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3,104,249

ORGANO-TITANIUM COMPOUNDS AND A PROCESS OF PREPARING THEM

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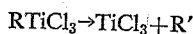
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Claims priority, application Germany Apr. 13, 1956

8 Claims. (Cl. 260-429.5)

The present invention relates to organo titanium compounds and a process of preparing them.

In spite of numerous attempts, it has hitherto been impossible to prepare organo-titanium compounds in which one or more alkyl groups are linked to the metal atom. It has, for example, been tried to prepare alkyl metal compounds of titanium by causing the ethereal solutions of magnesium alkyl halides or lithium alkyls to act upon titaniumtetrachloride. Such reactions did, however, not lead to the expected organo-titanium compounds. Instead, the transition of the tetravalent titanium to a lower valence was observed. From the course of the reaction it was suggested that a titanium alkyl halide, for example RTiCl_3 , was intermediately formed which, however, was not capable of existence and decomposed very rapidly according to the equation



Since all attempts to prepare titanium alkyls failed, it was generally assumed that, like in the other so-called transition metals, a combination of titanium and alkyl radicals which is capable of existence is not possible.

The present invention permits, inter alia, to prepare for the first time organo-titanium compounds in which compounds alkyl radicals are linked to the titanium and all other valences of the titanium are likewise bound by hydrocarbon radicals.

We have found that organo-titanium compounds in which one or more alkyl groups are linked to the metal atom can be obtained by causing titanium compounds of the general formula $(\text{R}_1)_2\text{TiX}_2$ wherein R_1 represents the cyclopentadienyl radical or a cyclopentadienyl radical substituted by one or more hydrocarbon radicals, and X represents alkoxy groups, halogen groups or another acid radical, to react, suitably in the presence of an inert diluent, with alkyl metal compounds of the elements of group I or II or subgroup II of the periodic table or of aluminum. As titanium compounds which can be converted with special advantage to organo-metal alkyl compounds according to the invention, there are mentioned the bis-cyclopentadienyl-titanium dihalides. It is to be understood that the term halogen is here meant to include also the pseudohalogens. X represents chlorine, bromine or iodine, the cyano group or thio-cyanate group, since the corresponding products are easier to obtain. Of these compounds there comes primarily into consideration the dichloride since it is easily accessible and can be prepared in a simple manner from cyclopentadienyl sodium and titanium tetrachloride. In many cases the bis-cyclopentadienyl-titanium-dialkoxy compounds are advantageously used. As alkoxy radicals are chiefly concerned those containing 1 to 4 carbon atoms such as methoxyl, ethoxyl, propoxyl, butoxyl or iso-butoxyl. If desired, the alkoxy groups may contain higher alkyl radicals, for example the ethylhexyl radical or the dodecyl radical.

Instead of the aforesaid compounds there may also be used the corresponding diacetates or the corresponding compounds with other acid groups for example sul-

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fate. If desired, compounds may be used in which the two radicals X are different.

The cyclopentadienyl radical may be substituted by one or more identical or different hydrocarbon radicals, preferably by aliphatic hydrocarbon radicals containing 1 to 4 carbon atoms. There come into consideration for example, methyl, dimethyl, ethyl, propyl, isopropyl or butyl compounds. If desired, there may also be used compounds such as dodecyl, phenyl, toluyl, benzyl or xylil compounds.

For reacting the above mentioned titanium compounds there are used according to the invention alkyl metal compounds of group I or II or sub-group II of the periodic table or of aluminum. In view of their high reactivity and easy preparation, magnesium alkyl halides, known as Grignard's compounds and lithium alkyl compounds, for example methyl compounds, are especially suitable. There may also be used with advantage magnesium dialkyls, zinc dialkyls, beryllium dialkyls, sodium alkyls or potassium alkyls. Of the aluminum alkyls there come chiefly into consideration aluminum trialkyl and dialkyl-aluminum chloride or the mixture of alkylaluminum chlorides known as "sesquichloride." In the alkyl compounds, the alkyl radical advantageously is a radical containing 1 to 4 carbon atoms, for example a methyl, ethyl, propyl, isopropyl, butyl or isobutyl radical. The reaction of the titanium compounds and the metal alkyls is suitably carried out in the presence of a diluent. In the case of a metal alkyl of low reactivity it is, however, also possible to use undiluted components.

