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COMPLEXES OF ACYCLIC TRIENES WITH IRON SUBGROUP TRICARBONYLS

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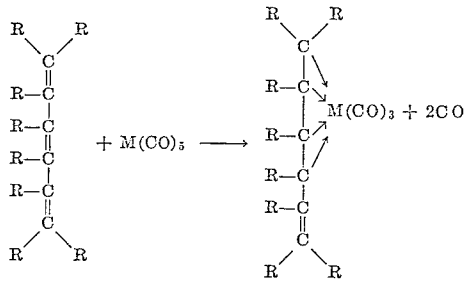
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6 Claims. (Cl. 260—439)

The present invention relates to organometallic compounds and processes for preparing them. More particularly, it relates to hydrocarbon compounds on which a hydrocarbon triene is coordinated with an iron subgroup metal and with carbonyl groups.

Butadiene iron tricarbonyl and related compounds are known wherein methyl and phenyl groups or the like are substituted in the butadiene moiety. In those compounds the double bonds each appear to donate a pair of electrons to the iron so that of the ten electrons needed to bring the iron to an inert gas structure, only six are contributed by carbonyl groups, two from each such group. It is also known that trienes such as cycloheptatriene coordinate with metal carbonyls in such manner that all three of the double bonds donate electrons to the metal atom thereby reducing the number of carbonyl groups required to donate the remaining electrons needed to reach an inert gas structure. It has now been found that for iron and other iron subgroup metals the three double bonds of acyclic trienes do not all contribute electrons. Surprisingly one of the double bonds remains uncoordinated so that tricarbonyl metal compounds of such trienes are formed. This is an important advantage since the uncoordinated double bond provides a very reactive site on which to conduct additional reactions.

Among the objects of the invention is the provision of novel organometallic compounds, as well as processes for preparing them.

According to the present invention the carbonyls of iron subgroup metals (iron, ruthenium and osmium) will react with acyclic trienes in the following manner:



The R's are preferably hydrogen or univalent hydrocarbyl radicals containing from 1–8 carbon atoms, with the total number of carbons in the molecule no more than about 20.

Alloocimene is a readily available triene of the above type and is accordingly a particularly preferred reactant for the above purposes. Other such trienes are hexatriene-1,3,5; decatriene-3,5,7; 2-methyl hexatriene-1,3,5; 3-methyl heptatriene-2,4,6; 5,8-dibutyl dodecatriene-4,6,8; 3,4-diethyl hexatriene-1,3,5; 1-phenyl hexatriene-1,3,5; 1-(2'-methyl cyclohexyl)-octatriene-2,4,6; as well as any other such triene that can be prepared by dehydrating corresponding alcohols in which H and OH substitutents appear on adjacent carbons that are to be connected by a double bond.

The process conditions for forming the triene metal tricarbonyl are not particularly critical since the reactants need only be brought together at reaction temperatures.

Agitation is helpful and the reaction may be carried out in an inert atmosphere or in air if desired. In general, any nonreactive solvent can be used although in many cases no solvent is necessary. The simple mononuclear carbonyl reactants are all liquids as are a good many of the trienes, particularly at reaction temperatures, but the use of a common solvent such as high boiling hydrocarbons inert to the reactants can be used to raise the reaction temperature without increasing the pressure.

The following examples serve to illustrate but not to limit the invention.

Example I

A mixture of 136 g. (1.0) mole of alloocimene and 98 g. (0.5 mole) of iron pentacarbonyl was refluxed 8.5 hours under nitrogen, during which time 0.43 cu. ft. of gas was evolved, amounting to 48% based on the calculated amount of CO that should be liberated. After cooling, the mixture was noted to have only a trace of solids. Fractionation through a helix-packed column was then carried out. Iron carbonyl was distilled over at 46° (81 mm.); alloocimene between 78–81° (12 mm.); and alloocimene iron tricarbonyl at 117–118° (5 mm.). The last named material is obtained in good yield as an orange oil which analyzes very closely.

Calculated for $C_{13}H_{16}FeO_3$: C, 56.55; H, 5.84; Fe, 20.23. Found: C, 56.5; H, 5.89; Fe, 19.9.

Infrared analysis showed carbon-hydrogen stretching at 3.3–3.5 microns and metallo carbonyl bands at 4.9 and 5.1 microns similar to those observed in the spectra of butadiene and isoprene iron carbonyls.

Larger yields are obtained if the reaction time is lengthened.

Example II

A mixture of 136 g. (1.0 mole) of alloocimene, 98 g. (0.5 mole) of iron pentacarbonyl, and 0.5 g. of hydroquinone was heated to reflux for fourteen hours under a nitrogen atmosphere. After eight cubic feet (100% plus of theory) of gas had been evolved, the reaction was stopped.

Very little iron pentacarbonyl was recovered when the dark colored reaction mixture was distilled at 46° under 81 mm. pressure. Distillation at 62° and 5 mm. gave 64 g. of unreacted alloocimene.

A final distillation through a small helix-packed column gave 109.9 g. (90.5%) of alloocimene iron tricarbonyl boiling at 108–109.5°/4 mm.

Example III

Hexatriene-1,3,5 and ruthenium pentacarbonyl are mixed in 1:1 molar proportion, and the mixture dissolved in twice its weight of ethyl benzene. The resulting material is refluxed in an argon atmosphere for 18 hours, and an excellent yield of hexatriene-1,3,5 ruthenium tricarbonyl is recovered as in Example I.

