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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 borines formed from various phosphines and various difunctional borines; these phosphine borines may be added to gasoline which may contain tetraethyl lead (TEL), 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 gasolines.

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

Broadly, this invention concerns phosphine borines of the general formula $R_3P{:}BX_2R'X_2B{:}PR_3$ where each X represents F, Br or Cl, each R may be the same or different and represents H or lower alkyl (1–8 carbons) and R′ represents a lower alkylene group.

These materials may be added to gasoline and serve as excellent preignition additives when the said gasoline contains TEL or similar metal-containing anti-detonants such as methyl-cyclopentadienyl 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 the presence of TEL in gasoline 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 readily soluble in hydrocarbons, are relatively insoluble in water and this also 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 superior to mixtures of individual commercially available preignition additives containing phosphorus on the one hand and boron on the other. Further, the 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 effectiveness 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 compounds is as follows: A difunctional borine, the bis(dihaloborino)-alkane, is placed in a suitable reaction vessel and to this is added incrementally an equimolar quantity of the primary, secondary or tertiary phosphine to be reacted therewith. The reaction vessel initially is held at a sufficiently low temperature, as in a bath of liquid nitrogen or in a Dry Ice bath, that little or no reaction takes place. On warming after each incremental addition, the heat evolved by the exothermic reaction is dissipated and the reaction is controlled. The reverse addition may be used but is somewhat less convenient. The stoichiometry of the reaction calls for 2 moles of the phosphine material for each mole of the difunctional borine.

A large number of primary, secondary and tertiary phosphines are known; see, for example, Kosolapoff, Organophosphorus Compounds, John Wiley & Sons, Inc., New York, 1950, 30–37. Preparation of the various boron-containing precursors is described in the co-pending application of David R. Stern and Lahmer Lynds, Serial No. 707,124, filed January 6, 1958, entitled, Organoboron Compounds.

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

Example.—A quantity of bis(dibromoborino)ethane, $C_2H_4(BBr_2)_2$, was obtained by the process set forth in the afore-mentioned co-pending application and 66.870 g. thereof (0.181 mole) were placed in a 250 ml. round-bottom flask which had previously been flushed with nitrogen. The flask was held in a Dry Ice bath and 27.541 g. (0.362 mole) trimethylphosphine run incrementally into the flask. As the reaction proceeded, the temperature increased. The addition compound

$$[(CH_3)_3P{:}BBr_2CH_2—]_2$$

was obtained in good yield.

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

Phosphine	Bis(dihaloborino)alkane	Phosphine Borine Product
$(C_2H_5)_3P$	$C_2H_4(BCl_2)_2$	$[(C_2H_5)_3P{:}BCl_2CH_2—]_2$
$(CH_3)_3P$	$C_4H_8(BCl_2)_2$	$[(CH_3)_3P{:}BCl_2CH_2CH_2—]_2$
$(CH_3)_2HP$	$C_2H_4(BCl_2)_2$	$[(CH_3)_2HP{:}BCl_2CH_2—]_2$
$(CH_3)H_2P$	$C_2H_4(BBr_2)_2$	$[(CH_3)H_2P{:}BBr_2CH_2—]_2$
H_3P	$C_2H_4(BBr_2)_2$	$(H_3P{:}BBr_2CH_2—)_2$
$(C_4H_9)_3P$	$C_2H_4(BBr_2)_2$	$[(C_4H_9)_3P{:}BBr_2CH_2—]_2$
$(C_2H_5)_3P$	$C_3H_6(BCl_2)_2$	$[(C_2H_5)_3P{:}BCl_2CH_2—]_2CH_2$
$(CH_3)_3P$	$C_2H_4(BF_2)_2$	$[(CH_3)_3P{:}BF_2CH_2—]_2$

As afore-mentioned, 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 flames in a given cycle, which flames occur in the combustion chamber prior to the time at which the normal flame produced by the spark occurs. Efficiency of the preignition additive can be measured by the preignition index which is a percentage of such abnormal flames occuring 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 only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. Compounds of the general formula

$$R_3P{:}BX_2R'X_2B{:}PR_3$$

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

2. The compound $[(CH_3)_3P{:}BBr_2CH_2—]_2$.
3. The compound $[(C_2H_5)_3P{:}BCl_2CH_2—]_2$.
4. The compound $[(CH_3)_3P{:}BCl_2CH_2CH_2—]_2$.
5. The compound $[(CH_3)_2HP{:}BCl_2CH_2—]_2$.
6. The compound $[(CH_3)H_2P{:}BBr_2CH_2—]_2$.
7. The compound $(H_3P{:}BBr_2CH_2—)_2$.
8. The compound $[(C_4H_9)_3P{:}BBr_2CH_2—]_2$.
9. The compound $[(C_2H_5)_3P{:}BCl_2CH_2—]_2CH_2$.
10. Compounds of the general formula

$$R_3P{:}BX_2R'X_2B{:}PR_3$$

where each R is lower alkyl, X is halogen and R' is a lower alkylene group.

11. Compounds of the general formula

$$H_3P{:}BX_2R'X_2B{:}PH_3$$

where each X is halogen and R' is a lower alkylene group.

12. Compounds of the general formula

$$(CH_3)_3P{:}BX_2R'X_2B{:}P(CH_3)_3$$

where each X is halogen and R' is a lower alkylene group.

13. Compounds of the general formula

$$(C_2H_5)_3P{:}BX_2R'X_2B{:}P(C_2H_5)_3$$

where each X is halogen and R' is a lower alkylene group.

14. Compounds of the general formula

$$R_3P{:}BX_2C_2H_4X_2B{:}PR_3$$

where each R is selected from the group consisting of H and lower alkyl and X is halogen.

15. Compounds of the general formula

$$R_3P{:}BCl_2R'Cl_2B{:}PR_3$$

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

16. Compounds of the general formula

$$R_3P{:}BBr_2R'Br_2B{:}PR_3$$

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

No references cited.