylenic group, i.e. a vinyl or vinylidene group, are preferred. Typical examples of such compounds include, but are not restricted to, the following: vinyl-dimethyl-boron, vinyl-diethyl-boron, vinyl-dipropyl-boron, vinyl-dibutyl-boron, vinyl-diamyl-boron, vinyl-diphenyl-boron, vinyl-dicyclohexyl-boron, vinyl-methyl-ethyl-boron, vinyl-ethyl-propyl-boron, vinyl-methyl-phenyl-boron, vinyl-ethyl-cyclohexyl-boron, allyl-dimethyl-boron, allyl-diethyl-boron, allyl-dipropyl-boron, allyl-dibutyl-boron, allyl-ditolyl-boron, allyl-dicyclopentyl-boron, isopropenyl-dimethyl-boron, isopropenyl-diethyl-boron, isopropenyl-dipropyl-boron, isopropenyl-dibutyl-boron, isopropenyl-methyl-ethyl-boron, isopropenyl-ethyl-propyl-boron, isopropenyl-dixyl-boron, beta-vinyl-triethyl-boron, (beta-vinyl-ethyl)-dimethyl-boron, (beta-vinyl-ethyl)-dipropyl-boron, isobutenyl-dibutyl-boron, (4-vinyl-cyclohexyl)-dimethyl-boron, (4-vinyl-n-butyl)-diethyl-boron, (6-vinyl-n-hexyl)-dimethyl-boron, vinyl-dimethyl-aluminum, vinyl-diethyl-aluminum, vinyl-dipropyl-aluminum, vinyl-dibutyl-aluminum, vinyl-diamyl-aluminum, vinyl-diphenyl-aluminum, vinyl-dicyclohexyl-aluminum, vinyl-methyl-ethyl-aluminum, vinyl-ethyl-propyl-aluminum, vinyl-methyl-phenyl-aluminum, vinyl-ethyl-cyclohexyl-aluminum, allyl-dimethyl-aluminum, allyl-diethyl-aluminum, allyl-dipropyl-aluminum, allyl-dibutyl-aluminum, allyl-ditolyl-aluminum, allyl-dicyclopentyl-aluminum, isopropenyl-dimethyl-aluminum, isopropenyl-diethyl-aluminum, isopropenyl-dipropyl-aluminum, isopropenyl-dibutyl-aluminum, isopropenyl-methyl-ethyl-aluminum, isopropenyl-ethyl-propyl-aluminum, isopropenyl-dixyl-aluminum, (beta-vinyl-ethyl)-dimethyl-aluminum, (beta-vinyl-ethyl)-dipropyl-aluminum, isobutenyl-dibutyl-aluminum, (4-vinyl-cyclohexyl)-dimethyl-aluminum, (4-vinyl-n-butyl)-diethyl-aluminum, (6-vinyl-n-hexyl)-dimethyl-aluminum, crotyl-dimethyl-boron, crotyl-diethyl-boron, crotyl-dipropyl-aluminum, etc.

Such intermediate compounds as listed in the preceding paragraph can be prepared according to well-known, standard reactions of dialkyl boron halides and dialkyl aluminum halides with appropriate Grignard reagents, such as vinyl magnesium chloride, allyl magnesium bromide, etc., or by reaction of these same halides with divinyl tin, tetravinyl lead, etc. Such reactions are illustrated as follows:



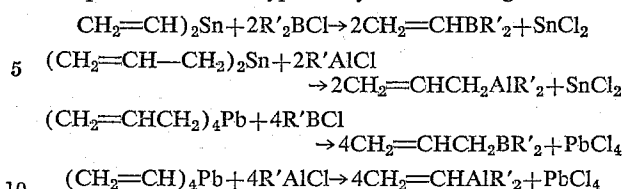
Such reactions can be represented by the following general reaction:



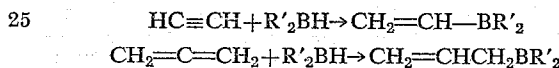
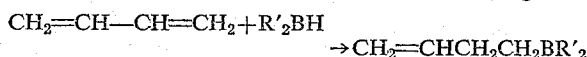
wherein R, M, R', and m are as defined above.

