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MOTOR FUELS

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This invention relates to motor fuels and methods of making the same, and more particularly to motor fuels containing metal organo compounds to improve their properties.

In more recent years, motor fuels containing tetraethyl lead have become widely used. More recently, the production of metallic organo derivatives within the motor fuel, in situ, have been developed eliminating the hazards and expense of the prior methods of making tetraethyl lead extraneously of the fuel, and also yielding motor fuels of pronouncedly improved characteristics.

Among the objects of the present invention is the production of motor fuels which contain novel types of metallo organo derivatives, widely departing from the metallo aryls and alkyls of the prior art, and giving to such products as motor fuels, not only improved characteristics but new properties.

Still further objects and advantages will appear from the more detailed description set forth below, it being understood, however, that such more detailed description is given by way of illustration and explanation only, and not by way of limitation, since various changes therein may be made by those skilled in the art, without departing from the scope and spirit of the present invention.

This application is a continuation-in-part of application Serial No. 236,785, filed October 24, 1938, entitled Metallo organo derivatives.

In accordance with the present invention, metallo organo compounds are produced in which the organic radicle contains an unsaturated linkage, such as the olefinic —C= C— , or the acetylenic $\text{—C}\equiv\text{C—}$, the organic radicles containing such groups being of any desired character, such as aliphatic or acyclic, aromatic or isocyclic, heterocyclic, etc., aliphatics being preferred, and the metallo component being any desired heavy metal, but preferably one of the metals and non-metals of accepted use for antidetonants in motor fuels, such as lead, tin, antimony, zinc, phosphorus, silicon, arsenic, mercury and thallium, etc.

In producing these modified motor fuels, for example, various methods are available, but the simplest is that in which the metallo aryl or alkyl, is reacted with the desired unsaturated compound under conditions wherein the unsaturated compound forms a radicle containing the olefinic or acetylenic linkage, and the latter replaces the saturated alkyl or aryl group of the original metallo organo compound, producing new types of metallo organics. Where the unsaturated re-

actant is a gas like ethylene, propylene or acetylene, a current of said gas may be passed through the liquid metallo organo or a solution of the metallo aryl or alkyl, either in a solvent therefor or in a suspension thereof. Where the unsaturate is a liquid or solid, such as cyclopentadiene, for example, the liquid or solid may be added to the solution containing the metallo alkyl or aryl, or the latter may be dissolved in the liquid unsaturate. The reactions involving the gaseous unsaturates, such as ethylene, propylene and acetylene, may be carried out at ordinary room temperatures and pressures, the gases being well dried to remove any moisture. Higher temperatures and superatmospheric pressures may be used, particularly where unsaturated liquids are being treated; while even low temperatures and subatmospheric pressures may be used.

The process will be exemplified by the treatment of lead tetraethyl and Grignards, such as ethyl magnesium chloride (or other halide), with the gaseous unsaturates, it being understood that such illustrative reactions are exemplary of the use of other types of metallo organics.

Thus, a well dried current of acetylene is passed through the ethereal solution of ethyl magnesium bromide (prepared in the usual way) at ordinary temperatures, until the extent of reaction desired has taken place. The maximum conversion is reached after about twenty-four hours. The acetylenic magnesium bromide is produced together with ethane. The Grignard may be recovered and used for organic synthesis, or it may be added to motor fuel. It may be converted into any of the other metallo acetylenic derivatives by double decomposition in the usual way. See Patent No. 2,012,356, page 3, lines 3-25. Thus lead acetylenic derivatives may be produced and added to motor fuels. If only partial conversion into other metallo derivatives is carried out, mixed metallo derivatives are obtained.

Or the lead tetraethyl in solution in any desired solvent is treated with a current of well dried acetylene at ordinary temperatures. The lead acetylenic derivative is formed together with ethane.

Similarly zinc diethyl may be treated with acetylene to give the corresponding zinc acetylene derivative, ethane being formed at the same time.

