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PHOSPHINE BORINES AND THEIR PREPARATION

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This invention relates in general to phosphine borines and more particularly to phosphine borine compounds formed from various borines and various difunctional phosphines; these phosphine borines may be added to gasoline which may contain tetraethyl lead (TEL) and which will probably contain ethylene dichloride and dibromide (in the case of automotive fuels) and ethylene dibromide alone (in the case of aviation fuels), the phosphine borines serving to reduce preignition of gasoline used as a motor fuel.

It is an object of this invention to provide for the preparation of certain phosphine borines which are particularly useful as preignition additives for gasoline; that is, the new compounds to which this invention is directed serve to reduce preignition of gasoline.

Ancillary objects and advantages of this invention, if not specifically set forth, will become apparent during the course of the description which follows.

Broadly, this invention concerns phosphine borines of the general formula $R'_3B{:}PR_2R''R_2P{:}BR'_3$, where each R' may be the same or different and represents H or lower alkyl, each R' may be the same or different and represents F, Br, Cl, lower alkyl (1–6 carbons) or H, and R'' is a lower alkylene group.

These materials may be added to leaded or unleaded gasoline and serve as excellent preignition additives, especially when the said gasoline contains TEL or a similar metal-containing anti-detonant such as methylcyclopentadienyl manganese tricarbonyl, as set forth in greater detail in our co-pending application Serial No. 796,223, filed even date herewith.

When the phosphine borines of this invention are added to motor fuel, the resulting motor fuel is found to have a low preignition index and a high resistance to detonation knocking. Another effect of the use of these phosphine borines is to decrease the tendency of gasoline containing TEL to raise the octane requirement of the engine in which the gasoline is used. A further advantage of these phosphine borines as gasoline additives is that such phosphine borines are highly resistant to hydrolysis, as a result of which they have little tendency to be "leached" from the fuel by the action of such free water as may be present.

In this respect, the phosphine borines as a class are decidedly advantageous as compared with most other boron-containing gasoline additives which are highly vulnerable to hydrolysis. A further desirable feature of such phosphine borines is that they are liquids or low-melting solids amply soluble in hydrocarbons. These properties are important in gasoline additives since additives which have high-melting points or low solubilities have a strong tendency to precipitate and form solid deposits when the fuel mixture is vaporized in the carburetor. Such deposits cause malfunctioning of the engine in addition to defeating the purpose of feeding the additive into the combustion chamber. Liquids are also desirable from a material-handling standpoint, since they may be blended conveniently with liquid fuels.

The phosphine borines of the present invention, while highly soluble in hydrocarbons, are relatively insoluble in water; this tends to maintain quantitative requirements at low levels since there is essentially no loss by extraction.

Finally, the fact that halogen may here be introduced in the form of the phosphine borine compound permits a reduction in the amount of ethylene dihalide normally required in leaded gasoline; this enables a reduction in costs by providing means for simultaneously controlling ignition and scavenging lead with a single additive.

Such a phosphine borine, when used as a preignition additive for gasoline, combines the known beneficial effects of both boron and phosphorus in a single molecule of relatively small size and low molecular weight, but, unexpectedly, small amounts of the phosphine borines are found superior to mixtures of individual commercially-available preignition additives containing phosphorus on the one hand and boron on the other. Further, these phosphine borines are relatively non-reactive and resist decomposition, even at relatively high temperatures.

The range of effective concentrations for these materials and details of their effects upon gasoline will not be further described here, as this information is set out in the afore-mentioned co-pending application.