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Preparation from alkenyl tin and alkenyl lead starting compounds are also typified by the following reactions:



Such intermediate compounds can also be prepared by the reaction of dialkyl boron hydrides and dialkyl aluminum hydrides, or corresponding compounds having aryl or cycloaliphatic hydrocarbon groups in place of the alkyl groups, with a considerable excess of an acetylenic or diolefinic hydrocarbon, in such a manner, for example by controlling the temperature and time of reaction, that the metal hydrides react only to the extent that there is hydrogen attached to the metal atom in the compound and that the acetylenic or diolefinic material reacts only to the extent of half of the unsaturation therein, e.g.



etc. Corresponding reactions can be performed with R'_2AlH to give the corresponding intermediates. These intermediates are then further reacted in accordance with the practice of this invention.

Typical monosubstituted metal hydrides that can be used as starting materials in preparing the compounds of this invention according to the above reaction I include, but are not restricted to, the following: methyl boron hydride, ethyl boron hydride, propyl boron hydride, butyl boron hydride, octyl boron hydride, phenyl boron hydride, tolyl boron hydride, phenethyl boron hydride, cyclohexyl boron hydride, (cyclohexylethyl)-boron hydride, methyl aluminum hydride, ethyl aluminum hydride, propyl aluminum hydride, butyl aluminum hydride, heptyl aluminum hydride, phenyl aluminum hydride, xylyl aluminum hydride, phenethyl aluminum hydride, cyclohexyl aluminum hydride, (cyclohexyl-ethyl)-aluminum hydride, etc. In cases where such compounds are difficult to prepare or are unstable, polymeric counterparts of such compounds which give the same addition derivatives as the monomeric materials can be used, such as, for example, symmetrical dimethyl diborane, symmetrical diethyl diborane, symmetrical dimethyl dialane, symmetrical diethyl dialane, symmetrical trimethyltriborane, etc.

Unsaturated compounds that can be used as intermediates in preparing the compounds of this invention by the above reaction II can be represented by the formula



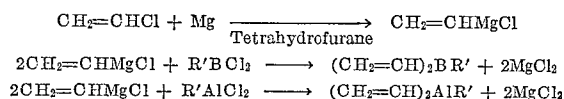
wherein R, R', M, and m are as defined above. Compounds having a terminal ethylenic group, i.e. a vinyl or vinylidene group, are preferred.

Typical examples of such compounds include, but are not restricted to, the following: divinyl-methyl-boron, divinyl-ethyl-boron, divinyl-propyl-boron, divinyl-butyl-boron, divinyl-amyl-boron, divinyl-phenyl-boron, divinyl-cyclohexyl-boron, vinyl-allyl-methyl-boron, vinyl-allyl-ethyl-boron, vinyl-allyl-propyl-boron, vinyl-allyl-phenyl-boron, vinyl-allyl-cyclohexyl-boron, diallyl-methyl-boron, diallyl-ethyl-boron, diallyl-propyl-boron, diallyl-amyl-boron, diallyl-tolyl-boron, diallyl-cyclopentyl-boron, diisopropenyl-methyl-boron, diisopropenyl-ethyl-boron, diisopropenyl-butyl-boron, diisopropenyl-xylyl-boron, diisopropenyl-cyclohexyl-boron, vinyl-isopropenyl-methyl-boron, allyl-isopropenyl-ethyl-boron, vinyl-isopropenyl-butyl-boron, allyl-isopropenyl-cyclohexyl-boron, bis-(beta-vinyl-ethyl)-methyl-boron, bis-(beta-vinyl-ethyl)-propyl-boron, bis-(4-vinyl-cyclohexyl)-methyl-boron, bis-(4-