In an analogous way the olefinic derivatives may be produced of the Grignards, of lead, zinc, tin, etc., and utilized in motor fuels or other hydrocarbon fractions and distillates.

To exemplify the production of an olefinic metallic derivative, a liquid olefine will suffice.

One molecular weight of ethyl magnesium bromide is prepared in the usual way. Cyclopentadiene (1.3) is maintained at the boiling point, and the ethyl magnesium bromide introduced. The reaction takes about 12 hours for completion. Cyclopentadienyl magnesium bromide is formed together with ethane. If in lieu of using an ethereal solution of the ethyl magnesium bromide, part of the ether is distilled off and replaced by benzol (desirably free from thiophene), the reaction is more rapid, being completed in 5 or 6 hours at 60° C. The process can be further improved by using ligroin (boiling 60 to 80° C.) as the medium, and dissolving the cyclopentadiene therein and reacting with the Grignard. Even though the latter is not soluble in the ligroin, by the use of agitation, the reaction is very rapid, and is completed in 3 hours at temperatures of 45 to 50° C.

Other unsaturated compounds, such as indene and fluorene, may be used to give corresponding Grignard type reaction products. Or as pointed out above, the metallo alkyls, for example, may be similarly treated with these various olefinic materials to give corresponding metallo olefinic compounds.

Many of these metallo derivatives are new compounds including, for example, the lead acetylenic and olefinic derivatives, the Grignard olefinic derivatives of ethylene and propylene, etc. They are desirably used herein in motor fuels, but may be used in organic syntheses of far reaching importance.

While the preparation of these metallo organics has been illustrated above in the production of individual organic compounds, complex mixtures of metallo derivatives are produced and at the same time hydrocarbons are formed, which latter may be left in the complex or separated therefrom depending on the use to which the material is put. Where the hydrocarbons are of such type as to be desirably present in a motor fuel such as gasoline, they may be retained in the complex. Such complex organo derivatives of the metal when treated with the unsaturate yield lead derivatives of the unsaturate, such as lead ethylenic or lead propylenic or lead acetylenic, etc. derivatives, while higher hydrocarbons are formed. The latter raise the octane number of the motor fuel, while the metallo derivatives act as antioxidants. For example, a well dried stream of acetylene is passed through a motor fuel containing lead alkyls produced in situ, normal temperatures being employed, the reaction being continued for six hours. Lead acetylide is formed, together with paraffin hydrocarbons. The alkyl radicles set free in nascent condition recombine in various ways.

Analogously, a gasoline containing a complex mixture of Grignards produced in accordance with Patent No. 2,012,356 is treated at 40-70° C. with a current of ethylene for three to six hours. The corresponding magnesium ethylene halide is produced, together with paraffins of various types.

In lieu of using pure gaseous unsaturates, gaseous mixtures containing the unsaturates may be employed. Gases from cracking units may thus be used, since they contain relatively high contents of olefines, and may be directly applied to the production of the olefinic plumbanes and other metallo organics. As exemplary of the use of such products there may be mentioned the gas from a vapor phase cracking plant containing 6% of butylenes, 17% propylene, 27% ethyl-

ene and 50% methane. Such a gas may desirably be employed to treat the lead alkyl or analogous derivative as set forth above. The metallo organo compound such as lead alkyl, may be in solution and the gas run through the solution at a temperature of from 20 to 50° C., and if desired under pressure, as for example, about 90 pounds per square inch. The current of gas is run through for five hours to produce the conversion. More desirably counter current contact of gas with liquid is utilized, and with slightly elevated temperatures and pressures, the process of conversion is quite rapid. By the use of still gases, vapor phase cracking gases, etc., utility is made of products readily available in the refinery. Very complex mixtures of metallo ethenyls, propenyls, butenyls, etc. are produced.

Where polymerization of the unsaturates takes place, the motor fuels may be redistilled. But the conditions of reaction can be chosen to avoid so extensive polymerization as to require distillation.

