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CYCLOMATIC MANGANESE COMPOUNDS

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This invention relates to novel hydrocarbon manganese compounds and to a process for their preparation.

Attendant with the development and evolution of the internal combustion engine for passenger car and heavy-duty service, the petroleum industry has been continually called upon to effect improvements in the antiknock quality of hydrocarbon fuels. These improvements have, in general, been brought about by two distinct methods. One of these methods comprises improvements in refining operations such as thermal and catalytic cracking and reforming or alkylating processes. The other method comprises the use of fuel additives to effect an increase in the antiknock qualities of the hydrocarbon fuels. Inasmuch as improvements in refinery techniques involve considerable capital expenditures, the use of fuel additives has attained greater and more widespread acceptance as the more effective method, particularly from the economic standpoint. The instant invention is therefore concerned with providing novel hydrocarbon manganese compounds useful as additives to fuel and lubricating oils and also useful in the synthesis of other manganese compounds which are capable of improving combustion characteristics of hydrocarbon fuels and as additives to lubricating oils and greases, and the like.

It is therefore an object of our invention to provide novel hydrocarbon manganese compounds. It is also an object of this invention to provide hydrocarbon manganese compounds which are useful as additives for liquid and solid combustion fuels, and lubricating oils and greases, as well as for other uses. It is likewise an object to provide a process for the preparation of novel hydrocarbon manganese compounds. Additional important objects of this invention will become apparent from the discussion which follows.

The above and other objects are accomplished by providing novel hydrocarbon cyclomatic manganese compounds having the general formula

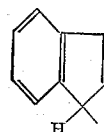


wherein R and R' can be the same or different and are cyclomatic hydrocarbon radicals having from 5 to about 17 carbon atoms which embody a group of 5 carbons having the general configuration found in cyclopentadiene, said compound being further characterized in that the cyclomatic hydrocarbon radical is bonded to the manganese through the carbons comprising the cyclopentadienyl-group configuration.

When employing the compounds of our invention in the synthesis of other hydrocarbon fuel and lubricating oil additives, we especially prefer compounds in which at least one of the carbon-to-carbon double bonds in the cyclopentadienyl-group configuration is olefinic in nature. In other words, in this preferred embodiment not more than two carbons of the cyclopentadienyl ring should be shared with a fused aromatic ring such as a benzene ring.

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An example of one of the cyclomatic radicals of this preferred embodiment is the indenyl radical.



When R and R', the cyclomatic radicals, have this type of configuration or structure, the resulting cyclomatic manganese compounds are found to have the optimum characteristics for use as fuel and lubricating additives.

Reference to the generic formula described above indicates that there are two types of constituents in the new composition of matter of the present invention. These are, first, the cyclomatic constituents R and R' and, second, the metallic constituent Mn. As stated previously, the cyclomatic constituents R and R' are cyclopentadienyl-type radicals, i. e., radicals containing the cyclopentadienyl moiety. In general, such cyclomatic groups can be represented by the four generic formulae presented hereinafter, having from 5 to about 17 carbon atoms. Thus, any substituents attached to the cyclopentadienyl group in the radical can have from 1 to about 12 carbon atoms. However, radicals in which the substituents have from 1 to about 20 or more carbon atoms are also within our invention.

When a cyclomatic radical of the compounds of our invention is substituted with univalent aliphatic radicals, these substituents can be radicals having from 1 to about 12 or more carbon atoms selected from the group consisting of alkyl, alkenyl, aralkyl and aralkenyl. Thus, when these substituents are univalent aliphatic radicals, they can be alkyl radicals, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, t-butyl, n-amyl, the various positional isomers thereof, as, for example, 2-methylbutyl; 1,1-dimethylpropyl; 1-ethylpropyl, and the corresponding straight and branched chain isomers of hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tetradecyl, hexadecyl, nonadecyl, eicosyl, and the like. Likewise, the univalent aliphatic substituent can be an alkenyl radical, such as ethenyl, Δ^1 -propenyl, Δ^2 -propenyl, isopropenyl, Δ^1 -butenyl, Δ^2 -butenyl, Δ^3 -butenyl, and the branched chain isomers thereof as Δ^1 -isobutenyl, Δ^2 -isobutenyl, Δ^1 -sec-butenyl, Δ^2 -sec-butenyl, Δ^1 -pentenyl, Δ^2 -pentenyl, and the branched chain isomers thereof Δ^1 -hexenyl, Δ^3 -hexenyl, Δ^4 -hexenyl, and the branched chain isomers thereof, including 3,3-dimethyl- Δ^1 -butenyl; 2,3-dimethyl- Δ^2 -butenyl; and 1-methyl-1-ethyl- Δ^2 -propenyl; and the various isomers of heptenyl, octenyl, nonenyl, decenyl, undecenyl, dodecenyl, tetradecenyl, heptadecenyl, octadecenyl, eicosenyl, and the like.

