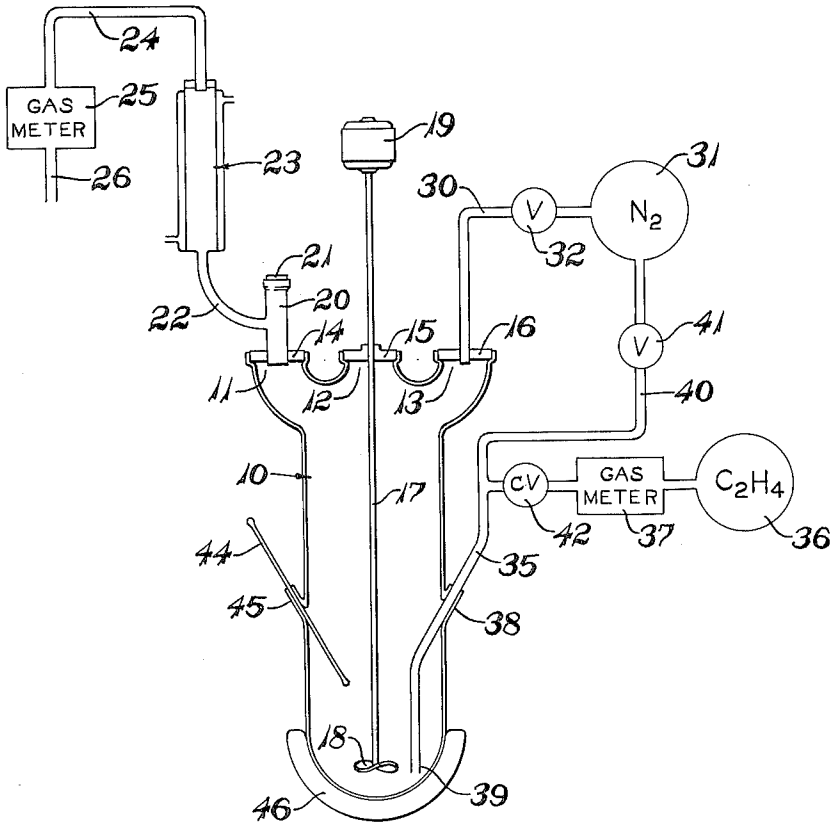
March 28, 1961 M. E. ROHA ET AL 2,977,381

ORGANO-METAL COMPOUNDS AND PRODUCTION THEREOF

Filed Jan. 16, 1956



United States Patent Office 2,977,381
Patented Mar. 28, 1961

2,977,381

ORGANO-METAL COMPOUNDS AND PRODUCTION THEREOF

Max E. Roha, Brecksville, and Warren L. Beears, Cleveland, Ohio, assignors to Goodrich-Gulf Chemicals, Inc., Pittsburgh, Pa., a corporation of Delaware

Filed Jan. 16, 1956, Ser. No. 559,505

11 Claims. (Cl. 260—448)

This invention relates to certain organo-metal compounds and more especially to hydrocarbon-metals containing hydrocarbon chains having moderately high numbers of carbon atoms, which higher organo-metals are adapted to serve as intermediates for the production of a variety of organic chemicals.

This invention in its principal embodiments relates to a novel process for producing higher hydrocarbon-metals, and to higher hydrocarbon-metals produced thereby, and comprises in substance starting with a simple or lower hydrocarbon-metal and by chain growth from alpha-olefin units insert hydrocarbon groups between a carbon of the original hydrocarbon groups and the metal, and thus to build up higher hydrocarbon-metals by increasing the number of carbon atoms in each of the hydrocarbon groups. These higher hydrocarbon-metals may be converted into the corresponding higher alcohols by oxidation of the higher hydrocarbon-metals and then by hydrolyzing the resulting oxidation products, as described in our copending application, Serial No. 555,273, filed December 27, 1955.

An object of this invention is to produce higher hydrocarbon-metals of high quality by chain growth of alpha-olefin units built into a simple or lower hydrocarbon-metal between the hydrocarbon and the metal at substantially atmospheric pressures and at room or moderate temperatures, in relatively short times, and in simple inexpensive equipment that brings the cost of plant and equipment down to a point which makes the production of the higher hydrocarbon-metals a practical commercial operation and that produces higher hydrocarbon-metals the chain lengths of which can be controlled.

A further object of this invention is to produce higher hydrocarbon-metals by a novel process that makes it possible to produce, from low hydrocarbon-metals, by gradual chain growth, higher hydrocarbon-metals having substantially any desired number of carbon atoms in the higher hydrocarbon chains, and to stop the chain growth at a point in the building up of the hydrocarbon chains which will provide higher hydrocarbon-metals of the desired chemical structure. Other objects will be apparent from the following specification.

It is well known that certain metals combine with simple hydrocarbon radicals, a carbon atom of the hydrocarbon radical linking directly with the metal atom to form a class of compounds herein referred to as lower hydrocarbon-metals.

The metals of the lower hydrocarbon-metals which constitute a starting material in the process of this invention include those metals occurring on the right hand side of the "periodic chart of the elements," which is a well-known chart reproduced on pages 392 and 393 of "Handbook of Chemistry and Physics," published by Chemical Rubber Publishing Company, Cleveland, Ohio, in 1954. The preferred lower hydrocarbon-metals of this application are hydrocarbon-aluminums, although the metal-organic compounds in which the organic component is a

hydrocarbon radical having from 2 to 8 carbon atoms and the metal component is an element occurring on the right-hand side of the "Periodic Chart of the Elements," as charted on page 393 of the above identified "Handbook," which metal-organic compounds are well known, being listed on pages 624 to 663 of the above identified "Handbook." The metal components of the lower hydrocarbon-metals include, among others, aluminum, antimony, bismuth, cadmium, copper, gallium, germanium, indium, lead, mercury, thallium, tin and zinc.

In the specification and claims of this application, the above identified "periodic chart of the elements," as it appears on pages 392 and 393 of the said "Handbook of Chemistry and Physics," is referred to simply as "the periodic chart of the elements"; the heavy metals charted on page 392 as "the heavy metals occurring on the left hand side of the periodic chart of the elements"; and include, among others, titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, iron, osmium, cobalt and nickel.