While motor fuel fractions, such as gasoline, have been particularly mentioned, other hydrocarbon fractions and distillates may be similarly treated. Diesel fuels may be so treated. The ethylene, propylene, etc. are illustrative of the class of olefinic materials, while acetylene illustrates the class of compounds containing the $\text{—C}\equiv\text{C—}$ group. The term "olefinyl" like the term "ethylenyl" and similar terms is intended to cover compounds in which the metal is joined directly to carbon of olefin group such as ethylene, etc. Furthermore, the term "metal" is used herein to cover both heavy metals and non-metals of the character set forth above which are found to be useful in motor fuels in connection with anti-detonating and other types of metal derivatives.

The desired derivatives may also be produced by reaction of alloys and amalgams, particularly of the alkali metals, with halogen derivatives of the unsaturated hydrocarbons. Thus sodium lead alloy may be reacted with ethenyl chloride ($\text{CH}_2=\text{CHCl}$) to produce the corresponding lead derivative. Such reactions may be carried out in any desired medium or vehicle as in the presence of the gasoline or other hydrocarbon vehicle.

The processes given above in which alkyl or aryl groups of metallo alkyls or aryls are replaced by unsaturated organic radicles are illustrative of the wide variety of processes which can be utilized to modify the metallo organo ingredients of motor fuels, by simple means in view of the great reactivity of the metallo organic derivatives such as lead alkyl, zinc alkyl, the Grignard reagents, etc. Processes can further be employed to modify the ingredients along other lines, and to introduce either other substituent groups, or partially to replace alkyls or alkylene groups in such metal derivatives. Thus, compounds are produced in which the metal is joined directly to a carbon atom of an alkylene group and at the same time is also joined to a carbon atom of an alkyl group. These mixed compounds represent metallo organo derivatives in which the metal constituent is joined directly to a carbon atom of each of two dissimilar organic radicles. The aliphatic radicles, particularly the olefins are preferred. The alkylene group attached to the metal in producing the metal alkylenes profoundly influences the character of these metallo organics in their use in motor fuels, the alkylene group having important characteristics differen-

tiating from the alkyl or aryl groups. Where it is desired to tone down the influence of such alkylene groups, the mixed derivatives may be utilized so that instead of having four alkylene groups attached to lead, for example, there may be from one to three alkylene groups and correspondingly three to one alkyl or aryl groups.

An important process in this connection is that in which an organic derivative containing a nitrogen group, is employed to replace alkyl or aryl or alkylene or acetylene groups in the corresponding metal derivatives, either completely or partially by nitrogen containing radicles, in which the nitrogen is directly attached to the metal. As a result amides or amido derivatives are readily produced. Amido derivatives of the metals, such as lead, zinc, etc. can be readily produced by direct treatment of the metal aryls or alkyls with ammonia, whereas if amines are employed, including, for example, primary and secondary amines, substituted amino derivatives of the metals are obtained. As noted, if the substitution for the alkyl or aryl or alkylene groups, is carried to the total elimination of such alkyl, aryl or alkylene or acetylene groups, metal amides or metal amido derivatives are produced containing no alkyl or aryl or other radicles, except those which may be attached to the nitrogen. A wide variety of different types of compounds can thus be produced, and by control of the processes, mixtures of complex substances of the character can all be produced simultaneously by simple means in the motor fuels themselves, and preferably are so produced. While these reactions can be carried out utilizing individual compounds, the simplicity of reactions by which the metal derivatives are treated in the motor fuels themselves, particularly when they have been produced in situ therein along lines indicated above, make such methods preferable to others. Various of these processes are illustrated below.

It should be kept in mind in this connection that where the metal derivative is being treated in situ in a motor fuel, hydrocarbon oil, etc., that such metallo organo derivative may be present in a concentrated degree in such vehicle, and after the modification of the metallo derivative, the resulting material containing a concentration of the new metallo derivative may be diluted with motor fuels, gasolines, etc., of any desired type, to reduce the content of metal derivative to the small amount required, such as only a fraction of a percent in the final commercial product.

