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PROCESS FOR PREPARING ORGANOMETAL COMPOUNDS

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This invention relates to a process for preparing organometal compounds and particularly to an improved electrolytic process, especially for the manufacture of tetraalkyl lead antiknock compounds.

Electrolytic syntheses of organometals are known. For example, Tafel, Ber., 44, 327 (1911), obtained tetraisopropyl lead by electrolyzing an aquesous acid solution of acetone at a lead cathode in the absence of air. Such method, however, is not general and appears impractical for organolead production because of low yields and side reactions. Later (in 1925) Calingaert and Mead disclosed tetraalkyl lead formation at a lead cathode by electrolyzing a catholyte consisting of an alkyl halide in either alcoholic caustic (Calingaert in U. S. Patent 1,539,297) or aqueous caustic containing casein (Mead in U. S. Patent 1,567,159). They hypothesized: "Apparently the hydrogen formed at the cathode reduces the reaction mass, forming lead di-ethyl, which is unstable at the temperature of the catholyte, and breaks up thermally into lead and lead tetraethyl." The above disclosure suggests that a potential source of hydrogen is necessary, such as the hydroxylic solvent employed, and further that, if diethyl lead is an intermediate, the yield based on lead can be no more than 50% of the consumed lead. In fact, under the disclosed conditions the tetraethyl lead yields tend to be low and the cathode deteriorates. Further, the ethylating agent tends readily to be destroyed in side reactions, by reaction for example with the caustic present, particularly in alcohol.

Besides the cathodic processes, anodic oxidations have also been employed to produce organometallics, as for example by Hein et al., Z. anorg. Allgem. Chem., 141, 161 (1924), who obtained tetraethyl lead by electrolyzing sodium zinc triethyl at a lead anode, and by Ziegler in British Patent 814,609 (1959) who discloses synthesis of Group II–V metal alkyls by electrolyzing a complex aluminum alkyl at an anode composed of the Group II–V metal. Numerous other references disclose similar processes. All such anodic processes are characterized by the fact that the source of the organic groups to begin with is invariably another organometal (often a complex of two or more such compounds), the net result of the electrolytic oxidation being replacement of metal in the starting material by metal of the anode. That the anodic process requires organometal starting material is an important disadvantage, for such materials normally are difficult or costly to make and require special storage and handling under inert atmospheres.

An object of the invention is to provide an improved process for making hydrocarbon metal compounds electrolytically from relatively inexpensive and readily available starting materials. A particular object is to make hydrocarbon lead antiknock compounds by such process which avoids the use of organometal starting materials. Another object is to provide an improved method of alkylating lead electrolytically, wherein the current, electrode material and alkylating agent are more efficiently utilized, and whereby tetraalkyl lead antiknock compounds

are obtained in better yields than by heretofore suggested methods of electrolytic reduction. Other objects are to advance the art. Still other objects will appear hereinafter.

The above and other objects may be accomplished in accordance with this invention which comprises the process for preparing organometal compounds having hydrocarbon radicals bonded directly to a metal selected from the group consisting of lead, tin, arsenic, antimony and bismuth, which process comprises electrolyzing, at a cathode of the selected metal, a solution of an alkylating agent in a normally liquid, non-hydroxylic catholyte which, exclusive of the alkylating agent, has a higher reduction potential than the alkylating agent, employing at least 0.01 mole of alkylating agent per kilogram of solution, said alkylating agent being at least one member of the group consisting of (a) esters of the formula RX wherein X is an anion whose conjugate acid, HX, has a molecular weight greater than 20 and a pKa in water of less than about 6 and R is a hydrocarbon radical of 1 to 10 carbon atoms having a saturated carbon atom attached to X and (b) onium salts of the formula G_nQY wherein G_nQ is an onium cation in which Q is an element selected from groups VA and VIA of the Periodic Table, n is an integer of 3 to 4, G is a hydrocarbon radical at least one of which is R as defined above, and Y is salt-forming anion, which onium salts are weakly acidic to weakly basic, their water solutions having a pH between 5 and 10, and recovering the organometal compound from said solution.