The hydrocarbon radicals of the lower hydrocarbon-metals are preferably the simple alkyl radicals, such as ethyl, propyl, butyl, amyl, hexyl, heptyl and octyl; simple cycloalkyl radicals such as cyclopentyl, methyl cyclopentyl, cyclohexyl, methylcyclohexyl and the like; simple aryl radicals, such as phenyl, tolyl, and xylyl; simple aralkyl radicals such as styryl, methylstyryl, ethyl-phenyl, indyl and the like.

The simple or lower hydrocarbon-metals into which the alpha-olefin units are built by chain growth are of the general formula

$$R_m—Me—X_n \qquad (1)$$

wherein R represents a hydrocarbon radical, either alkyl, cycloalkyl, aryl, or aralkyl, of the character enumerated in the preceding paragraph, Me represents one of the metals occurring on the right hand side of the periodic chart of the elements, X represents a monovalent substituent, either hydrogen or a halogen, such as chlorine, bromine, iodine or fluorine, and m and n are digits whose sum totals the valency of Me, and of which n, but not m, may be zero.

The novel process of this application for producing the higher hydrocarbon-metals may be represented by the following general equation:

$$R_m—MeX_n + N\cdot CH_2=\underset{R^2}{\overset{R^1}{C}} \longrightarrow \left[R\left(CH_2—\underset{R^2}{\overset{R^1}{C}} \right)_y \right]_n —Me—X_n \qquad (2)$$

wherein R, Me, X, m and n have the same significance as in Formula 1 above; N represents the number of alpha-olefin molecules entering into chain growth; R^1 and R^2 represent hydrogen or the same or different hydrocarbon radicals above set forth; and y represents the mean number of alpha-olefin molecules which are built into each of the m higher hydrocarbon chains as alkylidene radicals.

A preferred embodiment of the invention of this application as indicated by experience up to this time, is the production of higher hydrocarbon-aluminums in which the alpha-olefins are built into low hydrocarbon-aluminums by chain growth between the aluminum atom and a carbon of the original hydrocarbon groups linked to the aluminum atom.

The production of the higher hydrocarbon-aluminums is accomplished by the chain growth of alpha-olefin molecules into a low hydrocarbon-aluminum between the aluminum atom and a carbon atom of the original hydrocarbon radicals, the size of, or the number of carbon atoms in, the hydrocarbon chains so grown being controlled by regulating the amount of the alpha-olefin that is taken up in the chain-growth action.

GENERAL EXAMPLE

As illustrative of the fundamentals of this invention, the following general example is given:

Triethyl aluminum and aluminum trichloride are added to dry xylene in a suitable reaction vessel, or reactor, under a blanket of dry nitrogen, and the reactor contents stirred to obtain an intimate admixture. Then, titanium tetrachloride is added to the reactor contents with stirring continued for some time. There is formed in the reactor contents, which is a clear liquid, a catalyst complex that is capable of activating the gradual chain growth of alpha-olefin units in the triethyl aluminum in the manner indicated in the above Equation 2. However, up to this point, no chain growth has taken place.

An alpha-olefin in a gaseous state, for example, ethylene, is bubbled through the reactor contents containing the catalyst complex in a constant stream, until a sufficient amount of the alpha-olefin, as determined by means later described in detail, has been taken up by the low hydrocarbon-aluminum to produce the desired chain growth of the original hydrocarbon radicals.

Extensive experimentation indicates that chain growth continues under proper conditions as long as the alpha-olefin is bubbled through the reactor contents containing the catalyst complex, at least within the useful range of chain growth, and that chain growth is gradual and continuous, and involves the growing of alpha-olefin molecules into the low hydrocarbon-aluminum. In certain instances, it has been noted that all of the growing chains of the hydrocarbon-aluminum do not grow at the same rate. Experimental evidence to date, however, indicates that where one chain grows more slowly than another that the slow-growing chain is activated through chain transfer to grow more rapidly so as to tend to even up the chain growth in the several hydrocarbon chains. This is substantiated by experimental evidence which shows that in the process of this invention the chain sizes, or number of carbon atoms in the chain, produced by chain growth are for the most part within a definite range. Thus, if the hydrocarbon-aluminum chains are grown to an average C_{20} length, the resulting hydrocarbon chains are mainly of the C_{20} length and the remainder are largely in the C_{18} to C_{22} range. This makes it feasible to segregate by fractional distillation the higher hydrocarbon-aluminum having the C_{20} built-up chain length. For many uses as an intermediate it is unnecessary to separate out the major constituents, since the mixed higher hydrocarbon-aluminums constitute an intermediate that is useful for many purposes, and particularly for the production of plasticizers.

Taking a lower hydrocarbon-metal, in which the metal has a valency of 3, by way of illustration, the following starting hydrocarbon-metals may be employed in the process of this invention:

i. Lower trihydrocarbon-metal	R_3Me
ii. Lower dihydrocarbon-metal halide	R_2Me Halogen
iii. Lower hydrocarbon-metal dihalide	RMe $Halogen_2$
iv. Lower dihydrocarbon-metal hydride	R_2MeH
v. Lower hydrocarbon-metal dihydride	$RMeH_2$

all of which are herein referred to generically as lower hydrocarbon-metals for the purposes of this invention.

In the preparation of the lower hydrocarbon-metals, the end product frequently contains two or more of the above indicated, i to v, or similar lower hydrocarbon-metals. Such mixtures may be employed as the starting lower hydrocarbon-metals and such a mixture is herein generically referred to as a mixture of lower hydrocarbon-metals.

By the process of the above General Example, all of the lower hydrocarbon-aluminums are operative, either alone or in admixtures, to produce by chain growth useful higher hydrocarbon-aluminum intermediates. Just what chemical compounds are formed in the process of producing the higher hydrocarbon-aluminums are not now known, and the explanations in the succeeding paragraph are not to be considered in limitation of the invention or of the claims of this application.