For example, a motor fuel fraction containing lead alkyls produced in situ in such motor fuel by the methods set forth in Patent No. 2,012,356, is subjected to treatment with ammonia by passing a dry current of ammonia into the motor fuel containing the metallo alkyls and aryls. The process can be carried out at ordinary temperatures and under ordinary pressures, but if desired the reaction mediums can be heated to moderate temperatures and superatmospheric pressures can be employed. Counter-current methods can be utilized for contact of the gas with the liquid here as in other cases illustrated above. As a result of such treatment, depending on the extent to which the replacement is permitted to occur, that is the length of time treatment, there is produced as an ultimate derivative lead amide, in which the metal is directly attached to the nitrogen of the amido group. If the reaction, however, is interrupted before

complete displacement of the alkyls and aryls by the amido group, mixed compounds represented by the amido metallo alkyls or amido metallo aryls are obtained.

If it is desired to treat the metallo alkyls or aryls individually, and subsequently to add the produced products to motor fuels or other compositions, an analogous process may be employed. Thus a current of well dried ammonia is led into an ether solution of zinc ethyl under conditions analogous to those described immediately above with the production of zinc amide.

Similarly hydrazin may be employed to produce corresponding metal hydrazides. For example, hydrazine vapor is passed into the solutions containing the desired metallo organic derivatives, such as the lead alkyls or aryls as explained above. On such treatment of a solution containing a lead alkyl, for example, the hydrocarbon corresponding to the alkyl present is liberated, and the metal hydrazide is produced, in which event, in this instance, lead hydrazide would be obtained. Here too, the reaction may be interrupted before the complete replacement of alkyl or aryl groups as obtained by means of the hydrazide radicle, so that mixed hydrazide metallo alkyls or hydrazide metallo aryls are obtained.

Analogously, the lead ethylenyl, and other metallo organic derivatives produced as set forth above, which contain an unsaturated group, and in which the metal is joined directly to the carbon, may be treated with ammonia, hydrazin, or other nitrogen containing bases to obtain displacement, either completely or in part of the carbon-containing radicles by the nitrogen-containing group.

In lieu of using ammonia, hydrazin, or similar types of compounds, the substituted ammonias and hydrazines may also be employed. Thus, any of the amines, particularly the primary and secondary amines may be employed for reaction with the metallo derivatives of organic radicles to produce substituted compounds in which the metal is attached to the nitrogen of the amino radicle. Where the amines employed are gaseous or easily vaporized, as in the case of methylamine, ethylamine, etc., the gaseous amine may be conducted into the solution containing the metallo aryl, alkyl or analogous compound at ordinary temperatures, the reaction readily taking place, and producing corresponding metallo derivatives in which the metal is joined to the nitrogen of the amino group producing an alkyl amino metal derivative. Again, if the reaction is not permitted to go to completion, the substitution is effected in part only with the result that mixed derivatives, corresponding to alkyl or aryl, amido metallo alkyls or aryls are obtained. Where the amines are liquids and not readily vaporized, they may be utilized in liquid condition for reaction with the solution, such as the gasoline solution of the metal alkyls, etc.

By the methods set forth above, therefore, motor fuels and other hydrocarbon vehicles carrying metallo derivatives of carbon and nitrogen containing radicles are readily produced. Metallo derivatives of unsaturated organic compounds in which the metal is joined directly to the carbon, or metallo organic derivatives, including nitrogen-containing radicles, in which the metal is attached directly to the nitrogen, or combinations of such materials are readily produced. These various metallo derivatives are of great importance in the modification of mo-

tor fuels giving them new properties, particularly as anti-detonating agents, anti-gumming compounds, etc.

Having thus set forth my invention, I claim:

1. A motor fuel of hydrocarbon type containing a compound containing an unsaturated organic radicle of not more than four carbon atoms in which an element is joined directly to carbon, said element being selected from the group consisting of lead, tin, antimony, zinc, phosphorus, silicon, arsenic, mercury and thallium.