As diluents can be used all substances which are inert with respect to organo-metal compounds and liquid under reaction conditions such as ether, for example dimethyl ether, diethyl ether, dipropyl ether, diisopropyl ether, dibutyl ether, tetrahydrofuran, dioxan, saturated aliphatic or cycloaliphatic hydrocarbons such as butane, pentane, hexane, heptane, octane, cyclohexane, cyclopentane, the alkyl derivatives thereof such as methylcyclohexane, methylcyclopentane or benzene fractions containing the aforesaid or higher aliphatic hydrocarbons and which have been obtained for example from petroleum or by the Fischer-Tropsch synthesis. There come further into consideration aromatic hydrocarbons such as benzene, toluene or xylene, tertiary amines such as triethylamine, trimethylamine or tripropylamine. If desired, amines containing different hydrocarbon radicals may be used. In some cases chlorinated hydrocarbons such as methylene chloride or chlorobenzene may be employed. Diluents boiling below 100°C . are preferably used. The reaction conditions such as temperature, concentration and molar ratio of the components, depend on the reactivity of the components and the stability of the titanium alkyl compounds to be obtained. The reaction can be effected at a temperature within the range of -100°C . and $+100^\circ \text{C}$. Preferably a temperature between -20°C . and $+30^\circ \text{C}$. is used, this offering the technically simplest way. In some cases the preferred temperature is below 0°C . During the reaction the same working methods are used as in the case of other organo-metal compounds, i.e. the operation is carried out, inter alia, with the exclusion of air, for example under an atmosphere of nitrogen or another inert gas, and with the exclusion of moisture.

The organo-titanium compounds according to the invention are new. They correspond to the following formula



wherein R_1 represents a cyclopentadienyl radical which

may be substituted by hydrocarbon radicals if desired, R_2 represents an aliphatic hydrocarbon radical and Y is either identical with R_2 or X whose meaning has been explained above. The new compounds are soluble in the above mentioned diluents. They have a yellow to orange or red coloration and are crystallized compounds which are substantially stable when exposed to air. On exposure to a strong action of light or on being heated they decompose, in which case intermediate formation of alkyl radicals probably takes place. When heated to temperatures above 100°C ., the dialkyl-bis-cyclopentadienyl titanium compounds as well as the mono-cyclopentadienyl titanium compounds melt with decomposition, the latter substances being, however, somewhat more stable. The compounds of the invention are stable in water. They can be used as catalysts, for example for the polymerization of olefins.

In some cases it is of advantage, when reacting titanium compounds in which the two radicals X stand for halogen groups and/or alkoxy radicals, to use methyl compounds of metals of group I or II of the periodic table, while proceeding at a temperature below 0°C .

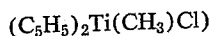
The following examples serve to illustrate the invention but they are not intended to limit it thereto:

EXAMPLE 1

In a vessel of a capacity of 250 ml. which was provided with a stirrer, a dropping vessel and a device for intense cooling, 2.5 g. (10 millimols) of bis-cyclopentadienyl-titanium dichloride were stirred, at 20°C . under a pure nitrogen atmosphere, with 80 ml. of dry methylene chloride, and in the course of $\frac{1}{2}$ hour a solution of 1.0 g. (14 millimols) of trimethylaluminum in 50 ml. of pentane was added dropwise. The dark red solution was allowed to react for 1 hour. Subsequently 30 ml. of absolute ether were added for deactivating any organo-aluminum compounds in excess. The solvents were removed under reduced pressure as far as possible, and the residue was mixed with 30 ml. of pentane and cooled to -80°C . The orange-red precipitate was suction-filtered on a cooled suction filter with the exclusion of air, washed with cooled pentane and dried under reduced pressure. In this manner 2.05 g. of small orange-red crystals of bis-cyclopentadienyl-methyl-titanium chloride were obtained which melted at 168°C . to 170°C . with decomposition. The yield amounted to 90% of the theoretical. As could be seen from decomposition by means of an acid, the substance was already pure. It could be well recrystallized from cyclohexane and methylcyclohexane. The methyl compound was soluble in water, in the cold, without decomposition; on the addition of acid the orange-yellow solution turned red with formation of methane.

Analysis by Decomposition by Means of an Acid

320 mg. of substance yielded 30.9 ml. of methane (at 0°C . under a pressure of 760 millimeters of mercury). Theory: 31.4 ml. of methane (calculated for



EXAMPLE 2

In a Schlenk tube 10.0 ml. (about 100 millimols) of dimethylaluminum chloride were added under a pure nitrogen atmosphere to a suspension of 10.0 g. (40 millimols) of powdered bis-cyclopentadienyl-titanium dichloride in 20 ml. of absolute toluene. The whole was thoroughly shaken and allowed to stand overnight at room temperature. After this time, solution was practically complete, 50 ml. of absolute ether were slowly added, while cooling and shaking, during which procedure a crystallized red precipitate was obtained. The whole was allowed to stand for 2 hours at -80°C . The red mother liquor was then cautiously removed, and the crystals were washed several times with absolute ether and pentane and dried under reduced pressure. The yield

amounted to about 7.5 g. of orange-colored crystal powder.