In general the organometal compounds so obtained are well known to the art and are known to be useful for a wide variety of purposes. The lower hydrocarbon lead compounds are well known antiknock agents. The other organometal compounds are known to be useful as catalysts, as fungicides, as insecticides, as antiknock agents, and the like.

In general, the process comprises passing a direct electric current through a cathode of the metal to be alkylated, through a non-hydroxylic electrolyte containing an alkylating agent in contact with the cathode and then, to complete and repeat the circuit, to an anode and back to the cathode. The organometal compound is recovered from the catholyte by conventional means, the properties and handling characteristics of the organometal compounds being known. No special or unusual equipment or cell conditions are required. The process is easy and economical to operate and may be conducted at relatively low voltages and current densities and at ordinary ambient temperatures and pressures.

The apparatus employed for carrying out the process and the method of operating such apparatus may be any of those which are conventional for carrying out electrolytic processes. Suitable apparatus and methods are described by S. Swann, Jr., in the chapter beginning on page 385 of "Technique of Organic Chemistry," A. Weissberger, editor, vol. II, 2nd ed. (1956), Interscience New York, N. Y. Preferably, the process is carried out in an electrolytic cell in which the catholyte is separated from the anolyte by a membrane which is permeable to an electric current, that is, in which the cell is divided into a catholyte compartment and an anolyte compartment by such a membrane. Suitable apparatus of this character is disclosed by S. Swann, Jr., above, by Calingaert in U. S. Patent 1,539,297, by Mead in U. S. Patent 1,567,159, and by Ziegler et al. in U. S. Patent 2,985,568. While the membrane may be omitted, optimum results are obtained when it is present. Usually, the membrane will be made of a porous substance which permits transport of ions from one solution to the other, i.e., an ion-permeable membrane. A variety of such membrane materials are known to the art and may be employed in the process of this invention, it being understood that such materials may differ considerably in their resistance to the flow of electric current which will affect the selection of the particular material for a particular apparatus and condition of operation. Examples of suitable membrane materials are porous porcelain, asbestos, parchment, polyethylene, glass fiber paper, films and sheets of ion exchange resins and the like, all of which are available commercially. Usually, it will be preferred to employ a cation-permeable membrane formed of a cation-ion exchange resin. The anode may be made of any desired electrode material chosen with regard to the composition of the anolyte with which it will be in contact. While the catholyte employed in the process of this invention must be non-hydroxylic, the anolyte may be either hydroxylic or non-hydroxylic, provided it has the required conductivity for the electric current. The cell may also be provided with means for heating, cooling, and agitating the electrolytes, for maintaining an inert atmosphere when desired, and for refluxing or maintaining superatmospheric pressures where volatile materials are employed or produced, such means being conventional and well known to the art.

The alkylating agent, preferably, is an ester of the formula RX wherein X is an anion whose conjugate acid, HX, has a molecular weight greater than 20 and a pKa in water of less than about 6, most preferably less than 4, and R is a hydrocarbon radical of 1 to 10 carbon atoms having a saturated carbon atom attached to X. The hydrocarbon radical is usually acyclic and may be saturated or unsaturated, including ethylenically and acetylenically unsaturated, and may contain carbocyclic substituents, such as cycloaliphatic and aromatic groups. The chain length of the radical R does not appear to be critical for operability. Normally, however, it will have less than about 10 and preferably less than 6 carbon atoms. Usually, the most valuable metal compounds to be produced are those in which the organo radical is a primary alkyl radical, particularly of 1 to 2 carbon atoms, i.e., methyl or ethyl, and hence R most preferably will be such an alkyl radical. The anion X may be that of an inorganic acid or an organic acid. Thus, the RX esters include halides in which the halogen has an atomic number of at least 17, sulfates, sulfonates, phosphates, phosphonates, carboxylates, and the like. Preferably, the esters are the esters of non-oxidizing mineral acids, including sulfuric acid, and most preferably the halides.