Example IV

0.05 mole of 3-methyl heptatriene-2,4,6 mixed with 0.01 mole osmium pentacarbonyl is heated for 6 hours in a nitrogen atmosphere, by contact with a bath of diphenyl ether held at 150° C. The mixture is then cooled and fractionally distilled to give a small amount of 3-methyl heptatriene-2,4,6 osmium tricarbonyl, and elemental as well as infrared analysis confirms this.

Example V

A reaction time of only two hours produces a measurable yield as shown when 13.6 grams decatriene-3,5,7 mixed with 12.0 grams ruthenium pentacarbonyl is refluxed in air for this length of time and then promptly distilled.

Example VI

In some cases it is advantageous to have an excess of the pentacarbonyl in the reaction mixture, as when the triene is available in only limited amounts. As an instance of such an operation 8.0 grams (0.04 mole) of iron pentacarbonyl is reacted with 2.2 grams (0.008 mole) 5,8-dibutyl dodecatriene-4,6,8, at 180° C. in nitrogen for ten hours. The progress of the reaction is readily followed by collecting and measuring the amount of non-condensible water-insoluble gas evolved. At the end of the ten hours over 50% of the theoretical amount of gas is collected, and fractional distillation yields over one cubic centimeter of the desired product.

The uncomplexed double bond in my compounds has been shown to be present by hydrogenation reactions and the characteristic uncomplexed C=C absorption in the infrared region.

The new compounds of the present invention decompose at elevated temperatures, generally above 350° C., and deposit films of metal upon such decomposition. This film deposit is in the form of a metallic mirror when carried out gradually, and more or less irregular when the decomposition is vigorous. The presence of halogen in the compound reduces the deposit formation, so that for vapor coating use, the unhalogenated products are preferred.

The unsaturated triene iron carbonyls as well as all the above derivatives can be used to improve the combustion of fuels such as domestic fuel oil, bunker fuel oil, diesel fuel, kerosene, jet engine fuel and paraffin wax. The triene iron carbonyls themselves all have very low melting points, most of them being liquid at ordinary temperatures, so that they make more desirable combustion additives than ferrocene, for example. As little as 0.1% of these additives reduces soot formation materially in the above fuels, notwithstanding the presence of olefinic unsaturation which heretofore has been considered to promote soot formation. The triene iron carbonyls as well as the dihydroxylated derivatives referred to above, are also suitable for use as antioxidants in protecting natural as well as synthetic rubbers against the deteriorating influences of ultraviolet light and air.

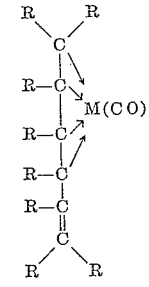
The range of temperatures at which the triene iron carbonyls are formed from the above-mentioned reactants, is quite broad. At 80° C. there is a definite reaction although it is quite slow. Above about 275° C. the trienes tend to decompose too rapidly. A preferred temperature range is from 110° to 230° C. The reaction times can vary from about one-half hour to twenty hours and substantially quantitative yields are obtained by carrying out the reaction until the gas evolution is 100% of the theoretical. The addition of 0.01 to 1% of a polymerization inhibitor, as in Example II, reduces losses of triene to by-product formation.

Inasmuch as the more complex carbonyls of the iron subgroup metals are more or less freely convertible to a simpler and more reactive form, especially under the reaction conditions, any of these complex carbonyls can be used in the reaction. These carbonyls appear to behave as though they form a metal tricarbonyl moiety which is consumed about as fast as it is formed, so that the same triene reaction takes place even when the trienes contain substituents which are inert to the reaction mixture. Thus, halogen atoms or ether groups can be contained in the trienes without changing the essential results.

Obviously many modifications and variations of the present invention are possible in the light of the above teachings. It is, therefore, to be understood that within the scope of the appended claims the invention may be practiced otherwise than as specifically described.

What is claimed:

1. A triene metal tricarbonyl having the formula

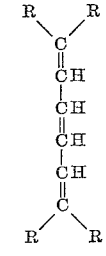


wherein the R radicals are selected from the class consisting of hydrogen and univalent hydrocarbyl radicals containing from one to eight carbon atoms, said radicals being selected from the class consisting of alkyl, aryl, and cycloalkyl radicals, the total number of carbon atoms in the triene molecule being from 6 to about 20 and M is an iron subgroup metal.

2. The compounds of claim 1 wherein the triene is alloocimene.

3. Alloocimene iron tricarbonyl.

4. A process for preparing a triene tricarbonyl compound of an iron subgroup metal comprising the step of reacting an acyclic triene hydrocarbon having the formula



wherein the R radicals are selected from the class consisting of hydrogen and univalent hydrocarbyl radicals containing from one to eight carbon atoms, said radicals being selected from the class consisting of alkyl, aryl, and cycloalkyl radicals, the total number of carbon atoms in the molecule being from 6 to about 20, with a pentacarbonyl of an iron subgroup metal.

5. Process for preparing alloocimene iron subgroup metal tricarbonyl compounds comprising the step of reacting alloocimene with an iron subgroup metal pentacarbonyl.

6. Process for preparing alloocimene iron tricarbonyl, said process comprising the step of reacting alloocimene with iron pentacarbonyl.

References Cited in the file of this patent

Burton et al.: Chemistry and Industry, Nov. 29, 1958, page 1592.