Wide experience with the hydrocarbon-aluminums indicates that when a dihydrocarbon-aluminum halide, as diethyl aluminum chloride, is employed as the starting lower hydrocarbon-metal, the chain growth is built up only on the two hydrocarbon groups, the chlorine atom attached to the metal atom blocking any chain growth between the halide and the metal. However, chain growth restricted to the two hydrocarbon groups produces a higher hydrocarbon-aluminum with carbon chains of determinate size, that is, the number of carbon atoms resulting from the chain growth. Such higher hydrocarbon-metals are useful intermediates, as in the production of higher alcohols. Similarly, starting with a hydrocarbon-aluminum dichloride, chain growth is restricted to the one hydrocarbon attached to the aluminum, and is operable to produce useful intermediates, although it would seem at present that such intermediates are less desirable. In the case of the lower hydrocarbon-aluminum hydrides, the alpha-olefin reacts to convert the hydride to a hydrocarbon group during the chain growth reaction, and the hydride may be so converted prior to the chain growth reaction and this is commonly done.

In brief, the lower hydrocarbon-aluminums are all capable by chain growth of producing higher hydrocarbon-aluminums which are useful intermediates.

As has been indicated above, other lower organometals, that can be converted to hydrocarbon-metals of the Formula 1 above, can also be used as starting materials.

As to the catalyst complex referred to in the above General Example, all that can be stated at present is that a catalyst complex is formed in the mixture of the lower hydrocarbon-aluminum, aluminum trichloride and titanium tetrachloride. What interaction takes place between these chemical compounds and what is the nature of the catalyst complex formed, is not known, although extensive experimentation has been carried on to find the answer to these questions. All that is known at present is that a catalyst complex is formed which directs a gradual chain growth of hydrocarbon units between the original hydrocarbon groups and the metal of the lower hydrocarbon-metal.

However, it has been ascertained that in the place of each of these three chemical compounds, other chemical compounds may be employed in the process of this invention.

(*a*) In place of the triethyl aluminum of the General Example, there may be employed the hydrocarbon-metals of the formula R_m—Me—X_n (1) above, more fully hereinabove described.

(*b*) In place of the aluminum trichloride of the General Example, there may be employed a compound containing a halogen linked to a metal occurring on the right hand side of the periodic chart of the elements, which compound has a generic formula

$$Y_h\text{—Me—}(Ha)_k \qquad (3)$$

in which Y is any monovalent substituent, Me is a metal occurring on the right hand side of the periodic chart of the elements, Ha is a halide or an oxyhalide, and *h* and *k* are digits whose sum totals the valency of Me and of which *h* but not *k* may be zero.

It will be seen that the compounds of Formula 1 may overlap the compounds of Formula 3. Thus, by way of illustration, if R of Formula 1 and Y of Formula 3 are each ethyl, Me in each formula is aluminum, and X in Formula 1 and Ha in Formula 3 are each chlorine, then diethyl aluminum chloride and ethyl aluminum dichloride would come within both the Formula 1 and the Formula 3. In the event that the lower hydrocarbon-metal, or any substantial part thereof, falls within the Formula 3,

then it becomes unnecessary to add to the lower hydrocarbon-metal a compound of the formula

$$Y_h—Me—(Ha)_k$$

since it is already present in the starting hydrocarbon-metal. However, its addition is permissible.

In other words, the whole or a substantial part of the admixture of compound (*a*) plus compound (*b*), to which the compound (*c*) is added, need be a compound of the Formula 3 in order to secure high yields of the higher hydrocarbon-metals.

(*c*) In place of the titanium tetrachloride of the above General Example, there may be employed a compound containing a halogen linked to a heavy metal occurring on the left hand side of the periodic chart of the elements, which compound has the general formula

$$Me^t(An)_p \qquad (4)$$

wherein Me^t is a heavy metal occurring on the left hand side of the periodic chart of the elements. An is an anion, and *p* is the maximum valency of Me^t. Thus, the heavy metals include, among others, titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, rhenium, iron, ruthenium, osmium, cobalt, rhodium, iridium, nickel, palladium, platinum, thorium and uranium. Especially effective are the soluble halides and acetyl acetonates of the heavy metals Me^t.

The molar ratios of the chemicals above referred to under (*a*), (*b*) and (*c*) above, may be varied widely. Thus, the molar ratios of (*a*) and (*b*) combined to (*c*) preferably range from 50:1 to 400:1, although higher and lower ratios may be employed. The molar ratios of (*a*) to (*b*) above are not critical, since it is possible for (*a*) and (*b*) each to be wholly of the Formula 1 and at the same time of the Formula 3. Where, however, the compound (*a*) of the Formula 1 does not fall within the scope of Formula 3, then the molar ratio of (*a*):(*b*) should be preferably within a range of 1.5–5.0:1, although higher and lower molar ratios, give satisfactory results.

The process of this invention is carried out in circumambient inert fluid medium, either a gaseous medium or a combined inert liquid and gaseous medium, which media are practically non-reactive with the constituents of the reaction as well as with the resulting higher hydrocarbon-metals. The inert gaseous media include nitrogen, helium, argon and like gases. The inert liquid media include the inert liquid hydrocarbons, such as a saturated alkane, among which are butane, hexane, pentane, heptane, octane and the like, or mixtures thereof, such as "Deobase" kerosene, or the mixture of alkanes resulting from the "Fischer-Tropsch" process, or a cyclo-alkane, such as cyclohexane or methyl cyclohexane and the like, or a benzene hydrocarbon, such as benzene, toluene, xylene and the like, or mixtures of any of them. It is important that both the liquid and gaseous media be free of oxygen and water, and also preferably from impurities, especially peroxides, sulfur compounds, and compounds containing active hydrogen.

It is here noted that the amount of the inert solvent with relation to the amount of the active chemicals, hereinabove set out in detail, is not critical. In fact, where a mobile liquid hydrocarbon-metal is employed, such as triethyl aluminum, triisobutyl aluminum and the like, the inert solvent may be dispensed with and the reaction carried on without the solvent in an inert atmosphere of dry nitrogen. An inert solvent of the character hereinabove in the preceding paragraph set forth, is however desirable, since it acts as a diluent and slows down the chain growth of the alpha-olefin molecules into the hydrocarbon-metal, and thus makes it possible to regulate and more accurately control the rate of chain growth and to stop chain growth at the proper build-up of the chains. There are therefore no critical limits to the amount of solvent relative to the amounts of the other ingredients. It will normally be desirable to have the ratio of solvent to lower hydrocarbon-metal from 10 : 1 to 100 : 1, with a ratio of 40–50:1 being preferred.