A general preparative method for these new compounds is as follows: The difunctional phosphine and the boron compound (either diborane or a substituted borine) are introduced into the reaction vessel consecutively. The order of addition does not affect the final product; the choice of which compound is first introduced is dictated by the convenience of handling each of the reagents. If one or both of the reagents is reasonably volatile, the exothermic addition reaction is run under reflux or with external cooling or both to prevent loss of the reagents. For simplicity, the reaction temperature is adjusted to maintain a liquid reaction mixture throughout the synthesis, sometimes requiring external heating. If the product or reactants are thermally unstable at the melting point of the mixture, the synthesis is most conveniently carried out in an inert solvent. Hydrocarbons are the preferred solvent media. The stoichiometry of the reaction calls for 2 moles of the borine for each mole of the difunctional phosphine.

A large number of difunctional phosphines are known; see, for example, co-pending application Serial No. 695,241, filed November 8, 1957, for Phosphines.

The preparation of various boron-containing precursors is described in the literature; see, for example, M. L. Lappert, Organic Compounds of Boron, Chem. Rev., 56, 959 (1956).

Preparation of the various of the boron compounds which may be used in preparing materials of this invention is also set forth in application Serial No. 707,124, filed January 6, 1958 for Organoboron Compounds and application Serial No. 720,067, filed March 10, 1958 for Preparation of Dihaloborines. Still another disclosure of the preparation of these borines is that in application Serial No. 745,248, filed June 30, 1958 for Alkyldihaloborines.

The preparation of various other possible reactants, compounds of the formula $ArBX_2$, where Ar is an aryl group, is set forth in co-pending application Serial No. 787,106, filed January 16, 1959, for Preparation of Aryldihaloboranes and Poly(dihaloborane)benzenes.

Specific examples are set forth below showing the preparation of the materials of this invention, but these are for illustrative purposes only and are not to be interpreted as imposing limitations on the scope of the invention other than as set forth in the appended claims.

Example 1. Preparation of 1,3-trimethylene-P,P'-bis-(methylphosphine borine).—Into a nitrogen-swept, 250

ml. round-bottom flask containing 29.2 g. (0.214 mole) of 1,3-bis(methylphosphino)propane maintained at 10° C., was added a mixture of diborane and nitrogen. The addition of diborane was stopped when it appeared in the exit gas which passed through a mercury bubbler into a Bunsen burner flame. Excess diborane was then removed by degassing the phosphine borine adduct under high vacuum at room temperature.

1,3-trimethylene-P,P'-bis(methylphosphine borine) is a colorless solid melting at 28–30° C. The liquid form supercools easily and is metastable at room temperature for long periods of time. The supercooled liquid has the following physical properties: density, 0.895 g./ml. at 25° C.; refractive index, n_D^{25} 1.5215; miscible with acetone and benzene, soluble in petroleum ether (65–110° C.) 0.15 g./100 g. at 25° C. Vapor tensions in the range 0.5–3.0 mm. determine the equation

$$\log_{10}P\text{mm.} = 5.494 - 2118/T$$

from which the normal boiling point is calculated to be 537° C. At temperatures above 150° C. (ca. 3.3 mm. vapor pressure) the compound decomposes with loss of hydrogen.

Example 2. Preparation of 1,3-trimethylene-P,P'-bis-(phosphine borine).—Into a nitrogen-swept, 250 ml. round-bottom flask containing 26.3 g. (0.243 mole) of 1,3-bis(phosphino)propane intermittently cooled in an ice bath, was added a mixture of diborane and nitrogen. The addition of diborane was stopped when it appeared in the exit gas which passed through a mercury bubbler into a Bunsen burner flame. Excess diborane was then removed by degassing the phosphine borine adduct under high vacuum at room temperature.

1,3-trimethylene-P,P'-bis(phosphine borine) is a colorless solid melting at 55–56° C. The solid is soluble in petroleum ether (65–110° C.) 4.7 g./liter at 25° C. and has vapor tensions in the range 0.5–3.0 mm. determining the equation $\log_{10}P\text{mm.} = 14.49 - 5235/T$ from which the normal boiling point is calculated to be 182° C. At temperatures above 100° C. (ca. 3.6 mm. vapor pressure) the compound decomposes with loss of hydrogen.

Following the method set forth above, various other materials may be prepared; see the table below.