When the organic radical substituted in the cyclomatic group is a univalent aliphatic radical, it can be an aralkyl radical such as, for example, benzyl, α -phenylethyl, β -phenylethyl, α -phenylpropyl, α -phenylisopropyl, α -phenylbutyl, α -phenylisobutyl, β -phenyl-t-butyl, α' -naphthylmethyl, β' -naphthylmethyl, α -(α' -naphthyl)-ethyl, β -(α' -naphthyl)-ethyl, α -(α' -naphthyl)-propyl, α -(β' -naphthyl)-isopropyl, γ -(α' -naphthyl)-butyl, α -(α' -naphthyl)-isobutyl, β -(β' -naphthyl)-sec-butyl, the corresponding α' - and β' -naphthyl derivatives of n-amyl and the various positional isomers thereof, and the like. Other such aralkyl radicals include the α' -, β' -, and γ' -anthryl derivatives of alkyl radicals, such as α' -anthrylmethyl, β -(γ' -anthryl)-ethyl, Δ -(β' -anthryl)-2-methylamyl, and the like; and the corresponding alkyl derivatives of phenanthrene, fluorene, acenaphthene, crysene, pyrene, triphenylene, naphthacene, etc. The univalent aliphatic radical can be an aralkenyl radical, such as α -phenylethenyl, β -phenylethenyl, α -phen-

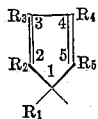
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yl- Δ^1 -propenyl, and the phenyl derivatives of the isomers of butenyl, pentenyl, heptenyl, and the like, up to about eicosenyl. Other such arylalkenyls include α -(α' -naphthyl)-ethenyl, α -(β' -naphthyl)-ethenyl, α -(α' -naphthyl)- Δ^1 -propenyl, α -(α' -naphthyl)- Δ^2 -propenyl, α -(β' -naphthyl)-isopropenyl, and the like. In addition, such aromatic derivatives of alkenyls, that is, aralkenyl radicals include derivatives of phenanthrene, fluorine, acenaphthene, chrysene, naphthacene, and the like.

When the organic radicals comprising the substituents in the cyclomatic groups of the compounds of our invention are univalent alicyclic radicals, these can be radicals selected from the group consisting of cycloalkyl and cycloalkenyl radicals. Thus, such univalent alicyclic radicals can be cycloalkyl radicals such as, for example, cyclopropyl, cyclobutyl, cycloamyl, cyclohexyl, cyclononyl, cyclodecyl, cyclododecyl, cyclooctodecyl, cycloeicosyl, and such cycloaliphatic radicals as α -cyclopropylethyl, α -cyclobutylpropyl, and the like. Similarly, the alicyclic radical substituents can be cycloalkenyl radicals such as α -cyclohexylethenyl, α -cycloheptyl- Δ^1 -propenyl, β -cyclooctyl- Δ^2 -propenyl, α -methylene- β -cyclododecylethyl, and the like.

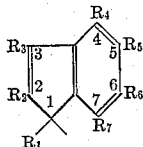
When the organic radicals substituted in the cyclomatic groups of our compounds are univalent aromatic radicals, they can be selected from the group consisting of aryl and alkaryl radicals. Thus, these univalent aromatic radicals can be aryl radicals, such as, for example, phenyl, naphthyl, anthryl, and the like including the various monovalent radicals of such aromatics as indene, acenaphthene, fluorene, naphthacene, chrysene, and the like. Moreover, these univalent aromatic radicals can be alkaryl radicals such as, for example, tolyl, 3,5-xylyl, p-cumenyl, mesityl, ethylphenyl, 2-methyl- α -naphthyl, 1-ethyl- β -naphthyl, and the like.