It is also here noted that the inert circumambient gas, such as nitrogen, may be replaced by the alpha-olefin gas, such as ethylene, entering into the chain growth of the hydrocarbon-metal. It is generally preferable to start with nitrogen as the inert gaseous blanket, and, after the reaction has started, to wash out the nitrogen with the ethylene, and then to utilize the ethylene as the blanket over the reacting liquids throughout the reaction period. After the reaction, nitrogen gas can be bubbled through the liquid reactor contents to remove excess ethylene from the liquid contents and to replace the overlying blanket of ethylene with nitrogen.

While this invention is not limited to any specific apparatus for carrying out the novel process thereof, it is believed that the process may be more readily understood by reference to the apparatus of the drawing in which Fig. 1 is a schematic representation of an apparatus in which the novel process of this invention may be carried out. The invention is not, however, limited to any specific apparatus.

In the drawing, a reactor, or reaction vessel **10**, is equipped at its upper end with three necks **11**, **12**, **13**, connecting with the reaction vessel **10** and sealed with stoppers **14**, **15**, **16**. Through the central neck **12** and stopper **15** is mounted a stirring rod **17** having at its lower end a turbine stirrer **18** and at its upper end a motor **19**. One of the side necks **11** has mounted in the stopper **14** a tube **20** having a stopper **21** fitting into its upper end, and a branch tube **22** extending laterally and upwardly to a condenser **23** which may be of any of the usual types of reflux condenser. The stopper **21** may be removed for charging materials into the reactor **10**, but is otherwise sealed into tube **20**. Also, liquid may be charged into the reactor **10** by a hypodermic syringe through tube **20**. The tube **22** conducts the gases discharged from reactor **10** to the condenser **23** and also the condensate from the condenser **23** back to the reactor **10**. The gases discharged from the condenser **23** are conducted through pipe **24** to a standard wet gas meter **25**, where the volume of gases passing pipe **24** is measured and the measurement recorded, prior to discharge through pipe **26**. The other side neck **13** of reactor **10** and its stopper **16** are connected with a pipe **30** connecting a source of dry nitrogen, as pressure tank **31**, with the reactor **10**, a valve **32** in pipe **30** being provided to control the flow of nitrogen into reactor **10**.

A tube **35** conducts the alpha-olefin in gaseous form from a source of supply **36**, as a pressure cylinder, through a standard gas meter **37** for measuring dry gases and recording the volume, the gases passing through pipe **35**, which enters reactor **10** through a branch tube **38**, to the bottom of reactor **10**, as shown at **39**.

A pipe **40** having a control valve **41** leads from the source of dry nitrogen **31** to pipe **35**, so as to be able to bubble nitrogen through the end **39** of pipe **35** beneath the surface of the reactor contents. A check valve **42** in pipe **35** between the point where pipe **40** joins pipe **35** and the ethylene inlet gas meter prevents the nitrogen from entering the inlet gas meter. A thermometer **44** is mounted in a branch tube communicating with the reactor **10** so as to be normally below the reactor contents.

Heating and cooling elements for the reactor may be provided. As shown, a heat exchanger unit **46** is contiguous to the outside of the lower part of reactor **10**.

EXAMPLE I

Heat the reactor **10** and at the same time flow dry nitrogen gas through pipe **30** from supply **31** through the reactor **10** to remove any absorbed moisture, discharging the gases and vapors through pipe **22**, condenser **23** and meter **25** to atmosphere. This may be done over

a considerable period of time to assure complete displacement of air and moisture in the apparatus by nitrogen. Cool the reactor **10**, and, while maintaining a positive nitrogen pressure in reactor **10**, add to reactor **10**, as through tube **20**, 8.85 g. (0.066 mole) of anhydrous aluminum trichloride from a weighing bottle and then add 90 milliliters of dry xylene. Seal the reactor **10** and stir contents of reactor **10** for several minutes at room temperature. A red colored liquid forms. Now, add 10.37 g. (0.091 mole) of triethyl aluminum to reactor **10**, as through tube **20**, while maintaining a positive pressure of nitrogen in the reactor. Close the reactor. A colorless liquid results with the evolution of some gas. Stir the reactor contents for several minutes at room temperature, and then bubble ethylene gas through pipe **35** through the contents of reactor **10** for 20 minutes while heating to 120° C. Cool reactor contents to room temperature, while bubbling ethylene gas through the reactor contents, which are now a straw colored liquid. The ethylene reacts with any hydride so as to eliminate it from the reactor contents. Cut off flow of ethylene gas and bubble nitrogen gas through the reactor contents for one hour to remove the ethylene from the solution. Add 8 milliliters of a benzene solution containing 0.2 millimoles of titanium tetrachloride per cc. of solution, in all 0.0016 mole of titanium tetrachloride, as through tube **20**, while keeping a positive pressure of nitrogen in reactor. Dilute with 210 milliliters of dry xylene. A clear amber colored liquid results. The reactor contents now contains the catalyst complex for the chain growth action. Up to this time no ethylene has been taken up in chain growth by the triethyl aluminum.