Representative RX esters which are suitable for use in the process of the present invention are ethyl bromide, diethyl sulfate, ethyl iodide, ethyl chloride, ethyl acetate, dibutyl sulfate, methyl chloride, methyl iodide, methyl bromide, allyl chloride, benzyl bromide, n-butyl bromide, dimethyl sulfate, isopropyl bromide, isobutyl iodide, hexyl bromide, octyl bromide, cyclohexylmethyl bromide, crotyl chloride, 5-hexenyl iodide, 3-butenyl bromide, dipropyl sulfate, ethyl hexyl sulfate, butyl methanesulfonate, ethyl p-toluenesulfonate, benzyl diethyl phosphate, methyl benzoate, ethyl trifluoroacetate, and allyl propionate. Mixtures of any two or more of such alkylating agents may be employed if desired, including those wherein the radical R is different to produce mixtures of organometallic compounds and mixed organometallic compounds containing two or more different hydrocarbon radicals in the molecule.

Another, less preferred, group of alkylating agents are the onium salts of the formula G_nQY wherein G_nQ is an onium cation in which Q is an element selected from groups VA and VIA of the Periodic Table, *n* is an integer of 3 to 4, G is a hydrocarbon radical at least one of which is an alkylating hydrocarbon radical corresponding to R in the RX esters above defined, i.e., a hydrocarbon radical of 1 to 10 carbon atoms having a saturated hydrocarbon radical attached to QY, and Y is a salt-forming anion, which onium salts are weakly acidic to weakly basic, that is, water solutions of such onium salts must have a pH between 5 and 10. Preferably, the anion Y corresponds to the anion X in the RX esters. The onium salts are well known compounds which are readily obtainable by the reaction of an RX ester with an alkylatable onium-forming amine, phosphine, arsine, thioether, or the like. They may be formed in situ in the non-hydroxylic catholyte solvent, thereby providing an alkylating, current-carrying catholyte. In solution in the catholyte, such onium salts may reform and be in equilibrium with the RX ester. For example, an acetonitrile solution, prepared by adding methyl diethyl sulfonium iodide or by separately adding methyl iodide and diethyl sulfide, will contain methyl diethyl sulfonium iodide in equilibrium with such species as methyl iodide, ethyl iodide, diethyl sulfide and methyl ethyl sulfide.

Representative onium salts which are suitable for use as alkylating agents in the process of the present invention include

tetraethylammonium bromide
triethylsulfonium bromide
ethyltriphenylphosphonium bromide
tetraethylammonium iodide
methyldiethylsulfonium iodide
tetramethylammonium bromide
trimethylsulfonium iodide
tetraethylammonium diethyl phosphate
tetrapropylammonium bromide
tetraethylammonium ethyl sulfate
tetrabutylphosphonium bromide
tetrabenzylarsonium bromide
dioctadecyldimethylammonium chloride
benzyltriethylammonium propionate
triethylsulfonium iodide
triethylselenonium bromide
allyltriethylammonium acetate
ethyltriphenylphosphonium iodide, and
tetra-n-amylammonium fluoride.

The RX esters are the more efficient alkylating agents, particularly as to the utilization of current, and usually result in higher yields of the desired compounds. Also, the RX esters are the more economical source of the alkylating agents since the onium salts are ordinarily prepared from them. However, the onium salts are current-carrier compounds and, when dissolved in a non-hydroxylic organic solvent, impart current-carrying characteristics to the solution. In preferred embodiments of the invention, an RX ester is used in combination with one or more of the onium salts, or with a catholyte-soluble current-carrying halide of a metal of groups IA or IIA of the Periodic Table. The alkylating radical in the onium salt may be the same or different from the radical R in the particular RX ester. In such combination, the onium salt or salts function primarily as the current-carrier. Due to the greater reactivity of the RX esters, the organometal compound produced usually will contain the hydrocarbon radical from the RX ester predominantly, with little or none of the alkylating radical from the onium salts, even when the alkylating radical of the onium salt is different from the alkylating radical in the RX ester employed.