According to a total analysis the product obtained was a mixture of bis-cyclopentadienyl-methyl-titanium chloride and bis-cyclopentadienyl-titanium dichloride.

$(\text{C}_5\text{H}_5)_2\text{Ti}(\text{CH}_3)\text{Cl}$: Found—Ti, 21.0; Cl, 18.17; C, 54.81; H, 5.50; Al, <0.02 . Calculated—Ti, 228.57; Cl, 20.96; C, 15.51; H, 57.80; Al, 5.73.

The mixture could be severed by boiling with methylcyclohexane in which the methyl compound is moderately soluble but the dichloride is substantially insoluble.

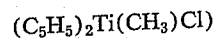
From the solution small orange-colored crystals were obtained on cooling. By adding pentane to the mother liquor and cooling to -80°C ., a further quantity of methyl compound could be obtained; it proved suitable to protect the solutions against light.

The yield amounted to about 4.5 g. of pure bis-cyclopentadienyl-methyl-titanium chloride or 50% of the theoretical. In addition thereto, a portion of the starting product was recovered.

Analysis.—Found: Ti, 21.38; Cl, 15.48; C, 57.58; H, 5.89. Calculated: Ti, 20.96; Cl, 15.51; C, 57.80; H, 5.73.

Analysis by Decomposition by Means of an Acid

198 mg. of substance yielded 19.2 ml. of methane (at 0°C . under a pressure of 760 millimeters of mercury). Theory: 19.4 ml. of methane (calculated for



EXAMPLE 3

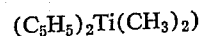
In a vessel of a capacity of 500 ml. provided with a stirrer, a reflux condenser, a dropping vessel and a thermometer, there were introduced 11.5 g. (46 millimols) of powdered bis-cyclopentadienyl-titanium dichloride and 200 ml. of absolute ether and the mixture was kept under a pure nitrogen atmosphere. In the course of about 2 hours, 100 ml. of an ethereal 1-molar methyl-lithium solution were added dropwise, while stirring and cooling to 10 to 15°C . and while avoiding strong action of light. The whole was stirred for a further hour and the yellow to orange colored solution was then decomposed by addition of ice water.

The ethereal solution was agitated two to three times with water, dried with a small amount of sodium sulfate and the solvent was removed under reduced pressure, and the crude bis-cyclopentadienyl-dimethyl-titanium was obtained in the form of fine orange colored crystals of characteristic odor. The crude product was obtained in almost quantitative yield. It was dissolved at room temperature in about 200 ml. of pentane and caused to precipitate in the form of long orange-yellow needles by slowly cooling to -80°C . The product is suitably stored in the dark at a low temperature (solid carbon dioxide). The decomposition point was $+97^\circ\text{C}$., varied however a little depending on the velocity of heating. The yield of pure substance amounted to about 8.5 g. (89% of the theoretical).

Analysis.— $(\text{C}_5\text{H}_5)_2\text{Ti}(\text{CH}_3)_2$: Found: Ti, 23.5; C, 68.58; H, 7.86; Cl. ——. Calculated: M.W., 208.15; Ti, 23.01; C, 69.24; H, 7.75; Cl. ——.

Analysis by Decomposition by Means of an Acid

133.5 mg. of substance yielded 28.7 ml. of methane (at 0°C . under a pressure of 760 millimeters of mercury). Theory: 28.8 ml. of methane (calculated for



EXAMPLE 4

In a vessel of a capacity of 250 ml. provided with a stirrer, a suspension of 6.76 g. (20 millimols) of finely powdered bis-cyclopentadienyl-titanium dibromide in 100 ml. of absolute ether was introduced and kept under a pure nitrogen atmosphere, and in the course of 1 hour 40 ml. of an ethereal 1.0-molar methyl-lithium solution

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were added dropwise at about 0° C. During this procedure the starting product dissolved with an orange coloration. The whole was stirred for a further hour and 50 ml. of ice water were then added. The ethereal solution was freed from lithium salts by washing with water, dried with sodium sulfate and freed from solvent under reduced pressure. The bis-cyclopentadienyl-dimethyl-titanium was obtained as a well crystallized orange colored mass. The yield of crude product amounted to 80% of the theoretical.

For complete purification the crude product was dissolved at room temperature in just the sufficient amount of pentane and crystallized out by cooling to -80° C. 3.0 g. of orange colored needles were obtained (decomposition point 97° C.). Yield of the pure product: 72%.