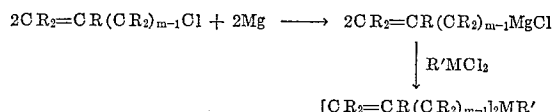
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vinyl-n-butyl)-ethyl-boron, bis-(6-vinyl-n-hexyl)-propyl-boron, vinyl-propyl-methyl-boron, allyl-crotyl-propyl-boron, dicrotyl-amy-ethyl-boron, divinyl-methyl-aluminum, divinyl-ethyl-aluminum, divinyl-propyl-aluminum, divinyl-butyl-aluminum, divinyl-amy-ethyl-aluminum, divinyl-phenyl-aluminum, divinyl-cyclohexyl-aluminum, vinyl-allyl-methyl-aluminum, vinyl-allyl-ethyl-aluminum, vinyl-allyl-propyl-aluminum, vinyl-allyl-phenyl-aluminum, vinyl-allyl-cyclohexyl-aluminum, diallyl-methyl-aluminum, diallyl-ethyl-aluminum, diallyl-propyl-aluminum, diallyl-amy-ethyl-aluminum, diallyl-tolyl-aluminum, diallyl-cyclopentyl-aluminum, diisopropenyl-methyl-aluminum, diisopropenyl-ethyl-aluminum, diisopropenyl-butyl-aluminum, diisopropenyl-xylyl-aluminum, diisopropenyl-cyclohexyl-aluminum, vinyl-isopropenyl-methyl-aluminum, allyl-isopropenyl-ethyl-aluminum, vinyl-isopropenyl-butyl-aluminum, allyl-isopropenyl-cyclohexyl-aluminum, bis-(beta-vinyl-ethyl)-methyl-aluminum, bis-(beta-vinyl-ethyl)-propyl-aluminum, bis-(4-vinyl-cyclohexyl)-methyl-aluminum, bis-(4-vinyl-n-butyl)-ethyl-aluminum, bis-(6-vinyl-n-hexyl)-propyl-aluminum, vinyl-propyl-methyl-aluminum, allyl-crotyl-propyl-aluminum, dicrotyl-amy-ethyl-aluminum, etc.

Such intermediate compounds as listed in the preceding paragraph can be prepared in the standard manner by reaction of alkyl boron dihalides and alkyl aluminum dihydrides with appropriate Grignard reagents, such as vinyl magnesium chloride, allyl magnesium bromide, etc., or by reaction of these same halides with divinyl tin, tetravinyl lead, etc. Such reactions are illustrated as follows:

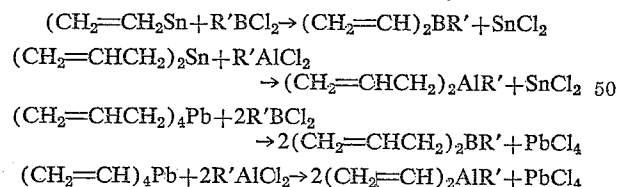


Such reactions can be represented by the following general reaction:



wherein R, R', M, and m are as defined above.

Preparation from alkenyl tin and alkenyl lead starting compounds are also typified by the following reactions:



Typical disubstituted metal hydrides that can be used as starting materials in preparing compounds of this invention according to the above reaction II include, but are not restricted to, the following: dimethyl boron hydride, diethyl boron hydride, dipropyl boron hydride, dibutyl boron hydride, diphenyl boron hydride, diphenethyl boron hydride, dicyclohexyl boron hydride, di-(cyclohexyl-ethyl)-boron hydride, dimethyl aluminum hydride, diethyl aluminum hydride, dipropyl aluminum hydride, dibutyl aluminum hydride, diphenyl aluminum hydride, dipentyl aluminum hydride, diphenethyl aluminum hydride, dicyclohexyl aluminum hydride, di-(cyclohexyl-ethyl)-aluminum hydride, etc. In some cases, where such compounds are difficult to prepare or are unstable, the polymeric counterparts of such compounds which give the same addition derivatives as the monomeric materials can be used, such as, for example, tetramethyl diborane, hexamethyl triborane, tetraethyl diborane, tetramethyl dialuane, tetraethyl dialuane, etc. In addition various mixed hydrocarbon compounds also can

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be used, such as, for example, methyl ethyl boron hydride, ethyl propyl aluminum hydride, methyl propyl aluminum hydride, ethyl butyl boron hydride, etc.