Having amply described the meaning of the term "organic radical," the discussion with regard to cyclomatic radicals has been facilitated. As stated hereinabove, the cyclomatic groups of the compounds of the present invention can be represented by four general formulae. The first class of cyclomatic radicals can be represented by the general formula



wherein each of R_1 , R_2 , R_3 , R_4 and R_5 can be the same or different and is selected from the group consisting of hydrogen and organic or hydrocarbon radicals having from about 1 to about 12 or more carbon atoms. Illustrative examples of such cyclomatic radicals include cyclopentadienyl; methylcyclopentadienyl; 1,2-dimethylcyclopentadienyl; ethylcyclopentadienyl; 1,3,4-tripropylcyclopentadienyl; 1,5-dipentylcyclopentadienyl; 1-methyl-3-*t*-butylcyclopentadienyl; isopropenylcyclopentadienyl; 1,2-di(Δ^2 -isobutenyl)cyclopentadienyl; 1-methyl-3-(Δ^1 -pentenyl)cyclopentadienyl; 3-(β -phenylethyl)-cyclopentadienyl; 3-cyclohexylcyclopentadienyl; 2-phenylcyclopentadienyl; 1-ethyl-3-(α -methyl)-cyclopentadienyl; 2-(*o*-tolyl)cyclopentadienyl; 1-acetyl-cyclopentadienyl; and the like.

The second type of cyclomatic radical is the indenyl-type radical represented by the general formula

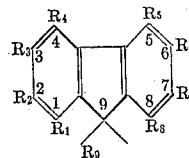


wherein each of R_1 , R_2 , R_3 , R_4 , R_5 , R_6 and R_7 can be the same or different and is selected from the group consisting of hydrogen and organic and hydrocarbon radicals

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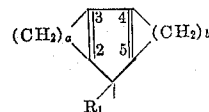
having from 1 to about 12 or more carbon atoms. Illustrative examples of such cyclomatic radicals include indenyl; 2-methylindenyl; 3-sec-butyindenyl; 3,4-diethenylindenyl; 5-(α -phenylbutyl)-indenyl; 3-cyclohexylindenyl; 3-phenylindenyl; 4,5-diphenylindenyl, and the like.

The third type of cyclomatic radical of the new compositions of matter of the present invention is a radical of the fluorenyl type which can be represented by the general formula



wherein each of R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , R_8 and R_9 can be the same or different and is selected from the group consisting of hydrogen and organic and hydrocarbon radicals having from 1 to about 12 or more carbon atoms. Illustrative examples of such radicals include fluorenyl; 3-ethylfluorenyl; 4,5-dipropylfluorenyl; 9-methylfluorenyl; 6-ethylfluorenyl; 4-benzylfluorenyl; 2-*m*-tolylfluorenyl, and the like.

The fourth type of cyclomatic radical, that is, a radical containing the cyclopentadienyl moiety can be represented by the general formula



wherein a and b can be the same or different and are small whole integers including 0 and excluding 1, the sum $a+b$ being at least 2, and wherein R_1 is selected from the class consisting of hydrogen and organic radicals. Thus, when a is zero each of the carbon atoms designated as 2 and 3 have attached thereto a monovalent radical selected from the class consisting of hydrogen and organic radicals. Furthermore, the monovalent radicals so attached can be the same or different. The same discussion applies to each of the carbon atoms designated as 4 and 5 when b is zero. Illustrative examples of this type of cyclomatic radical include 4,5,6,7-tetrahydroindenyl; 1,2,3,4,5,6,7,8-octahydrofluorenyl; 3-methyl-4,5,6,7-tetrahydroindenyl, and the like.

Non-limiting examples of the compounds of this invention in which the cyclomatic radical has the configuration shown in structure I above are bis(cyclopentadienyl)-manganese; bis(methylcyclopentadienyl)-manganese; bis(ethylcyclopentadienyl)-manganese; bis(propylcyclopentadienyl)-manganese; bis(butenylcyclopentadienyl)-manganese; bis(*t*-butylcyclopentadienyl)-manganese; bis(hexylcyclopentadienyl)-manganese; bis(cyclohexylcyclopentadienyl)-manganese; bis(heptylcyclopentadienyl)-manganese; bis(decylcyclopentadienyl)-manganese; bis(dodecylcyclopentadienyl)-manganese; bis(1,2,3,4-tetramethylcyclopentadienyl)-manganese; bis(1,2,3,4,5-pentamethylcyclopentadienyl)-manganese; bis(1,3-dibutylcyclopentadienyl)-manganese; bis(1,2-dipropyl-3-cyclohexylcyclopentadienyl)-manganese; bis(tolylcyclopentadienyl)-manganese; bis(1,3-diphenylcyclopentadienyl)-manganese; bis(acetyl-cyclopentadienyl)-manganese; cyclopentadienyl-(indenyl)-manganese, and the like.