Difunctional Phosphine	Borine	Phosphine Borine Product
$(CH_2)_2(PHCH_3)_2$	B_2H_6	$(CH_2)_2(HCH_3P:BH_3)_2$
$(CH_2)_4(PHCH_3)_2$	B_2H_6	$(CH_2)_4(HCH_3P:BH_3)_2$
$(CH_2)_2(PH_2)_2$	B_2H_6	$(CH_2)_2(H_2P:BH_3)_2$
$(CH_2)_4(PH_2)_2$	B_2H_6	$(CH_2)_4(H_2P:BH_3)_2$
$(CH_2)_2[P(CH_3)_2]_2$	B_2H_6	$(CH_2)_2[(CH_3)_2P:BH_3]_2$
$(CH_2)_3[P(CH_3)_2]_2$	B_2H_6	$(CH_2)_3[(CH_3)_2P:BH_3]_2$
$(CH_2)_4[P(CH_3)_2]_2$	B_2H_6	$(CH_2)_4[(CH_3)_2P:BH_3]_2$
$(CH_2)_5[P(CH_3)_2]_2$	B_2H_6	$(CH_2)_5[(CH_3)_2P:BH_3]_2$
$(CH_2)_3[P(C_2H_5)CH_3]_2$	B_2H_6	$(CH_2)_3[CH_3(C_2H_5)P:BH_3]_2$
$(CH_2)_2[P(C_2H_5)_2]_2$	B_2H_6	$(CH_2)_2[(C_2H_5)_2P:BH_3]_2$
$(CH_2)_3[P(C_2H_5)_2]_2$	B_2H_6	$(CH_2)_3[(C_2H_5)_2P:BH_3]_2$
$(CH_2)_4[P(C_2H_5)_2]_2$	B_2H_6	$(CH_2)_4[(C_2H_5)_2P:BH_3]_2$
$(CH_2)_4[P(i\text{-}C_3H_7)_2]_2$	B_2H_6	$(CH_2)_4[(i\text{-}C_3H_7)_2P:BH_3]_2$
$(CH_2)_2[P(n\text{-}C_4H_9)_2]_2$	B_2H_6	$(CH_2)_2[(n\text{-}C_4H_9)_2P:BH_3]_2$
$(CH_2)_4[P(n\text{-}C_8H_{17})_2]_2$	B_2H_6	$(CH_2)_4[(n\text{-}C_8H_{17})_2P:BH_3]_2$
$PH(CH_3)(CH_2)_3(C_2H_5)HP$	B_2H_6	$H_3B:PH(CH_3)(CH_2)_3(C_2H_5)HP:BH_3$
$(CH_2)_2[P(CH_3)_2]_2$	$B(CH_3)_3$	$(CH_2)_2[(CH_3)_2P:B(CH_3)_3]_2$
$(CH_2)_4[P(CH_3)_2]_2$	$B(CH_3)_3$	$(CH_2)_4[(CH_3)_2P:B(CH_3)_3]_2$
$(CH_2)_2[P(C_2H_5)_2]_2$	$B(C_2H_5)_3$	$(CH_2)_2[(C_2H_5)_2P:B(C_2H_5)_3]_2$
$(CH_2)_4[P(C_2H_5)_2]_2$	$B(C_2H_5)_3$	$(CH_2)_4[(C_2H_5)_2P:B(C_2H_5)_3]_2$
$(CH_2)_2[P(C_2H_5)_2]_2$	$B(CH_3)_3$	$(CH_2)_2[(C_2H_5)_2P:B(CH_3)_3]_2$
$(CH_2)_4[P(C_2H_5)_2]_2$	$B(CH_3)_3$	$(CH_2)_4[(C_2H_5)_2P:B(CH_3)_3]_2$
$(CH_2)_2[P(CH_3)_2]_2$	BCl_3	$(CH_2)_2[(CH_3)_2P:BCl_3]_2$
$(CH_2)_2[P(CH_3)_2]_2$	BBr_3	$(CH_2)_2[(CH_3)_2P:BBr_3]_2$
$(CH_2)_3(PHCH_3)_2$	BCl_3	$(CH_2)_3(HCH_3P:BCl_3)_2$
$(CH_2)_4(PHCH_3)_2$	BF_3	$(CH_2)_4(HCH_3P:BF_3)_2$
$(CH_2)_3[P(CH_3)_2]_2$	BCl_2CH_3	$(CH_2)_3[(CH_3)_2P:BCl_2CH_3]_2$
$(CH_2)_2[P(CH_3)_2]_2$	$B(n\text{-}C_4H_9)_3$	$(CH_2)_2[(CH_3)_2P:B(n\text{-}C_4H_9)_3]_2$