The optimum temperature for effecting the addition reaction depends on a number of factors. The use of a catalyst, such as an ether compound, as listed above, permits the addition to take place at room temperature or only slightly raised temperatures. In the absence of a catalyst, higher temperatures are required. However, the use of a catalyst is preferred so as to avoid formation of byproducts which accompanies the use of higher temperatures.

The type of unsaturated group in the hydrocarbon also influences the ease of addition and, therefore, the temperature required to effect the same. For example, terminal ethylenic groups, such as vinyl, vinylidene, and propargyl groups permit additions at lower temperatures than is the case with non-terminal ethylenic groups. Generally, in cases which require higher temperatures to effect the hydride addition, the same factors cause a corresponding increase in the temperature which will effect replacement of hydrocarbon groups from the metal atoms.

Also, as a general rule, the addition of boron hydride compounds requires a lower temperature than the corresponding addition of aluminum hydride compounds. For that reason, it is generally advantageous to effect the aluminum hydride compound addition prior to the addition of the boron hydride compound, lowering the temperature after the first addition, so that the temperature used in the aluminum addition will not cause displacement of the hydrocarbon groups in the boron compound. In the aforesaid preliminary step of aluminum addition, an excess of the hydrocarbon can be used to retard any formation of dialuminum compounds. This excess of hydrocarbon can be removed prior to the boron addition by the application of reduced pressure, or, if the presence of diboron products are not objectionable, an appropriate amount of the boron compound can be used to make the mixed boron-aluminum compound and an amount of diboron compound corresponding to the excess hydrocarbon compound used.

In cases where the boron compound is to be added first, a temperature will be selected for the aluminum compound addition that is below the temperature which will effect hydrocarbon displacement from the boron atom. In such cases, longer reaction times can be used to compensate when the selected temperature is lower than is used ordinarily for such aluminum addition.

In the absence of a catalyst, the addition of the aluminum compound can be effected easily at temperatures in the range of 90°-95° C. With ethers and other types of catalysts, the addition can be effected at temperatures of 70°-80° C. or even lower. Temperatures even below 50° C. can be used by using the catalyst indicated and longer reaction periods. It is preferred to keep the temperature below 100° C. to avoid displacement of the hydrocarbon groups from the aluminum.

With the boron compound, it is possible to effect the addition to the unsaturated hydrocarbon group at temperatures below 40° C. and with the catalysts indicated, it is possible to effect the addition at room temperature or at even lower temperatures. In some cases, temperatures above 50° C. may favor displacement of the hydrocarbon groups from the boron.

It is preferred for two reasons that the R' groups of the metal hydrides be small aliphatic groups. First, the use of smaller groups results in a higher proportion of metal in the resulting compounds. Secondly, the larger bulky groups retard somewhat the addition of the metal compounds to the unsaturated compounds, thereby necessitating more drastic reaction conditions and longer reaction periods. Therefore, methyl, ethyl, and propyl groups are preferred in place of the bulkier groups, such

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as phenyl, cyclohexyl, and aliphatic groups having groups attached to that carbon atom which will become attached to the metal atom, such as alpha, beta-dimethylpropyl, etc.

The new compounds of this invention are either liquids or solids. When it is desired to use the solid compounds of this invention in systems designed for high-energy liquid fuels, these compounds can be converted to liquids by dilution or dissolving in the simpler or lower melting compounds of this invention so as to avoid lowering the proportion of metal in the fuel compositions.

Various methods of practicing the invention are illustrated by the following examples. These examples are intended merely to illustrate the invention and not in any sense to limit the manner in which the invention can be practiced. The parts and percentages recited therein and all through this specification, unless specifically provided otherwise, refer to parts by weight and percentages by weight.