EXAMPLE 5

A suspension of 4.32 g. (10 millimols) of bis-cyclopentadienyl-diiodide in 100 ml. of absolute ether was reacted, as described in Example 4, with an ethereal solution of 20 millimols of methyl-lithium. During this process the color turned yellow-orange. After decomposition with water and the usual working up, a yield of crude bis-cyclopentadienyl-dimethyl-titanium of 85% of the theoretical was obtained. After recrystallization from pentane, the yield amounted to 1.58 g. or 76%.

EXAMPLE 6

A suspension of 2.35 g. (8 millimols) of finely powdered bis-cyclopentadienyl-titanium dithiocyanate in 80 ml. of absolute ether was reacted, as described in Example 4, at room temperature with an ethereal solution of 60 millimols of methyl-lithium. The dark substance originally present at the bottom of the liquid disappeared and the liquid turned orange-yellow. After the usual aqueous working up, 1.5 g. of crude bis-cyclopentadienyl-dimethyl-titanium (90%) were obtained. After recrystallization from pentane, the yield of the pure product amounted to 1.38 g. or 83%.

EXAMPLE 7

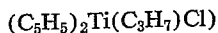
A suspension of 2.5 g. (10 millimols) of bis-cyclopentadienyl-titanium dichloride in 80 ml. of absolute ether was reacted at room temperature as described in Example 4 with 11.0 ml. of an ethereal 2-molar methylmagnesium-iodide solution. After the usual working up, 1.2 g. of bis-cyclopentadienyl-dimethyl-titanium decomposing at 97° C. were obtained. The yield amounted to 58%.

EXAMPLE 8

In a vessel of a capacity of 500 ml. provided with a stirrer, 110 ml. of a 0.4-molar n-propyl-lithium solution in pentane were slowly introduced dropwise into a suspension of 10.0 g. (40 millimols) of bis-cyclopentadienyl-titanium dichloride in 100 ml. of absolute ether. The red substance at the bottom of the liquid dissolved. Towards the end of the reaction, the reaction mixture was red-orange. Stirring was continued for a further hour at -50° C. and decomposition was then effected by addition of water. After the usual working up, 3.4 g. of bis-cyclopentadienyl-n-propyl-titanium chloride were obtained in the form of an orange powder of a decomposition point of about 160° C. The substance was only sparingly soluble in cold pentane but easily soluble in benzene, toluene etc.

Analysis by Decomposition by Means of an Acid

234 mg. of substance yielded 19.6 ml. of propane (at 0° C. under a pressure of 760 millimeters of mercury). Theory: 20.4 ml. of propane (calculated for



EXAMPLE 9

In the usual vessel provided with a stirrer (capacity 250 ml.), a solution of 2 g. (about 20 millimols) of dimethyl-zinc in 30 ml. of pentane was added, under a pure nitro-

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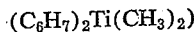
gen atmosphere, slowly and uniformly and while stirring vigorously, to a suspension of 2.5 g. (10 millimols) of bis-cyclopentadienyl-titanium dichloride in 100 ml. of absolute pentane. After the addition the mixture was kept for 2 hours at the boil and worked up as usual. After recrystallization from pentane, 0.5 g. of orange-yellow needles decomposing at 97° C. were obtained, i.e. 24% of the theoretical of bis-cyclopentadienyl-dimethyl-titanium.

EXAMPLE 10

A suspension of 5.6 g. (20 millimols) of bis-[1-methyl-cyclopentadienyl]-titanium-dichloride in 80 ml. of absolute ether was reacted, as described in Example 4, at 10° C. to 15° C. while stirring with 40 ml. of ethereal 1.1-molar methyl-lithium solution. Stirring was continued for 1 hour and after the usual aqueous working up 3.1 g. of bis-[1-methyl-cyclopentadienyl]-dimethyl-titanium (65%) were obtained. The substance was very easily soluble in cold pentane and on cooling to -80° C. crystallized in the form of yellow wart-like crystal clusters. The intensive odor of the compound was similar to that of bis-cyclopentadienyl-dimethyl-titanium.