When there is only one organo or hydrocarbon substituent on the cyclopentadienyl ring, its position is not specified since, according to theory, the cyclopentadienyl ring or group is bonded to the manganese by five equivalent bonds running from each of the five carbons in the cyclopentadienyl ring to the manganese. Since all these bonds are equivalent and all five carbons in the ring are equidistant from the manganese, it is immaterial to which of the five carbons a single substituent is attached. When,

however, more than one substituent is attached to the cyclopentadienyl ring, the positions are given so as to indicate the relative positions of the different substituents with respect to each other on the cyclopentadienyl ring.

Examples of compounds having the configuration of structure II given hereinabove are bis(indenyl)manganese; bis(3-methylindenyl)manganese; bis(3-ethenylindenyl)manganese; bis(2,3-dimethylindenyl)manganese; bis(1,3-diethylindenyl)manganese; bis(1,7-diisopropylindenyl)manganese; bis(1,2,3,4,5,6,7-heptamethylindenyl)manganese; 5-phenylindenyl(3(2-ethylphenyl)indenyl)manganese, etc.

Examples of compounds having the configuration of structure III above are bis(fluorenyl)manganese; bis(3-ethylfluorenyl)manganese; bis(4-propylfluorenyl)manganese; bis(2,3,4,7-tetramethylfluorenyl)manganese, and the like.

Examples of compounds having the configuration of structure IV above are bis(4,5,6,7-tetrahydroindenyl)manganese; bis(3-methyl-4,7-dihydroindenyl)manganese; bis(2-ethyl-3-phenyl-4,5,6,7-tetrahydroindenyl)manganese; bis(1,2,3,4,5,6,7,8-octahydrofluorenyl)manganese; bis(1,4,5,8-tetrahydrofluorenyl)manganese, and the like.

The general methods for the preparation of the cyclomatic compounds of the instant invention comprise reacting manganese in a suitable active form, such as a metallic compound or a metal per se, with a cyclomatic hydrocarbon or a metallic cyclomatic compound to form a manganese cyclomatic compound.

One method for the preparation of the compounds of the instant invention involves the formation of a cyclomatic manganese compound by the reaction of active cyclomatic metal compounds, such as cyclomatic magnesium halides, cyclomatic alkali metal compounds, cyclomatic zinc halides, and the like, with a compound of manganese, such as a manganese salt.

Another method comprises reacting manganese with a cyclomatic hydrocarbon in the presence of an active metal catalyst, to produce a bis(cyclomatic)manganese compound; for example, bis(methylcyclopentadienyl)manganese, etc.

Another embodiment of our invention comprises introducing cyclopentadiene into a mixture of manganous salt and alkali metal to produce the cyclomatic manganese compounds of our invention.

The reaction of active manganese metal with cyclopentadiene is commercially attractive because of the simplicity of the reagents involved. The active manganese metal can be obtained by electro-deposition or by other methods of reduction, such as the reduction of manganese salts as, for example, the reduction of manganese halides by other metals as, for example, sodium. An example of this is the reaction of 55 parts of freshly reduced manganese with 132 parts of cyclopentadiene under an inert atmosphere, such as nitrogen at temperatures ranging from 0° C. to 300° C. to give bis(cyclopentadienyl)manganese. The Grignard method, or, in general, the synthesis of bis(cyclomatic)manganese compounds by the reaction of cyclomatic group II metal salts, such as cyclomatic magnesium halides with manganese salts, such as manganous halides, has the advantage of being less hazardous than other methods of preparation. The process of the instant invention, however, is preferred because of the high yields obtained in the synthesis of the bis(cyclomatic)manganese compounds.