Example I

A reaction vessel equipped with stirrer, reflux condenser, and a gas inlet is flushed out with oxygen-free nitrogen and an atmosphere of nitrogen maintained therein. A solution of 250 parts of diethyl ether and 138 parts of vinyl dimethyl borane (prepared from dimethyl boron chloride and tetravinyl tin according to paper 69, page 26M, Abstract of Papers, 135th meeting American Chemical Society, April 5, 1959) (is added to the reaction vessel) and the mixture is cooled to 10° C. Symmetrical dimethyl diborane is fed into the reaction mixture at a rate such that 28 parts are absorbed over a period of approximately two hours, after which the reaction mixture is allowed to come to room temperature and the stirring continued for another six hours. The greater part of the ether is then removed by distillation at no more than 40° C. Then while the nitrogen atmosphere is still maintained in the system, the reaction product is transferred to distillation equipment provided with means for effecting distillation at reduced pressures. The pressure is reduced gradually to effect removal of the last traces of ether and unreacted reagents, leaving the desired product which is isolated in the boiling range of 35–75° C. at 0.1 to 0.5 mm. Product analysis shows 17.8 percent boron which is in good agreement with the theoretical value of bis-(dimethylboro-ethyl)-methyl borane,



Methane and ethane are given off upon decomposition of a sample of the product with water.

Example II

When the procedure of Example I is repeated using 176 parts of allyl dimethyl borane instead of vinyl dimethyl borane, there is obtained the corresponding derivative which is isolated in the range of 40°–82° C. at 0.1 to 0.6 mm. Product analysis shows 15.9 percent boron which is in good agreement with the theoretical value for bis-(dimethylboro-propyl)-methyl borane, $\text{CH}_3\text{B}[\text{CH}_2\text{CH}_2\text{CH}_2\text{B}(\text{CH}_3)_2]_2$. Methane and propane are given off when this compound is decomposed with water.

Example III

Using the procedure of Example I, 94 parts of diallyl methyl borane is reacted with 82 parts of tetramethyl diborane to give the same product as obtained in Example II. This example illustrates the alternate synthesis described hereinabove.

Example IV

The procedure of Example I is repeated using an equivalent weight of diglyme instead of ethyl ether, with 58 parts of ethyl aluminum dihydride and 100 parts of vinyl diethyl borane, and heating the mixture to 60°–70° C. There is isolated bis-(diethylboro-ethyl)-ethyl aluminum, $\text{C}_2\text{H}_5\text{Al}[\text{CH}_2\text{CH}_2\text{B}(\text{C}_2\text{H}_5)_2]_2$, which on analysis

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shows a total metal content of 19.58 percent, of which 10.78 percent is aluminum and 8.80 percent is boron, and which is in good agreement with the theoretical values for this compound. Ethane is released when this compound is decomposed with water.

Example V

The procedure of Example I is repeated using 70.8 parts of butyl boron dihydride and 200 parts of ethyl dimethyl aluminum. There is isolated a product whose analysis corresponds to $\text{C}_4\text{H}_9\text{B}[\text{CH}_2\text{CH}_2\text{CH}_2\text{Al}(\text{CH}_3)_2]_2$.

Example VI

The procedure of Example IV is repeated using 58 parts of ethyl aluminum dihydride and 200 parts of allyl dimethyl aluminum, to give a product which on analysis shows an aluminum content of 31.85 percent and which checks closely to the theoretical value for the compound of the structure $\text{C}_2\text{H}_5\text{Al}[\text{CH}_2\text{CH}_2\text{CH}_2\text{Al}(\text{CH}_3)_2]_2$.