According to the process of this invention, the catholyte must be non-hydroxylic, usually a solution of a non-hydroxylic current-carrying compound in a normally liquid non-hydroxylic organic solvent. However, it is not necessary to maintain rigorous anhydrous conditions and to completely exclude ordinary atmospheric components from the cell or the cathode. In other words, traces of water, such as those present in the atmosphere, are permissible. The catholyte must be normally liquid, i.e., liquid at normal room temperatures and pressures, and have a reduction potential greater than that of the alkylating agent. In other words, the catholyte should be substantially inert to the rest of the system, particularly to the organometal compounds being produced, and should not undergo reaction at the cathode in preference to the alkylating agent.

The non-hydroxylic organic solvents are substantially non-acidic, that is, they have a pKa of at least about 20, as determined by the method of Pearson and Dillon, JACS, 75, p. 2439 (1953). Suitable non-hydroxylic organic solvents are the organic amides, preferably of secondary amines, including carboxamides, sulfonamides, phosphoramides, and cyanamides; nitriles; sulfoxides; sulfones; ethers; halohydrocarbons; thiocyanates; carboxylic esters; and ketones. Specifically, there may be used acetonitrile, propionitrile and higher homologs; N,N-dimethylformamide, N,N-dimethyl acetamide, N-methylcaprolactam, N-methylpyrrolidone, N,N-diethyl formamide; hexamethylphosphoramide, hexaethylphosphoramide; N,N-dimethylethanesulfonamide; dimethyl sulfoxide and other lower alkyl sulfoxides such as diethyl sulfoxide; acetone, methyl ethyl ketone and diethyl ketone; diethylene glycol dimethyl ether and diethylene glycol methyl ethyl ether; ethyl thiocyanate, propyl thiocyanate; propylene carbonate; N,N-dialkylamino nitriles such as N,N-dimethylcyanamide and homologs. Mixtures of any two or more of such solvents may be used as the catholyte solvent. Where the alkylating agent is normally liquid and can be rendered sufficiently conductive of electric current, it can be used as the catholyte solvent.

The current-carrying compound, which may be dissolved in the catholyte solvent to render it electrically conductive and hence to form the catholyte of the present invention, may be varied widely. It need only be soluble in the non-hydroxylic organic solvent to the extent required to produce a catholyte having the required electric conductivity which in general should be at least about 0.0005 ohm^{-1} cm.$^{-1}$ and, preferably, from 10 to 100 times this value. For example, the conductivity of a 10% wt. solution of tetraethylammonium bromide in acetonitrile is 0.027 ohm^{-1} cm.$^{-1}$ at 50° C. It is well known to the art to impart electrical conductivity to normally non-conductive organic liquids, including non-hydroxylic organic liquids, by means of current-carrying solutes. This practice and the materials employed are disclosed by S. Swann, Jr., hereinbefore referred to, and in the following literature:

(a) Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed., Reinhold, New York (1950).

(b) Fuoss and Accascina, "Electrolytic Conductance," Interscience, New York, (1959).

(c) Tables Annuelles de Constantes et Donnies Numeriques 18, "Conductivity of Electrolytes," Hermann, Paris (1937).

(d) Audrieth and Kleinberg, "Non-Aqueous Solvents (Applications as Media for Chemical Reactions)," John Wiley and Sons, New York (1953).

In general, suitable inert current-carriers are dissolved inorganic or organic salts which are either neutral, weakly basic, or weakly acidic, i.e., show a pH between 5 and 10 in water solution. They include univalent and polyvalent salts exemplified by onium, alkali metal, alkaline earth metal, and rare earth metal halides, perchlorates, thiocyanates, sulfonates, phosphonates, and carboxylates. In the process of the present invention, it will generally be preferred to employ one or more onium salts of the formula G_nQY wherein G is a hydrocarbon radical of 1 to 10 carbon atoms having a saturated carbon atom attached to QY, *n* is an integer of 3 to 4, Q is an element selected from the groups VA and VIA of the Periodic Table, preferably nitrogen or sulfur, and Y is a salt-forming anion, which onium salts are weakly acidic to weakly basic, or one or more catholyte-soluble current-carrying halides of the metals of groups IA and IIA of the Periodic Table, i.e., halides of the alkali metal and alkaline earth metals which are soluble in the catholyte solvent.