The manganese salts employed are salts of organic or inorganic acids, preferably the respective manganous salts. Examples of these manganese salts are manganous acetate, manganous benzoate, manganous carbonate, manganous oxalate, manganous lactate, manganous nitrate, manganous phosphate, manganous sulfate, manganic phosphate, manganous fluoride, manganous chloride, manganous bromide, manganous iodide, and the like. In addition, manganese salts of β -diketones, such as tris(2,4-pentanedione) manganese and tris(2,4-hexanedione)-

manganese may also be employed, as well as manganese salts of β -keto esters, such as the manganese salts of ethylacetacetate, and the like. An example of the process employed is the reaction of cyclopentadienyl sodium with manganous halide to give bis(cyclopentadienyl)manganese. Cyclomatic alkali metal compounds are also reacted with naturally occurring manganese ores, such as manganosite (MnO), manganese dioxide (MnO_2), manganic sesquioxide (Mn_2O_3), manganous sulfide (MnS), manganic sulfide (MnS_2), rhodochrosite ($MnCO_3$), and the like, to give bis(cyclomatic)manganese compounds such as bis(methylcyclopentadienyl)manganese, etc.

The cyclomatic alkali metal compound used in the preparation of our compounds can be prepared by the reaction of a cyclomatic compound with an alkali metal directly, or with an alkali metal compound. Thus, a cyclomatic alkali metal compound can be prepared by reacting a cyclomatic compound with an alkali metal derivative of a compound which is less acidic than the cyclomatic compound. The process is carried out in an inert atmosphere, such as nitrogen, argon, helium, methane, etc., to prevent oxidation due to oxygen in the air. For example, cyclopentadienyl sodium can be prepared by reacting cyclopentadiene with a sodium alcoholate such as sodium methylate, sodium ethylate, sodium benzoate, etc. Potassium, rubidium and cesium can be used in place of sodium.

The cyclomatic alkali metal compounds can also be prepared by reacting hydrocarbon cyclomatic compounds containing the cyclopentadienyl group with alkali metal derivatives of amines, such as sodamide, and the alkali metal derivatives of alkyl and aryl hydrocarbon amines in which not more than two of the hydrogens in ammonia are substituted by alkyl and/or aryl hydrocarbon groups as, for example, sodioanilide, potassium ethyl amide, rubidium diisopropyl amide, cesium methylethyl amide, etc.; alkali metal aryl methanes, such as benzyl sodium, di(phenyl)methyl potassium, tri(2,4-dimethylphenyl)methyl rubidium, alkali metal arylalkyl methanes, such as sodiocumene, 5(α -naphthyl)decyl potassium, etc.; alkali metal acetylides, such as sodioacetylide, potassium acetylide, etc., and the like.

One preferred embodiment in the preparation of the bis(cyclomatic)manganese compounds of this invention is a process comprising reacting a manganese salt with an alkali metal cyclomatic hydrocarbon compound having from 5 to about 17 carbon atoms which embodies a group of 5 carbons having the general configuration found in cyclopentadiene. The reaction is preferably carried out in the presence of a suitable, preferably non-aqueous, solvent, examples of which are hydrocarbons, such as benzene, cyclohexane, diisobutylene, toluene; and ethers, such as diethyl ether, ethylene glycol dimethyl ether, ethylene glycol diethyl ether, propylene glycol methylphenyl ether, methylphenyl ether, tetrahydrofuran, dioxane, dodecyl ether, etc. In other words, hydrocarbon and ether solvents having up to about 20 carbon atoms may be employed.

The cyclomatic manganese product can be separated from the reaction mixture by solution in a solvent, such as ether, and the removal of the solid impurities by filtration, centrifugation, and the like. The product can also be separated from the reaction mixture by vacuum distillation or selective solvent extraction. The solvent may be removed from the product by fractional distillation and the product further purified by fractional distillation or sublimation. The method of preparation is further illustrated in the examples below.

EXAMPLE I

Bis(cyclopentadienyl)manganese

A reaction vessel equipped with means for charging and discharging liquids and solids, gas inlet and outlet means, temperature measuring devices, heating and cool-

ing means, means for agitation, and means for condensing vapors, was flushed with pre-purified nitrogen. To the flask were then added 400 parts of tetrahydrofuran and 23 parts of sodium dispersed in 23 parts of mineral oil. An atmosphere of nitrogen was maintained in the reaction vessel throughout the run. The vessel was cooled to 10° C. and 66.7 parts of freshly-distilled cyclopentadiene was added in small increments with agitation while maintaining the temperature below 15° C. After the addition of the cyclopentadiene, the temperature was allowed to rise to 23° C. over a period of about two hours, when the completion of the formation of the sodium cyclopentadiene was evidenced by the cessation of hydrogen evolution. To this solution of cyclopentadienyl sodium in tetrahydrofuran was added 63 parts of anhydrous manganous chloride. The mixture was heated and maintained at reflux temperature for 20 hours. At the end of this time, the solvent was removed by distillation under reduced pressure and the product purified by sublimation at a pressure of about 2 mm. of mercury at about 130° C., producing 48.64 parts, 52.3% yield, of lustrous, brown-black bis(cyclopentadienyl)manganese crystals. Analysis of the product showed it to contain 64.9 percent carbon and 5.44 percent hydrogen, corresponding to the formula $(C_5H_5)_2Mn$; calculated 64.9 percent carbon and 5.41 percent hydrogen. The bis(cyclopentadienyl)manganese oxides readily in air and should therefore be kept in an inert atmosphere, such as nitrogen.