Example VII

In an apparatus similar to that used in Example I, there is added 250 parts of diglyme, 86 parts of tetramethyl diborane, and the mixture cooled to 0° C. There is then introduced 160 parts of butadiene, stirring is continued for half an hour, and the mixture is then heated to 60° C. for 2 hours. The reaction mixture is next cooled to room temperature and the excess butadiene removed by heating to 40° C., after which the mixture is cooled again to 0° C. and there is introduced 28.5 parts of symmetrical dimethyl diborane. The reaction mixture is processed as in the preceding examples and there is isolated a product having 15.88 percent boron, which is in good agreement with a compound of the formula



Example VIII

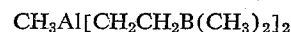
The procedure of Example VII is repeated except that 45 parts of dimethyl dialuane is used instead of dimethyl diborane and there is isolated a compound of the formula $\text{CH}_3\text{Al}[\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{B}(\text{CH}_3)_2]_2$.

Example IX

The procedure of Example VIII is repeated except that 78 parts of acetylene is used instead of the butadiene and there is isolated $\text{CH}_3\text{B}[\text{CH}_2\text{CH}_2\text{B}(\text{CH}_3)_2]_2$.

Example X

A reaction vessel equipped with stirrer, reflux condenser, and a gas inlet is flushed out with oxygen-free nitrogen and an atmosphere of nitrogen maintained therein. A solution of 250 parts of diglyme and 96 parts of divinyl monomethyl aluminum is added to the reaction vessel and cooled to 0° C. Symmetrical tetramethyl diborane is fed into the reaction at such a rate that 90 parts are absorbed over a period of approximately two hours, after which the reaction mixture is allowed to come to room temperature and then heated at 60°–75° C. for an additional two to three hours. The diglyme is removed by distillation under reduced pressure at a temperature not to exceed 75° C. The pressure is then reduced gradually to effect removal of the last traces of ether and unreacted reagents, leaving the desired product which can be isolated in the boiling range of 30°–80° C. at 0.1 to 0.6 mm. Product analysis shows 15.05 percent aluminum and 12 percent boron, which values are in good agreement with the theoretical values for



Methane and ethane are given off on decomposition with water.

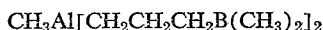
Example XI

The procedure of Example X is repeated using 44 parts of dimethyl dialuane, $(\text{CH}_3\text{AlH}_2)_2$, and 140 parts of di-

methyl vinyl borane to produce the same product as in Example X.

Example XII

The procedure of Example X is repeated using 120 parts of diallyl methyl aluminum instead of the divinyl derivative and there is obtained



which on analysis shows 13.0 percent aluminum and 10.2 percent boron, which values are in good agreement with the theoretical values for this compound. Methane and propane are given off on decomposition of the product with water.

Example XIII

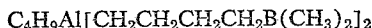
The procedure of Example X is repeated using 134 parts of diallyl ethyl aluminum and 150 parts of tetraethyl diborane $[(\text{C}_2\text{H}_5)_2\text{BH}]_2$ to give



which on analysis shows 10.2 percent aluminum and 8.2 percent boron, which values are in close agreement with the theoretical values for the compound.

Example XIV

In an apparatus similar to that used in Example X there is introduced 250 parts of diglyme, 86 parts of tetramethyl diborane, and the mixture cooled to 0° C. There is then introduced 150 parts of butadiene and the mixture heated to 40° C. for 2 hours, after which the excess butadiene is allowed to escape. The reaction mixture is cooled to 0° C. and there is then introduced 86 parts of n-butyl-aluminum dihydride and the mixture heated to 60° C. for two hours. The product is isolated as in Example X. Product analysis and the liberation of methane and butane on decomposition with water indicates that the compound is

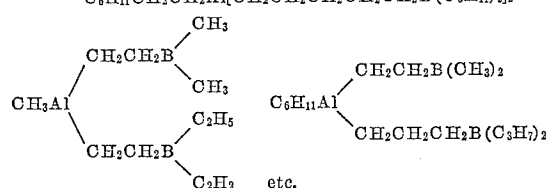
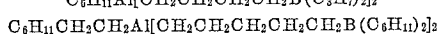
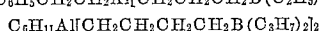
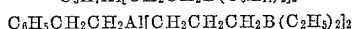
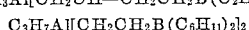
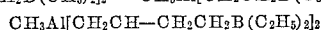
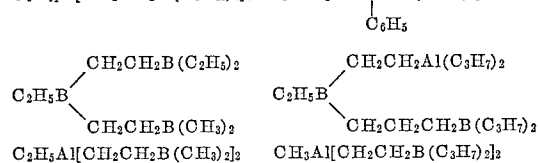
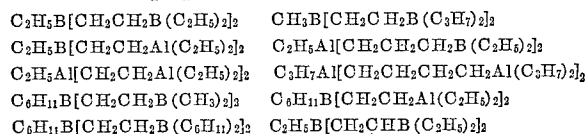