Heat the reactor contents to about 60° C. and maintain approximately that temperature, while bubbling ethylene gas through the reactor contents in a slow steady stream. Record at short intervals from the inlet gas meter the inlet volume of ethylene gas and from the outlet gas meter the outlet volume of gas. The difference is indicative of the amount of ethylene being taken up by the triethyl aluminum in chain growth. From these tabulated results can be computed the mean size of the chain growth on the aluminum triethyl:

Table I

Time of Reaction in Min.	Inlet Meter in Liters	Outlet Meter in Liters	Total Ethylene Take-Up		Mean Length of Alkyl Chains
			in Liters	in Moles	
0	0	0	0	0	C_2
10	7.8	7	0.8	0.033	C_4
20	18.5	14.5	4.0	0.163	C_6
30	29.1	21.0	8.1	0.333	C_8
41	39.2	27.5	11.7	0.476	C_{10}
51	50.4	34.5	15.9	0.647	C_{12}
74	67.2	48.5	18.7	0.762	C_{14}
93	83.0	57.0	26.0	1.06	C_{16}
115	99.5	69.5	30.0	1.22	C_{18}
128	108.5	75.0	33.5	1.36	C_{20}

It is to be noted from the above tabulation and calculations made thereon that the chain growth is gradual and continuous and that the mean number of carbon atoms in the growing alkyl chains can be determined at any stage and the addition of ethylene to the reactor contents cut off at a stage which will yield the desired mean number of carbon atoms in each of the built-up alkyl chains. Thus, if the reaction were stopped at the end of 51 minutes, the mean number of carbon atoms in the alkyl chains would be C_{12}; if at the end of 93 minutes, C_{16}; if at the end of 115 minutes, C_{18}; and at the end of 128 minutes, C_{20}. Since the purpose of this experiment was to produce higher triethyl aluminums of a mean chain size of C_{20}, the flow of ethylene to the reactor was cut off at 128 minutes.

Thus, it is possible by a close following of the chain growth build-up to stop the reaction at a point to give substantially the desired mean number of carbon atoms in the higher alkyl chain.

In the above Example I, the molar ratio of aluminum triethyl to titanium tetrachloride is 57:1, and of the aluminum trichloride to titanium tetrachloride, 41:1. That is, the molar ratio of aluminum triethyl to aluminum trichloride to titanium tetrachloride is 57:41:1.

As an illustration of the utility of higher hydrocarbon-metals produced as described in above Example I, a higher alcohol corresponding to the built-up hydrocarbon chain C_{20}, namely, n-eicosanyl alcohol, known commercially as n-eicosanol, may be produced from the tri-n-eicosanyl aluminum, formed in Example I, by oxidizing the higher hydrocarbon-metal and hydrolyzing the resulting oxidation product, all as fully set out in our copending application Serial No. 555,273.

EXAMPLE II

Utilizing the same apparatus and the same procedure as in Example I, flame the reactor while flowing dry nitrogen gas therethrough to remove absorbed moisture. Cool the reactor under nitrogen to room temperature. Place in the reactor 8.1 g. (0.06 mole) of anhydrous aluminum trichloride and 200 milliliters of dry xylene, all under a blanket of dry nitrogen. Stir the reactor contents for several minutes. A red colored liquid results. Add 17.8 g. (0.091 mole) of aluminum triisobutyl, as from a hypodermic syringe. A clear colorless liquid results. Bubble ethylene into the reactor contents before and after the addition of the aluminum triisobutyl to remove any hydride present. Up to this point no ethylene is taken up in chain growth by the aluminum triisobutyl.

Heat the reactor contents to about 80° C. while stirring. Add to reactor contents 3.6 milliliters of benzene solution containing 0.25 millimole of titanium tetrachloride to 1 cc. of benzene solution, in all 0.0009 mole of titanium tetrachloride.

Now, bubble ethylene in a steady continuous stream slowly through the reactor contents while stirring and record at short intervals from the inlet gas meter the inlet gas volume and from the outlet gas meter the outlet volume. The difference is indicative of the amount of ethylene gas being taken up by the aluminum triisobutyl in chain growth. From these recorded results and from computations made therefrom, the mean length of the chain growth at any time may be substantially determined.

Table II

Time of Reaction in Min.	Inlet Meter in Liters	Outlet Meter in Liters	Total Ethylene Take-Up		Mean Length of Alkyl Chains
			in Liters	in Moles	
0	0	0	0	0	C_4
15	7.3	2.52	4.82	1.96	C_6
30	14.2	4.7	9.5	3.86	C_8
50	22.8	7.6	15.2	6.15	C_{10}
70	31.8	11.8	20.0	8.1	C_{12}
90	40.5	15.35	25.15	10.06	C_{14}
110	48.2	18.0	30.2	12.4	C_{16}
130	57	22.1	34.9	14.3	C_{18}
155	68.0	26.7	41.3	17.8	C_{20}

It is to be noted from the above tabulation and calculations made thereon that the mean number of carbon atoms in the grown chains can be approximated at any stage of the chain growth, and the addition of ethylene stopped. In the above Example II, it was the purpose to obtain a higher isobutyl aluminum of a mean chain length of C_{20}.

Note also that in the above Example II, the molar ratio of aluminum triisobutyl to titanium is 100:1, and the molar ratio of aluminum triisobutyl to aluminum trichloride to titanium tetrachloride is 100:66:1.

EXAMPLE III

Utilizing the same apparatus and procedure as in Example I, but employing an alkyl metal halide, namely, diisobutyl aluminum chloride, a higher alkyl aluminum chloride is produced according to the following equation:

$$(C_4H_9)_2AlCl+nC_2H_2 \longrightarrow \left[C_4H_9(CH_2-CH_2)_n\right]_2-Al-Cl$$

without employing a Y_h—Me—$(Ha)_k$ compound.

As in the preceding examples, flame the reactor while flowing dry nitrogen therethrough to remove absorbed moisture. Cool the reactor under a positive pressure of dry nitrogen to room temperature. Place in the reactor 25.9 g. (0.151 mole) of diisobutyl aluminum chloride and add 290 milliliters of dry xylene, all while maintaining a positive pressure of dry nitrogen. Bubble ethylene through the reactor contents, and, while the bubbling is continuing, add 3.6 milliliters of an xylene solution containing 0.25 millimole of titanium tetrachloride per milliliter of solution, in all 0.0009 mole of titanium tetrachloride, all while stirring. Record as in previous examples and compute from the recorded results the mean size of the chain growth, having in mind that chain growth takes place only between the two original isobutyl groups and the aluminum, and that no chain growth takes place between the chlorine atom and the aluminum.