EXAMPLE II

Bis(methylcyclopentadienyl)manganese

The procedure of Example I was followed employing 400 parts of tetrahydrofuran, 23 parts of sodium dispersed in 23 parts of mineral oil, 80 parts of freshly-distilled methylcyclopentadiene, and 63 parts of powdered $MnCl_2$, containing 3.11 percent water. The manganous chloride was added to the methylcyclopentadienyl sodium solution at a temperature of 20° C. After maintaining the mixture at reflux temperature for two hours, the compound bis(methylcyclopentadienyl)manganese was separated by distillation at reduced pressure under nitrogen. It was a viscous, reddish-brown liquid which crystallized on standing. Analysis showed it to contain 66.7 percent carbon and 6.54 percent hydrogen, corresponding to the formula $(C_5H_7)_2Mn$; calculated 67.6 percent carbon and 6.62 percent hydrogen. The yield was 84.3 percent based on the amount of $MnCl_2$ employed. The bis(methylcyclopentadienyl)manganese is spontaneously combustible and therefore should not be exposed to oxygen of the atmosphere.

A variation of Example II, by which the same product is prepared, consists of adding methylcyclopentadiene to a mixture of manganous chloride and sodium dispersed in mineral oil.

EXAMPLE III

Bis(ethylcyclopentadienyl)manganese

Ethylcyclopentadiene was prepared by reaction of cyclopentadienyl sodium with ethyl bromide in tetrahydrofuran. Then, bis(ethylcyclopentadienyl)manganese was prepared according to the process described in Example I.

EXAMPLE IV

Bis(allylcyclopentadienyl)manganese

The procedure of Example III is followed by using allyl chloride in place of ethyl bromide, potassium in place of sodium, and tris(2,4-pentanedione)manganese in place of manganous chloride. A good yield of bis(allylcyclopentadienyl)manganese is obtained. Good yields are also obtained when lithium is used in place of potassium.

EXAMPLE V

Bis(phenylcyclopentadienyl)manganese

Phenylcyclopentadiene, obtained by treating cyclopentenone with phenyl lithium to give 1-phenyl-2-cyclopenten-1-ol which upon distillation yields phenylcyclopentadiene, is reacted with sodium according to the procedure described in Example I to give phenylcyclopentadienyl sodium. The latter is reacted with manganous bromide to give bis(phenylcyclopentadienyl)manganese in good yield.

EXAMPLE VI

The procedure of Example I is followed except that a mixture of cyclopentadiene and methylcyclopentadiene is employed in place of cyclopentadiene. A high yield of cyclopentadienyl(methylcyclopentadienyl)manganese is obtained.

EXAMPLE VII

Bis(indenyl)manganese

The procedure of Example I was followed using indene in place of cyclopentadiene. After addition of anhydrous manganous chloride to the indenyl sodium in tetrahydrofuran, the reaction mixture was refluxed for three hours. Separation of product according to Example I produced a good yield of bis(indenyl)manganese which, on analysis, was found to correspond to the formula $(C_9H_7)_2Mn$.

EXAMPLE VIII

Bis(1,2,3,4,5-pentamethylcyclopentadienyl)manganese

The procedure of Example II is employed using 136 parts of 1,2,3,4,5-pentamethylcyclopentadiene and 108 parts of manganous bromide ($MnBr_2$). Lithium was used in place of sodium. A good yield of bis(1,2,3,4,5-pentamethylcyclopentadienyl)manganese is obtained.

EXAMPLE IX

Bis(octylcyclopentadienyl)manganese

The procedure of Example II is followed using 178 parts of 2-octylcyclopentadiene, a dispersion of potassium instead of sodium, and 44 parts of manganese dioxide. A good yield of bis(octylcyclopentadienyl)manganese is obtained.