Representative current-carrying compounds which are suitable for use in the process of the present invention are lithium bromide, sodium iodide, potassium thiocyanate, lithium perchlorate, potassium iodide, calcium bromide, lanthanum chloride, lithium chloride, triphenylmethyl bromide, diphenyliodonium iodide, tetraethylammonium bromide, triethylsulfonium bromide, triphenylethylphosphonium iodide, dioctadecyldimethylammonium chloride, methyldiethylsulfonium iodide, and the other onium salts which have been disclosed hereinbefore as alkylating agents. Combinations of any two or more of such current-carrying compounds may be used.

The alkylating agent, the solvent, and the current-carrying salt are readily coordinated in a wide variety of combinations to provide suitable catholytes for the alkylation of the cathodic metals. In general, the non-hydroxylic solvent will be the major component of the catholyte. The alkylating agent will be present in the proportion of at least 0.01 mole per kilogram (1,000 grams) of the total catholyte, i.e., the total of catholyte solvent, current-carrier and alkylating agent, usually from about 0.01 to about 8.7 moles, and most preferably from about 0.25 to about 5 moles. When an RX ester is used in combination with an onium salt, the RX ester will usually be present in a concentration of from about 0.1 to about 8.7 moles per kilogram of solution, preferably at least about 0.4 mole, and most preferably at least about 1 mole. The upper limit of the alkylating agent will vary, depending on its molecular weight and its solubility in the non-hydroxylic organic solvent. The current-carrying compound may be employed in the proportion of from 0.001 to about 2 moles per kilogram of catholyte, usually from about 0.01 to about 0.5 mole, and preferably from about 0.05 to about 0.5 mole. The upper limit of the current-carrier will further depend upon its solubility in the total catholyte composition.

The electrolysis is accomplished by passing a direct current across the cell, that is, through the cathode, the catholyte, the anolyte, and the anode. The voltage applied across the cell is not critical so long as it is sufficient to overcome the resistance of the cell, including that of the catholyte and the anolyte, and to establish current flow through the cell. The minimum voltage depends upon such factors as cell design, the particular catholyte, particularly the particular current-carrying compound and the concentration thereof in the catholyte solvent, and the choice of alkylating agent. At least sufficient volts are required to reduce the alkylating agent at the cathode and to overcome the various resistances in the cell. In general, the reduction of the alkylating agent appears to require about 1 to 2 volts and, in the particular systems explored, the minimum total voltage required usually was of the order of 4 to 5 volts. It is seldom necessary to exceed about 15 volts in ordinary equipment and most catholytes, but higher voltages up to about 30 volts have been used. Much higher voltages can be employed if desired. The usual operating range is from about 4 to about 15 volts. The current density may range from 0.0001 amp./sq. cm. to about 1 amp./sq. cm. of cathode area, but preferably is kept below about 0.5 amp./sq. cm. The lower limit of current density will usually be dictated by the desired rate of production of the organometal compound under the existing conditions. Usually, the current density will be from about 0.1 to about 0.4 amp./sq. cm.

Usually, the process, i.e., the electrolysis in the cell, will be carried out at normal room temperatures and pressures. However, the operating temperatures may be higher or lower, consonant with a practical rate of production of the organometal compound and the thermal stability of the system. While temperatures of from about 20° C. to 70° C. are preferred, temperatures as low as 0° C. and as high as 100° C. may be used. The pressure on the system should be at least sufficient to maintain a liquid catholyte, and otherwise may be above or below atmospheric pressures. Reflux may be used in the usual way to retain volatile components in the cell and to aid in controlling reaction conditions. Also, where the materials employed or the organometal compounds produced are sensitive to atmospheric moisture or oxygen, an inert atmosphere such as nitrogen may be employed.

In the examples presented hereinafter, the process is carried out as a batch operation. However, the process is adaptable to continuous operation. The reaction times may be considerably less than those shown in the examples and, particularly in the tetraalkyl lead system, the tetraalkyl lead begins to appear in the catholyte almost immediately after the electrolysis is started and, while the conversion at short times is low, the yields are high, of the order of 90% or better on both current and lead. Thus, in the continuous process, the catholyte containing the product may be continuously removed, treated for recovery of the organometal product, and recycled and replaced in whole or in part by fresh catholyte.