2. A motor fuel of hydrocarbon type containing a compound containing an olefin of 2 to 4 carbons in which an element is joined directly to carbon, said element being selected from the group consisting of lead, tin, antimony, zinc, phosphorus, silicon, arsenic, mercury and thallium.

3. A motor fuel of hydrocarbon type containing an ethylenyl derivative of lead.

4. A motor fuel of hydrocarbon type containing a propylenyl derivative of lead.

5. A motor fuel of hydrocarbon type containing a butylenyl derivative of lead.

6. A motor fuel of hydrocarbon type containing an amido ethylenyl derivative of lead.

7. A motor fuel of hydrocarbon type containing an amido olefinyl derivative of an element selected from the group consisting of lead, tin, antimony, zinc, phosphorus, silicon, arsenic, mercury, and thallium.

8. A motor fuel of hydrocarbon type containing a compound, having an element directly joined to a carbon atom of an alkylene group of not more than four carbon atoms, said element being selected from the group consisting of lead, tin, antimony, zinc, phosphorus, silicon, arsenic, mercury and thallium.

9. A motor fuel of hydrocarbon type containing a compound, having an element directly joined to a carbon atom of an alkylene group of not more than four carbon atoms and to a carbon atom of an alkyl group of not more than four carbon atoms, said element being selected from the group consisting of lead, tin, antimony, zinc, phosphorus, silicon, arsenic, mercury and thallium.

10. A motor fuel of hydrocarbon type containing a compound, having an element directly joined to a carbon atom of each of two dissimilar aliphatic radicles, one of which at least is an alkylene group of not more than four carbon atoms, said element being selected from the group consisting of lead, tin, antimony, zinc, phosphorus, silicon, arsenic, mercury and thallium.

11. The method of producing a motor fuel of hydrocarbon type which comprises passing a substantially dry olefin in gaseous condition through

gasoline containing a lead compound selected from the group consisting of lead alkyls and lead aryls until a lead olefinyl is formed in amount sufficient for antiknock purposes.

12. A method of making a hydrocarbon vehicle containing an antiknock constituent which comprises passing a substantially dry unsaturated aliphatic hydrocarbon in gaseous condition through a liquid hydrocarbon vehicle containing a lead compound selected from the group consisting of lead alkyls and lead aryls, until a substantial amount of a lead compound with such unsaturate is formed, and treating the resulting product with a substantially dry compound in the vapor state which compound has the formula NH_2R in which R is selected from the group consisting of H, NH_2 , alkyl, alkylene and aromatic radicals, until a substantial amount of a metallo organic derivative including a nitrogen containing radicle and a carbon containing radicle in which the metal is directly attached to nitrogen and carbon is formed.

13. The method of producing hydrocarbon vehicles containing antiknock components which comprises passing a substantially dry compound of the formula NH_2R in gaseous condition, in which compound R is selected from the group consisting of H, NH_2 , alkyl, alkylene and aromatic radicals, through a liquid hydrocarbon vehicle containing a lead compound selected from the group consisting of lead alkyls and lead aryls.

14. The method of producing motor fuel products which comprises passing substantially dry ammonia in gaseous condition through gasoline containing a lead compound selected from the group consisting of lead alkyls and lead aryls until a substantial amount of a metallo organic derivative including a nitrogen containing radicle and a carbon containing radicle in which the metal is directly attached to nitrogen and carbon is formed.

15. A motor fuel of hydrocarbon type containing a compound having an element directly joined to a carbon atom of each of two dissimilar aliphatic radicals having not more than four carbon atoms, said element being selected from the group consisting of lead, tin, antimony, zinc, phosphorus, silicon, arsenic, mercury and thallium.

16. A motor fuel of hydrocarbon type containing a compound having an element directly joined to a carbon atom of each of two dissimilar aliphatic radicals having not more than four carbon atoms, one of which radicals at least is an alkylene group, said element being selected from the group consisting of lead, tin, antimony, zinc, phosphorus, silicon, arsenic, mercury and thallium.

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