Good results are also obtained when rubidium or cesium are used as the alkali metals and other manganese ores in place of MnO_2 , e. g., MnO , Mn_3O_4 , MnS , $MnCO_3$, etc.

EXAMPLE X

Bis(1-naphthyl-2-ethylcyclopentadienyl)manganese

The procedure of Example II is followed using 222 parts of 1-naphthyl-2-ethylcyclopentadiene and 63 parts of manganous fluoride. The reaction mixture upon separation treatment produced bis(1-naphthyl-2-ethylcyclopentadienyl)manganese in good yield.

EXAMPLE XI

Bis(1,3,4,7-tetramethylindenyl)manganese

The procedure of Example II is carried out employing 172 parts of 1,3,4,7-tetramethylindene and 86 parts of manganous acetate. Bis(1,3,4,7-tetramethylindenyl)manganese is separated in good yield from the reaction product.

EXAMPLE XII

Bis(3-cyclohexylindenyl)manganese

Following the procedure of Example II 192 parts of 3-cyclohexylindene is reacted with 150 parts of manganous benzoate and bis(3-cyclohexylindenyl)manganese is obtained in good yield.

EXAMPLE XIII

Bis(4,5,6,7-tetrahydroindenyl)manganese

According to the process of Example II 120 parts of

4,5,6,7-tetrahydroindene is reacted with 72 parts of manganous oxalate. A good yield of bis(4,5,6,7-tetrahydroindenyl)manganese is obtained.

EXAMPLE XIV

Bis(1,2,3,4,5,6,7,8-octahydrofluorenyl)manganese

The procedure of Example II is followed in reacting 174 parts of 1,2,3,4,5,6,7,8-octahydrofluorene with 76 parts of manganous sulfate and bis(1,2,3,4,5,6,7,8-octahydrofluorenyl)manganese is obtained.

EXAMPLE XV

Bis(1,8-diethylfluorenyl)manganese

Following the procedure described in Example II, 222 parts of 1,8-diethylfluorene is reacted with 93 parts of manganous nitrate and bis(1,8-diethylfluorenyl)manganese is obtained.

EXAMPLE XVI

Bis(fluorenyl)manganese

The procedure of Example II is followed in reacting 166 parts of fluorene with 59 parts of manganous phosphate, and bis(fluorenyl)manganese is obtained.

EXAMPLE XVII

Bis(methylcyclopentadienyl)manganese

Following the procedure of Example I, 80 parts of methylcyclopentadiene were slowly added to 39 parts of sodamide in 250 parts of tetrahydrofuran. The mixture was heated to, and held at, reflux temperature for a period of two hours. It was then cooled to 12° C. and 63 parts of MnCl₂ were added. Heat was then applied and the mixture kept at reflux temperature for a period of about 16 hours. A good yield of bis(methylcyclopentadienyl)manganese was separated from the reaction mixture.

The temperatures of the steps in our process may be varied. For example, the reaction of the alkali metal with the cyclomatic compound can be performed at temperatures up to the boiling point of the cyclomatic compound. For dicyclopentadiene, this is about 175° C. at which point cracking to the monomer occurs and the latter reacts with sodium to form cyclopentadienyl sodium. A preferred range of temperatures is from about 10° C. to about 65° C. when conducting the reaction in a solvent, such as tetrahydrofuran. The upper temperature represents the boiling point of tetrahydrofuran. The manganese salt, i. e., MnCl₂, MnBr₂, or MnSO₄, etc., may be added to the alkali metal cyclomatic compound at temperatures ranging from -20 to 65° C. and higher, depending on the boiling point of the solvent, and since there is no great temperature rise upon addition of the manganese halide, the temperature limits are not critical. However, we prefer to conduct this reaction at a temperature of from 20-65° C. in order to cut down the time of reaction. The reaction mixture need not be refluxed, however, reflux periods up to 16 hours have been employed with good success.

The time of reaction of any part of the processes depends on temperature and will vary over a wide range. For instance, the reaction of sodium with cyclopentadiene is practically instantaneous and the rate of admixture of reactants depends on the efficiency of cooling. Therefore, the time of reaction can vary from several minutes to a few hours, such as four hours.

Solvents other than tetrahydrofuran, ether, and benzene were used in other runs which are not included in the illustrative examples given hereinabove. Such other solvents, or mixtures thereof, which were employed are n-butyl ether, dioxane, toluene, and dimethyl ether of ethylene glycol.