In order to more clearly illustrate this invention, preferred modes of practicing it, and the advantageous results to be obtained thereby, the following examples are given in which the quantities are in parts by weight unless specifically indicated otherwise.

Example 1

A. An electrolytic cell is used which comprises a lead cathode, a platinum anode, and, separate catholyte and anolyte compartments separated by a cation-permeable membrane (a commercial product which is understood to be a sulfonic acid type cation-ion exchange resin). The catholyte solution consists of 29 parts of ethyl bromide (EtBr), 5 parts of tetraethyl-ammonium bromide (Et_4NBr) and 175 parts of acetonitrile (corresponding to 1.273 moles of EtBr and 0.114 mole Et_4NBr per kilogram of solution). The anolyte is 28 parts of sodium carbonate in 250 parts water. With the electrolytes at room temperature, the direct current is turned on and, over a 15 minute period, the voltage is increased gradually from about 6 to about 15 volts and the current from about 0.2 to about 1–1.5 amperes, corresponding to a final current density of about 0.02–0.03 amp./sq. cm. These conditions are continued for about 4 hours, during which time the temperature rises to about 60° C. The catholyte is removed, decanted from a trace of insoluble matter, thoroughly mixed with 800 parts water and 150 parts pentane, and the resulting two-layer system separated. Another 150 parts pentane is used to reextract the aqueous layer, and the total pentane extract is distilled under reduced pressure to obtain tetraethyl lead in 70% yield based on the current passed and 80% based on the weight lost by the cathode during the electrolysis.

Alternatively the electrolyzed catholyte composition may be fractionally distilled or steam distilled to give tetraethyl lead.

B. Similarly in the above electrolytic procedure, but with the anolyte a solution of 5 parts of tetraethyl-ammonium bromide in 175 parts of acetonitrile, the yield of tetraethyl lead is 77% based on current and 81% based on lead. During this latter procedure, bromide is oxidized at the anode; the oxidation product is present in the anolyte as polybromide ions, e.g., Br_3^-, from which molecular bromine may be recovered by known methods. If desired, a scavenger for oxidant bromine may be added to the starting anolyte. For example, the scavenger may be an olefin (e.g., ethylene or cyclohexane) to form the olefin dibromide, or it may be a strong base anion exchange resin in the halide form, such resins being known in the art to chemisorb bromine as polybromohalide ions.

C. Other current-carriers can replace tetraethyl-ammonium bromide in the catholyte. Typical examples, with results obtained by the procedure of Example 1A, are:

Current-Carrier	Mole/kg. Catholyte	Tetraethyl Lead Yield, Percent Based on Lead
Lithium bromide	0.524	100
Triethylsulfonium bromide	0.121	81
Sodium iodide	0.159	76
Potassium thiocyanate	0.243	100
Lithium perchlorate	0.149	100
Potassium iodide	<0.145	84
Triphenylethylphosphonium iodide	0.091	86
Calcium bromide	<0.012	100
Triphenylmethyl bromide	0.094	72

It should be noted that triphenylmethyl bromide, normally a covalent, i.e., non-dissociated molecule, apparently dissociates into current-carrying ions in acetonitrile under the conditions employed. Thus, the current-carrier need not be a preformed salt existing as ions in the solid state, but need only be capable of rendering the solution electrically conducting.

Example 2

The procedure of Example 1A is followed except that acetonitrile is replaced by an equal volume of a non-hydroxylic solvent listed below, the moles of ethyl bromide (EtBr) and of tetraethylammonium bromide (Et_4NBr) per kilogram of catholyte varying in accord with the variations in the density of the solvents, as shown.