Example XV

The procedure of Example XIV is repeated using 78 parts of acetylene instead of butadiene and there is obtained



Using the procedure of the foregoing examples or appropriate modifications thereof with appropriate unsaturated compounds and appropriate metal hydrides, the following compounds typical of the compounds of this invention are prepared:



It is also possible to use mixtures of the various types of reagents indicated above. For example, in the above reaction I, the monoalkenyl reagent can comprise a mixture of two or more monoalkenyl compounds in which the alkenyl radical, the metal atom, or the R' group, can each or all be different. As an illustration, a mixture of dimethyl vinyl borane and dimethyl vinyl aluane can be reacted with symmetrical dimethyl diborane to give a mixture of products in which the compounds contain 3 atoms of boron, 2 atoms of boron and 1 atom of aluminum, and 1 atom of boron and 2 atoms of aluminum respectively. The proportions of each compound in the product mixture and the relative proportions of metal atoms therein depend on the concentrations and the relative reactivities of the various reagents.

Another illustration is to react a mixture of dimethyl vinyl borane and dimethyl allyl borane with symmetrical dimethyl diborane. Another variation is to react symmetrical dimethyl dialuane with dimethyl vinyl borane and dimethyl allyl aluane. It is also possible to use mixtures of the metal hydrides, for example reacting a mixture of symmetrical dimethyl diborane and symmetrical dimethyl dialuane with dimethyl vinyl borane, diethyl allyl aluane, etc.

In the above reaction II, it is also possible to use various mixtures of reagents, for example divinyl methyl borane can be reacted with a mixture of tetramethyl diborane and tetramethyl dialuane to give a mixture of products varying in the number of the different types of metal atoms therein. The hydrocarbon groups on the various metal reagents can also differ either in the same compound or in the different compounds of the mixture. Likewise, a mixture of the dialkenyl metal compound also can be used. For example, two or more of the dialkenyl metal compounds containing the same or different metal atoms therein can be reacted with one or more of the disubstituted metal hydrides. For example, a mixture of divinyl methyl borane and diallyl ethyl aluane can be reacted with tetramethyl diborane or tetramethyl dialuane, or a mixture of the substituted hydrides.

In some cases, particularly where the compositions are to be used for fuel purposes, the product mixtures can be used directly without separation of the various compounds. In other cases, the various substituent compounds can be separated by frictional distillation and reduced pressures. The ease of such separation depends on the comparative sizes of the various substituent groups in the compound and resultant differences in boiling points of these products.

As indicated above, the compounds of this invention are particularly useful as high-energy fuels. The liquid products of this invention can be used as such in rocket and missile systems as presently designed for use of liquid fuels. The solid products of this invention can be dissolved in the simpler liquid compounds of this invention so as to give liquid compositions suitable for use in liquid fuel systems, and thereby do not suffer a decrease in energy content by virtue of the solvent used. These compounds can be used, also, for various other purposes, such as additives to improve the characteristics of conventional motor fuels, such as gasoline, jet engine fuels, etc. The methods of using these materials for such purposes employ the conventional methods now used.

While certain features of this invention have been described in detail with respect to various embodiments thereof, it will, of course, be apparent that other modifications may be made within the spirit and scope of this invention and it is not intended to limit the invention to the exact details shown above except insofar as they are defined in the following claims.