Analysis by Decomposition by Means of an Acid

151 mg. of substance yielded 13.8 ml. of methane (at 0° C. under a pressure of 760 millimeters of mercury). Theory: 14.3 ml. of methane (calculated for



EXAMPLE 11

In an apparatus provided with a stirrer was placed a suspension of 5 g. (20 millimols) of bis-cyclopentadienyl-titanium dichloride in 80 ml. of absolute ether. The suspension was cooled to -50° C. and kept under a pure nitrogen atmosphere. In the course of two hours, a solution of 20 millimols of ethyllithium in pentane was introduced dropwise, while stirring vigorously, and the whole was allowed to react for a further hour, while cooling. The ether-pentane-solution was then freed from lithium chloride by means of water, dried with sodium sulfate and evaporated to dryness under reduced pressure. The orange-yellow powder so obtained was dissolved in toluene, filtered and crystallized by addition of pentane. The yield of bis-cyclopentadienyl-ethyl-titanium chloride amounted to 1.8 g. (7.4 millimols) or 37% of the theoretical.

We claim:

1. Bis-cyclopentadienyl-methyl-titanium chloride.
2. Bis-cyclopentadienyl-dimethyl-titanium.
3. Bis-cyclopentadienyl-propyl-titanium chloride.
4. Bis-(1-methyl-cyclopentadienyl)-dimethyl-titanium.
5. Bis-cyclopentadienyl-ethyl-titanium chloride.
6. A process for preparing a cyclopentadienyl alkyl-titanium compound having the formula



- in which each R_1 is selected from the group consisting of the cyclopentadienyl radical and the cyclopentadienyl radical substituted by 1 to 2 alkyl radicals each containing 1 to 4 carbon atoms, R_2 is a saturated aliphatic hydrocarbon radical of 1 to 4 carbon atoms and Y is selected from the group consisting of a saturated aliphatic hydrocarbon radical of 1 to 4 carbon atoms, a chlorine, bromine, iodine, cyano and thiocyno radical which process comprises the steps of (A) contacting in a liquid diluent selected from the group consisting of a saturated hydrocarbon, an aromatic hydrocarbon and chlorination products thereof (1) a titanium compound of the formula



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wherein R_1 is as defined above and X is selected from the group consisting of a chlorine, bromine, iodine, cyano and thiocyano radical with (2) an aluminum alkyl compound containing at least one alkyl group, said alkyl group having 1 to 4 carbon atoms, (B) adding an ether to deactivate excessive aluminum alkyl compound, and (C) distilling off the solvents in vacuo to isolate the solid reaction product.

7. A process for preparing a cyclopentadienyl alkyl-titanium compound having the formula



in which each R_1 is selected from the group consisting of the cyclopentadienyl radical and the cyclopentadienyl radical substituted by 1 to 2 alkyl radicals each containing 1 to 4 carbon atoms, R_2 is a saturated aliphatic hydrocarbon radical of 1 to 4 carbon atoms and Y is selected from the group consisting of a saturated aliphatic hydrocarbon radical of 1 to 4 carbon atoms, a chlorine, bromine, iodine, cyano and thiocyano radical which process comprises the steps of (A) contacting in a liquid diluent selected from the group consisting of a saturated hydrocarbon, an aromatic hydrocarbon and chlorination products thereof (1) a titanium compound of the formula



wherein R_1 is as defined above and X is selected from the group consisting of a chlorine, bromine, iodine, cyano and

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thiocyano radical with (2) a zinc alkyl compound containing at least one alkyl group, said alkyl group having 1 to 4 carbon atoms, (B) adding an ether to deactivate excessive zinc alkyl compound, and (C) distilling off the solvents in vacuo to isolate the solid reaction product.

8. A compound of the formula



wherein each R_1 is selected from the group consisting of the cyclopentadienyl radical and the cyclopentadienyl radical substituted by 1 to 2 alkyl radicals each containing 1 to 4 carbon atoms, and R_2 is a saturated aliphatic hydrocarbon radical of 1 to 4 carbon atoms.

References Cited in the file of this patent

UNITED STATES PATENTS

2,356,476	Shappirio	Aug. 22, 1944
2,827,446	Breslow	Mar. 18, 1958

FOREIGN PATENTS

1,092,700	France	Nov. 10, 1954
1,108,869	France	Sept. 14, 1955

OTHER REFERENCES

Fischer et al.	"Zeit. Naturforschung" 8b, 217-219 (1953).
Summers et al.	"J.A.C.S." 77, 3604-3606 (1955).

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,104,249

September 17, 1963

Karl Clauss et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, lines 7 and 8, strike out "Calculated-Ti, 228.57; Cl, 20.96; C, 15.51; H, 57.80; Al, 5.73." and insert instead -- Calculated-M.W., 228.57; Ti, 20.96; Cl, 15.51; C, 57.80; H, 5.73 --.

Signed and sealed this 28th day of April 1964.

(SEAL)

Attest:

ERNEST W. SWIDER

Attesting Officer

EDWARD J. BRENNER

Commissioner of Patents