The alkali metals used in our process to make the metal derivatives of the cyclomatic compounds which are then reacted with a manganese metal or compound

to make the cyclomatic manganese compound include lithium, sodium, potassium, rubidium, and cesium. Metals other than the alkali metals that can be used are the group IIA metals, such as beryllium, magnesium, calcium, strontium, and barium, and group IIB metals such as zinc and cadmium. In the case of polyvalent metals, the compounds may contain halogen such as the Grignard reagent in the case of magnesium.

In the above examples, nitrogen was employed as the inert atmosphere to prevent oxygen from coming in contact with the reactants. Other inert gases are also used, e. g., argon, methane, ethane, propane, and other hydrocarbons and vapors of the solvents employed in the reaction.

Our compounds are useful in the synthesis of other manganese compounds which are capable of improving combustion characteristics of hydrocarbon fuels as stated hereinabove. An example of such use is the preparation of methylcyclopentadienyl manganese tricarbonyl as described in the following example.

EXAMPLE XVIII

Methylcyclopentadienyl manganese tricarbonyl

Bis(methylcyclopentadienyl)manganese, prepared as described in Example II, was added to a pressure resistant vessel under a nitrogen atmosphere and the vessel charged with carbon monoxide. The vessel and contents were then heated from 22° C. to about 148° C. while maintaining the pressure in the reaction vessel within the range of from about 680 to 2175 p. s. i. The uptake of carbon monoxide ceased in about one hour indicating the completion of the reaction, whereupon the vessel was cooled and methylcyclopentadienyl manganese tricarbonyl separated from the reaction mixture.

This compound, as well as other cyclomatic manganese tricarbonyl compounds, is found to be an exceptionally good agent for improving the antiknock quality of hydrocarbon fuels used in spark ignition engines. The use and preparation of these cyclopentadienyl manganese tricarbonyl compounds is more fully disclosed in our co-pending application Serial No. 521,364, filed July 11, 1955, now Patent No. 2,818,417.

The cyclomatic compounds of the present invention possess particular utility as additives. Thus, many of the cyclomatic derivatives can be used as fuel additives, such as for fuels for internal combustion engines of both the spark ignition and compression ignition types, fuels for jet engines and rocket fuels, and the like. Likewise, many of the cyclomatic compounds of the present invention can be successfully employed as additives to natural and synthetic lubricants as well as the more viscous unctuous materials exemplified by natural and synthetic greases.

Other important uses of the cyclomatic compounds of the present invention include the use thereof as chemical intermediates, particularly in the preparation of metal and metalloid containing polymeric materials. In addition, some of the cyclomatic derivatives of this invention can be used in the manufacture of medicinals and other therapeutic materials as well as agricultural chemicals such as, for example, fungicides, insecticides, defoliants, growth regulants, and so on.

A particular advantage of the new compositions of matter of the present invention is the fact that by proper selection of the cyclomatic groups attached to the manganese, compounds having "tailormade" characteristics can be obtained. For example, compounds such as bis(cyclopentadienyl)manganese, cyclopentadienyl indenyl manganese, methylcyclopentadienyl indenyl manganese, bis(indenyl)manganese, will possess different degrees of stability, volatility, and solubility due to the varying complexity of the cyclomatic groups in the molecule. Likewise, the selection of the cyclomatic constituents enables the preparation of compounds of diverse applicability.

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This application is a continuation-in-part of our earlier filed co-pending applications Serial Nos. 297,392, filed July 5, 1952, and 325,224, filed December 10, 1952, now Patent No. 2,818,416.

Having fully described the novel cyclomatic derivatives of the present invention, the need therefor, and the best methods devised for their preparation, we do not intend that our invention be limited except within the spirit and scope of the appended claims.

We claim:

1. Hydrocarbon cyclomatic manganese compounds having the general formula



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wherein R and R' are cyclomatic hydrocarbon radicals selected from the group consisting of cyclopentadiene and hydrocarbon substituted cyclopentadienes having from 5 to about 17 carbon atoms which embody a group of 5 carbons having the general configuration found in cyclopentadiene, said compound being further characterized in that the cyclomatic hydrocarbon radicals are bonded to the manganese through the carbons comprising the cyclopentadienyl-group configuration.

2. Bis(cyclopentadienyl)manganese.
3. Bis(methylcyclopentadienyl)manganese.

References Cited in the file of this patent

Kealy et al.: "Nature," vol. 168, #4285, pages 1039-40.