The invention claimed is:

1. A chemical compound having the formula



wherein M is a metal selected from the class consisting

of boron and aluminum, R is a radical selected from the class consisting of hydrogen, monovalent hydrocarbon groups having no more than 8 carbon atoms, and hydrocarbon groups having no more than 8 carbon atoms and having substituted thereon at least one MR'_2 group, the number of MR'_2 groups in said compound totaling no more than 10, R' is a monovalent hydrocarbon group of no more than 8 carbon atoms, and m is an integer having a value of at least 1 and no more than 8.

2. Methyl-bis-(beta-dimethylboro-ethyl)-borane.

3. Methyl-bis-(3-dimethylboro-propyl)-borane.

4. Ethyl-bis-(beta-diethylboro-ethyl)-borane.

5. Butyl-bis-(3-dimethylalumino-propyl)-borane.

6. Ethyl-bis-(3-dimethylalumino-propyl)-aluane.

7. Methyl-bis-(4-dimethylboro-butyl)-borane.

8. Methyl-bis-(4-dimethylboro-butyl)-aluane.

9. Methyl-bis-(beta-dimethylboro-ethyl)-aluane.

10. Methyl-bis-(3-dimethylboro-propyl)-aluane.

11. Ethyl-bis-(3-diethylboro-propyl)-aluane.

12. Butyl-bis-(4-dimethylboro-butyl)-aluane.

13. A process for the preparation of a compound consisting of hydrocarbon groups and at least 3 atoms of metal selected from the class consisting of boron and aluminum, comprising the step of reacting a mixture of reagents selected from the class consisting of (1) a monosubstituted metal hydride having the formula $R'MH_2$ with a metal compound having the formula



and (2) a disubstituted metal hydride having the formula R'_2MH with a metal-containing compound having the formula $R'M[(CR_2)_{m-1}CR=CR_2]_2$, in which formulas M is a metal selected from the class consisting of boron and aluminum, R is a radical selected from the class consisting of hydrogen, monovalent hydrocarbon groups having no more than 8 carbon atoms, and monovalent hydrocarbon groups having no more than 8 carbon atoms and having substituted thereon at least one MR'_2 group, the number of MR'_2 groups in said compound totaling no more than 10, R' is a monovalent hydrocarbon group of no more than 8 carbon atoms, and m is an integer having a value of at least 1 and no more than 8, at a temperature which effects such reaction without substantial displacement of said R' groups.

14. A process of claim 13, in which said reaction is catalyzed by a compound having at least one C—O—C structure therein and the remainder of said compound consisting of radicals selected from the group consisting of hydrocarbon groups and no more than one atom se-

lected from the class consisting of boron and aluminum atoms.

15. A process of claim 13, in which said reaction is catalyzed by a compound having a formula selected from the group consisting of $B(OR'')_3$ and $Al(OR'')_3$ in which at least one R'' is a monovalent hydrocarbon group and the remaining R'' groups are selected from the class consisting of hydrogen and monovalent hydrocarbon groups.

16. A process of claim 13 in which said reaction is the reaction of a mono-substituted metal hydride having the formula $R'MH_2$ with a metal compound having the formula $CR_2=CR(CR_2)_{m-1}MR'_2$.

17. A process of claim 13, in which said reaction is the reaction of a disubstituted metal hydride having the formula R'_2MH with a metal-containing compound having the formula $R'M[(CR_2)_{m-1}CR=CR_2]_2$.

18. A process for the preparation of a compound consisting of hydrocarbon groups and boron atoms, comprising the reaction of vinyl dimethyl borane with symmetrical dimethyl diborane, at a temperature which effects such reaction without substantial displacement of said methyl groups.

19. A process for the preparation of a compound consisting of hydrocarbon groups and aluminum and boron atoms, comprising the step of reacting divinyl methyl aluminum with tetramethyl diborane at a temperature which effects such reaction without substantial displacement of said methyl groups.

20. A process for the preparation of a compound consisting of hydrocarbon groups and aluminum atoms, comprising the step of reacting symmetrical dimethyl dialuane with vinyl dimethyl aluane, at a temperature which effects such reaction without substantial displacement of methyl groups.

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