Table III

Time of Reaction in Min.	Inlet Meter in Liters	Outlet Meter in Liters	Total Ethylene Take-Up		Mean Length of Alkyl Chains
			in Liters	in Moles	
0	0	0	0	0	C_4
10	4.8	1.6	3.2	1.30	C_6
20	9.4	3.0	6.4	2.57	C_8
34	15.2	5.0	10.2	4.1	C_{10}
47	21.2	7.8	13.4	5.4	C_{12}
60	27.0	10.2	16.8	6.71	C_{14}

It is to be noted from the above table that the mean number of carbon atoms in the built-up chains can be approximated at any stage of the chain growth. In the above Example III, it was the purpose to obtain a higher isobutyl aluminum chloride of the following formula:

$$\left[C_4H_9(CH_2-CH_2)_5\right]_2-Al-Cl$$

and therefore the flow of ethylene to the reactor was cut off at the end of 60 minutes.

EXAMPLE IV

It is the purpose of this example to demonstrate that a higher hydrocarbon-metal can be produced from a lower hydrocarbon-metal without the use of an inert solvent or an inert gaseous medium, such as is employed in Examples I, II and III, but that the process of this invention may be carried out in a circumambient atmosphere of a gaseous alphaolefin without the use of inert solvent or inert gaseous medium.

Heat the reactor and pass ethylene gas through the reactor to remove all the air and moisture. Cool the reactor, and, while maintaining a positive pressure of ethylene in the reactor, charge the reactor with 103 g. (0.52 mole) of triisobutyl aluminum, which is a thin mobile liquid, and then add 34.8 g. (0.26 mole) of anhydrous aluminum trichloride, as from a weighing bottle. The temperature in the reactor rises to near 100° C. After allowing the reactor contents to cool to say about 30° to 40° C. heat the reactor contents to around 80° C. and add 0.974 g. (0.0052 mole) of titanium tetrachloride, all with a positive pressure of ethylene in the reactor and continuous stirring of the reactor contents.

Now, bubble ethylene in a steady stream slowly through the reactor contents. Record at intervals from the gas inlet meter the inlet ethylene volume and from the outlet gas meter the outlet gas volume. The difference is indicative of the amount of ethylene gas taken up by the triisobutyl aluminum in chain growth. When 8.1 moles of ethylene has been taken up, which, from Table II indicates that a higher triisobutyl aluminum of mean chain length of C_{12} has been formed, the flow of ethylene gas is stopped, and dry nitrogen passed through the reactor to flush out the excess ethylene and to provide an inert gaseous blanket over the reactor contents. The resulting product is a mobile liquid, which, when analyzed, is found to be a higher triisobutyl aluminum in which the alkyl chains have a mean length of 12 carbon atoms, or largely a higher triisobutyl aluminum of the formula

$$\left[C_4H_9(CH_2-CH_2)_4\right]_3Al$$

EXAMPLE V

As a further example of the process of this invention and its controllability to produce higher hydrocarbon-metal of a desired mean chain length, aluminum triethyl is subjected to chain growth by the process of this invention in its preferred form, so as to produce a mean chain length of C_{16}.

Taking the process of Example I as a standard by which day-by-day operations are to be carried out, and utilizing the same reactants in the same proportions as those employed in Example I, namely, 0.091 mole of triethyl aluminum, 0.066 mole of anhydrous aluminum trichloride and 0.0016 mole of titanium tetrachloride, that is, the quantities and the molar proportions of triethyl aluminum to aluminum trichloride to titanium tetrachloride being 57:41:1, the same as in Example I. Carrying out the process in the way described in detail in Example I, with 300 milliliters of xylene as the inert solvent, it is only necessary to observe and preferably record, which, in practical operations, is done by mechanical means, the amount of ethylene being taken up by the triethyl aluminum. For instance, where it is desired to produce a higher triethyl aluminum having a mean chain size of 16 carbon atoms, it is only necessary to stop the flow of ethylene to the reactor when the measuring devices indicate that 26.0 liters of ethylene have been taken up by the triethyl aluminum, since Table I of the standard Example I, indicates that when 26.0 liters of ethylene have been taken up, a higher triethyl aluminum in which the mean chain length of the alkyl chains is 16 carbon atoms has been formed; thus

$$(C_2H_5)_3Al+21CH_2=CH_2 \longrightarrow \left[C_2H_5(CH_2-CH_2)_{7.5}\right]_3Al$$

Similarly, other higher triethyl aluminums of other mean alkyl chain lengths may be readily produced.

It is clear from the examples above given that in making the periodic records of ethylene take-up during the chain growth, that the amount of ethylene take-up can be determined as the chain growth proceeds. It is consequently possible, by utilizing the technique of determining the amount of up-take of ethylene to tailor-make the higher hydrocarbon-metals and to duplicate results in successive runs, which is distinctly a novel feature of the process of this invention and which distinguishes and gives value to the novel process of this invention and makes it an outstanding contribution to the art.

While, in several of the examples, it has been noted that a positive pressure of the overlying blanket of inert gaseous medium is maintained, it is to be understood that such pressure is only that which is necessary to cause the flow of inert gaseous medium through the apparatus and to provide for a flow of the inert gas from the reactor to the atmosphere in the event that the introduction of any of the ingredients to the reactor might otherwise permit air to enter the reactor. The reaction is preferably carried out at near atmospheric pressures, although higher pressures may be employed without departing from the scope and spirit of the invention.

EXAMPLES VI AND VII

The above fundamentals of the chain growth principle of the process of this application are demonstrated by taking the process and procedure of Example I and (1) continuing the bubbling of ethylene through the reaction mixture for a total period of 10 hours, without other change, and (2) doubling the rate of the addition of ethylene to the reaction mixture, without other change:

Example	Time, minutes	Rate of Addition of Ethylene	Mean Chain Growth
I (control)	128	Control	C_{20}
VI	600	Same as Control	C_{100}
VII	128	2 Times Control Rate	C_{36}

It is here noted that mean size of the chains resulting from chain growth may be widely varied. Chain lengths of C_{100} to C_{500} are plainly within the scope of this invention, and all the experimental work so far points to the feasibility of extending the chain growth process to the production of higher hydrocarbon-metals having much longer built-up hydrocarbon chains.

EXAMPLES VIII TO X

In all the above examples, the alpha-olefin employed has in each case been ethylene. It is generally the preferred alpha-olefin to employ in the chain growth processes of this invention. However, other alpha-olefins may be employed, including aliphatic alpha-olefins, such as propylene, butene-1, pentene-1, hexene-1, heptene-1, octene-1, and the like, or alicyclic alpha-olefins, such as cyclohexene-1, methyl cyclohexene-1, cycloheptene-1, methyl cycloheptene-1, and the like, or aralkylenes, such as styrene, alpha-methyl styrene, phenyl ethylene, indene and the like.