As aforementioned, a test for preignition has been devised and the new compounds of this invention have been compared with other closely related compounds, as a result of which the superiority of these compounds has been made apparent. Briefly, this test involves measuring the number of instances per unit time of motor operation in which flames occur in the combustion chamber prior to the time at which the normal flame produced by the spark occurs, in general following the procedure described by Hirschler, McCullough and Hall, SAE Trans 62 40 (1954). Efficiency of the preignition additive can be measured by the preignition index which is a percentage of such abnormal flames occurring in the additive-containing test gasoline as compared with the base fuel, i.e., the same TEL-containing gasoline which has not been treated with the preignition additive.

Obviously, many modifications and variations of this invention may be made without departing from the spirit and scope thereof and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. Compounds of the general formula

$$R'_3B:PR_2R''R_2P:BR'_3$$

where R'' is a lower alkylene group, each R' is selected from the class consisting of F, Br, Cl, H and lower alkyl, and each R is selected from the class consisting of H and lower alkyl.

2. The compound of claim 1 wherein one R is H, one R is lower alkyl and each R' is H.

3. The compound of claim 1 wherein one R is H, one R is lower alkyl and each R' is lower alkyl.

4. The compound of claim 1 wherein each R is H.

5. The compound $CH_2(CH_2PHCH_3:BH_3)_2$.

6. The compound $CH_2(CH_2PH_2:BH_3)_2$.

7. The compound $CH_2[CH_2P(CH_3)_2:BH_3]_2$.

8. Compounds of the general formula

$$H_3B:PR_2(CH_2)_2R_2P:BH_3$$

where each R is lower alkyl.

9. Compounds of the general formula

$$H_3B:PR_2(CH_2)_4R_2P:BH_3$$

where each R is lower alkyl.

10. Compounds of the general formula

$$R'_3B:PR_2(CH_2)_4R_2P:BR'_3$$

wherein each R is lower alkyl and each R' is lower alkyl.

11. Compounds of the general formula

$$R'_3B:PR_2(CH_2)_2R_2P:BR'_3$$

wherein each R is lower alkyl and each R' is lower alkyl.

12. Compounds of the general formula

$$Br_3B:PR_2R''R_2P:BBr_3$$

where R'' is a lower alkylene group and each R is selected from the class consisting of H and lower alkyl.

13. Compounds of the general formula

$$Br_3B:PR_2(CH_2)_2R_2P:BBr_3$$

where each R is selected from the class consisting of H and lower alkyl.

14. Compounds of the general formula

$$Cl_3B{:}PR_2R''R_2P{:}BCl_3$$

where R'' is a lower alkylene group and each R is selected from the class consisting of H and lower alkyl.

15. Compounds of the general formula

$$Cl_3B{:}PR_2(CH_2)_2R_2P{:}BCl_3$$

where each R is selected from the class consisting of H and lower alkyl.

16. The compound $(CH_2)_2[(CH_3)_2P{:}BCl_3]_2$.

17. The compound $(CH_2)_2[(CH_3)_2P{:}BBr_3]_2$.

No references cited.