In each of the Examples VIII to X, the process of Example I is repeated, the only change being the use of a different alpha-olefin. In each case, the lower hydrocarbon-metal is satisfactorily converted by chain growth to a higher hydrocarbon-metal.

Examples	Alpha-Olefin	Mean Chain Growth
I (control)	ethylene	C_{20}
VIII	propylene	C_{28}
IX	octene-1	C_{36}
X	indene-1	C_{58}

EXAMPLES XI AND XII

The temperature of the reaction mixture may be varied widely in the process of this invention. Thus, following the procedure of Example I above, in which a temperature of about 60° C. is maintained during chain growth, the reaction mixture of the Example I is cooled to 20° C. and chain growth developed the same as in Example I except for temperature (Example XI here). In another example (Example XII here) the reaction mixture is maintained during chain growth at a temperature somewhat below the boiling point of xylene (140° C.). In Example XI, the chain growth takes place similar to that of Example I, but at a slower rate, whereas in Example XII, the same chain growth takes place but at a somewhat faster rate:

Examples	Temperature, ° C.	Time, minutes	Mean Chain Growth
I (control)	60	128	C_{20}
XI	20	240	C_{16}
XII	120	90	C_{20}

EXAMPLES XIII TO XXXVI

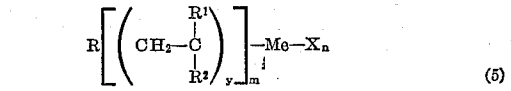
Following the general procedure of Example I, but utilizing (*a*) different starting hydrocarbon-metals of the formula R_m—ME—X_n; (*b*) different metal halides or oxyhalides of the formula R_h—Me—$(Ha)_k$; (*c*) different metal salts of the formula $Me^t(An)_p$; and (*d*) different molar ratios of the compounds (*a*), (*b*) and (*c*) above, similar higher hydrocarbon-metals are produced by chain growth as in the Example I.

In the interest of brevity and clarity, the Examples XIII to XXXVI, which yield useful higher hydrocarbon-metals with hydrocarbon chains from C_{12} to C_{100} chain lengths, are presented in tabulated form:

Table IV

Example	*a*	*b*	*c*	*a*:*b*:*c*
XIII	ethyl $AlCl_2$	$AlCl_3$	$TiCl_4$	50:10:1
XIV	diethyl AlH	$AlCl_3$	$TiCl_4$	50:25:1
XV	ethyl AlH_2	$AlCl_3$	$TiCl_4$	100:75:1
XVI	tripropyl Al	$AlCl_3$	$TiCl_4$	180:100:1
XVII	diisobutyl AlCl	$AlCl_3$	$TiCl_4$	100:66:1
XVIII	triisoamyl Al	$AlCl_3$	$TiCl_4$	180:45:1
XIX	tri-n-hexyl Al	$AlCl_3$	$TiCl_4$	75:50:1
XX	tri-n-heptyl Al	$AlCl_3$	$TiCl_4$	100:66:1
XXI	tri-n-octyl Al	$AlCl_3$	$TiCl_4$	159:40:1
XXII	di-n-octyl AlCl	$AlCl_3$	$TiCl_4$	240:100:1
XXIII	triphenyl Al	$AlCl_3$	$TiCl_4$	400:200:1
XXIV	tritolyl Al	$AlCl_3$	$TiCl_4$	380:100:1
XXV	trixylyl Al	$AlCl_3$	$TiCl_4$	180:45:1
XXVI	tricyclohexyl Al	$AlCl_3$	$TiCl_4$	400:100:1
XXVII	triethyl Sb	$ZnCl_2$	$FeCl_3$	100:66:1
XXVIII	tripropyl Cd	$BiCl_3$	$CoCl_3$	75:40:1
XXIX	triisobutyl Hg	$C_2H_5AlCl_2$	VCl_5	100:25:1
XXX	tetraethyl Ge	$C_2H_5AlCl_2$	$TiCl_4$	180:50:1
XXXI	pentacyclohexyl Bi	$BiCl_5$	$TiCl_4$	180:75:1
XXXII	triisobutyl Ga	$GaCl_3$	$TiCl_4$	100:66:1
XXXIII	diethyl Zn	$ZnCl_2$	$FeCl_3$	120:80:1
XXXIV	tetracyclohexyl Sn	$SnCl_4$	VCl_5	180:90:1
XXXV	diisobutyl In	$C_2H_5AlCl_2$	$TiCl_4$	360:100:1
XXXVI	diethyl Zn	$HAlCl_2$	$TiCl_4$	200:100:1

As has been above indicated, the lower hydrocarbon-metals of the formula R_m—Me—X_n, Formula 1 above, which constitute a starting material of the process of this invention, namely, lower hydrocarbon-metals in which R contains 10 or less carbon atoms, are known compounds. However, the higher hydrocarbon-metals produced by the chain growth process of this invention, namely, those in which the chain growth process of this invention has extended the original hydrocarbon chains to form higher hydrocarbon-metals having hydrocarbon groupings containing from 16 to 500 carbon atoms, and which are represented by the formula



(5)

in which all the symbols have the same significance as in General Equation 2, are new and useful chemical compounds and particularly, where *y* is 8 or more, novel and highly useful intermediates for the production of the higher alcohols and other compounds.

It is to be understood that variations in the procedure set forth in the specification and that modifications in the selection and proportions of the constituents utilized in the process, such as may be made by the usual knowledge of those skilled in the art, may be made without departing from the scope and spirit of the invention as set forth in the specification and in the following claims.

What is claimed is:

1. A method of producing at substantially atmospheric pressure a higher hydrocarbon-aluminum having a predetermined number of carbon atoms ranging from 10 to 100 in at least one of its hydrocarbon components by the chemical insertion of alkylidene radicals into a lower hydrocarbon-aluminum between the aluminum atom and a carbon atom of at least one of the hydrocarbon radicals of said lower hydrocarbon-aluminum, which carbon atom is linked directly to an aluminum atom, which method comprises preparing in inert circumambient fluid

media a liquid reaction medium initially consisting essentially of (*a*) a lower hydrocarbon-aluminum of the general formula R_m—Al—X_n, wherein R is a hydrocarbon radical having from 2 to 8 carbon atoms, X represents a monovalent substituent selected from the class consisting of hydrogen, chlorine, bromine and iodine, and *m* and *n* are digits whose sum totals 3 and of which *n*, but not *m*, may be zero, (*b*) aluminum trichloride, and (*c*) titanium tetrachloride; then passing an alpha-olefin having from 2 to 9 carbon atoms into intimate chemically reactive contact with the aforesaid liquid reaction medium at substantially atmospheric pressure gradually and relatively slowly over a period of time, measuring the amount of the alpha-olefin taken up in the chemical insertion of alkylidene radicals into the lower hydrocarbon-aluminum throughout the said period, and terminating the passing of the alpha-olefin into the liquid reaction medium when the measured amount of alpha-olefin so taken up indicates that the required number of alkylidene radicals have been chemically inserted into the said lower hydrocarbon-aluminum to yield the higher hydrocarbon-aluminum having the desired number of carbon atoms in at least one of its hydrocarbon radicals.

2. The method defined in claim 1 wherein the *n* of the formula R_m—Al—X_n is zero.

3. The method defined in claim 1 wherein the X of the above formula is chlorine and *n* is 1.

4. The method defined in claim 1 wherein the X of the above formula is chlorine and *n* is 2.

5. The method defined in claim 1 in which the formula R_m—Al—X_n represents triethyl aluminum.

6. The method defined in claim 1 in which the formula R_m—Al—X_n represents a tributyl aluminum.

7. The method defined in claim 1 in which the formula R_m—Al—X_n represents a trioctyl aluminum.

8. The method defined in claim 1 in which the formula R_m—Al—X_n represents diethyl-aluminum chloride.

9. The method defined in claim 1 in which the formula R_m—Al—X_n represents a dibutyl-aluminum chloride.

10. A method of producing at substantially atmospheric pressure a higher hydrocarbon-aluminum having a predetermined number of carbon atoms ranging from 10 to 100 in at least one of its hydrocarbon components by the chemical insertion of alkylidene radicals into a lower hydrocarbon-aluminum between the aluminum atom and a carbon atom of at least one of the hydrocarbon radicals of said lower hydrocarbon-aluminum, which carbon atom is linked directly to an aluminum atom, which method comprises preparing in inert circumambient fluid media a thoroughly admixed liquid catalyzed reaction medium consisting essentially of an anhydrous aluminum trichloride and a dry inert organic solvent, then adding to the resulting liquid composition with stirring a lower hydrocarbon-aluminum of the general formula R_m—Al—X_n, wherein R is a hydrocarbon radical having from 2 to 8 carbon atoms, X represents a monovalent substituent selected from the class consisting of hydrogen, chlorine, bromine and iodine, and *m* and *n* are digits whose sum totals 3 and of which *n*, but not *m*, may be zero; next bubbling in a gaseous state through the resulting liquid composition at substantially atmospheric pressure an alpha-olefin having from 2 to 9 carbon atoms to convert any aluminum hydrides present into hydrocarbon-aluminums, then bubbling through the liquid composition a stream of dry inert gas to wash out the residual alpha-olefin, adding to the resulting liquid composition with stirring titanium tetrachloride to complete the liquid catalyzed reaction medium, thereafter passing an alpha-olefin having from 2 to 9 carbon atoms into intimate chemically reactive contact with the resulting liquid reaction medium gradually and relatively slowly over a period of time, measuring the amount of the alpha-olefin taken up in the chemical insertion of alkylidene radicals into the lower hydrocarbon-aluminum throughout the said period, and terminating the passing of the alpha-olefin into the liquid reaction medium when the measured amount of alpha-olefin so taken up indicates that the required number of alkylidene radicals have been chemically inserted into the said lower hydrocarbon-aluminum to yield the higher hydrocarbon-aluminum having the desired number of carbon atoms in at least one of its hydrocarbon radicals.

11. A method of producing at substantially atmospheric pressure a higher hydrocarbon-aluminum having a predetermined number of carbon atoms in at least one of its hydrocarbon components by the chemical insertion of alkylidene radicals into a lower hydrocarbon-aluminum between the aluminum atom and a carbon atom of at least one of the hydrocarbon components of said lower hydrocarbon-aluminum, which carbon atom is linked directly to an aluminum atom, which method comprises preparing in inert circumambient fluid media a liquid catalyzed reaction medium consisting essentially of thoroughly intermixed anhydrous aluminum trichloride and dry xylene, then adding to said liquid composition with stirring a trialkyl aluminum in which the alkyl groups contain from 2 to 8 carbon atoms, thereafter bubbling through the resulting liquid composition ethylene to saturate the said resulting liquid composition with ethylene, next bubbling through the resulting liquid composition a stream of dry nitrogen to wash out the residual ethylene from the said liquid composition, then adding to the resulting liquid composition with stirring titanium tetrachloride to complete the liquid catalyzed reaction medium; thereafter passing ethylene into intimate chemically reactive contact with the liquid catalyzed reaction medium produced in the preceding step at substantially atmospheric pressure; gradually and relatively slowly over a period of time, measuring the amount of ethylene taken up in chemical reaction throughout the said period, and terminating the passing of ethylene into the liquid catalyzed reaction medium when the measured amount of ethylene taken up indicates that a requisite number of alkylidene radicals have been chemically inserted into said lower hydrocarbon-aluminum to yield a higher hydrocarbon-aluminum having the desired number of carbon atoms in at least one of its hydrocarbon radicals.

References Cited in the file of this patent

UNITED STATES PATENTS

2,181,640	Deanesly et al.	Nov. 28, 1939
2,699,457	Ziegler et al.	Jan. 11, 1955
2,826,598	Ziegler et al.	Mar. 11, 1958

FOREIGN PATENTS

534,792	Belgium	Jan. 31, 1955

OTHER REFERENCES

Grosse et al.: J. Organic Chemistry (1940), page 109.