Solvent	Moles/kg. catholyte		Tetraethyl Lead Yield, Percent Based on Lead
	EtBr	Et_4NBr	
N, N-Dimethylformamide	1.077	0.097	46
Dimethyl sulfoxide	0.943	0.085	16
1, 2-Dimethoxyethane	1.167	0.105	47
Methylene chloride	0.794	0.071	71
Propylene carbonate	0.869	0.078	40
Ethyl thiocyanate	1.031	0.093	84
N, N-Dimethylcyanamide	1.142	0.102	44

As in Example 1, the other current-carriers may be used, for example, diphenyliodonium iodide and lanthanum chloride in comparable amounts to render dimethylformamide suitably conductive.

Also, other non-hydroxylic solvent/current-carrier combinations are operable. For example, acetone containing dissolved therein either ethyltriphenylphosphonium iodide or a mixture of dioctadecyldimethylammonium chloride and lithium bromide has been used with good results.

Example 3

Tetraethyl lead is produced on repeating the method of Example 1A with other ethylating agents as exemplified below:

Ethylating Agent	Moles/kg. Catholyte	Tetraethyl Lead Yield, Percent Based on Lead
Diethyl sulfate	0.81	81
Ethyl iodide	4.24	72
Ethyl chloride	1.51	93
Ethyl acetate	1.40	10
Tetraethylammonium bromide	0.13 (total)	12
Triethylsulfonium bromide[1]	0.14	33

[1] No tetraethylammonium bromide added.

The last two agents, onium salts, are also current-carriers (Example 1). Thus, in the method of the invention, the same substance may provide alkylating radicals and current-carrying ions. While the RX esters themselves do not ordinarily conduct the current, they may be used to produce current-carrying onium salts in situ in the catholyte solvent, for example, by reacting an alkylating agent such as ethyl iodide with a suitable onium-forming base such as triethylamine to form tetraethylammonium iodide or such as diethyl sulfide to form triethylsulfonium iodide.

Example 4

Example 1A procedure is repeated with 290 grams (2.66 moles) ethyl bromide, 7.8 grams acetonitrile and 10 grams (0.0171 mole) dioctadecyldimethylammonium chloride as catholyte. (The concentrations of EtBr and current-carrier are, respectively, 8.66 and 0.056 mole/1000 grams catholyte.) The yield of tetraalkyl lead as TEL is 23% on current and 26% on metal. EtBr alone plus the salt was a poorer electrical conductor than the solution containing the acetonitrile.

The preceding examples illustrate the process of the invention, applied to the preparation of tetraethyl lead, wherein the catholyte solvent is a non-hydroxylic substantially inert organic solvent. In comparison, when the above procedure was used, employing an alkylating agent such as ethyl bromide in a catholyte consisting also of ethanolic sodium hydroxide (as suggested by Calingaert in U.S. Patent 1,539,297), the yield of tetraethyl lead was practically nil. With aqueous sodium hydroxide containing ethyl iodide emulsified therein with casein (as described by Mead in U.S. Patent 1,567,159), yields of tetraethyl lead of up to 25% based on current and up to 33% based on lead may be obtained. The above Examples 1 and 3, utilizing ethyl halides in the acetonitrile-based catholyte, provides tetraethyl lead in significantly greater yield, on the order of 70–100% based on current and lead.

Example 5

A catholyte consisting of 200 ml. acetonitrile, 2 ml. methyl chloride (MeCl), and 15 g. tetraethylammonium bromide (Et_4NBr), corresponding 0.23 mole MeCl and 0.41 mole Et_4NBr per kg. of catholyte, is electrolyzed by the method of Example 1B (i.e., the anolyte consists of 15 g. tetraethylammonium bromide in 200 ml. acetonitrile). Voltage and current are raised over a period of about 15 minutes to about 15 volts and 1–1.5 amperes, corresponding to a current density of about 0.02–0.03 amp./sq. cm. After 4 hours, the catholyte is decanted from a trace of sludge and analyzed. The tetraalkyl lead content, calculated as tetramethyl lead (probably the predominant product), corresponds to a 93% yield based on lead consumed and 75% based on current.

Satisfactory results are also obtained in the above procedure, on utilizing methyl iodide or methyl bromide. Likewise, mixtures of methylating and ethylating esters may be employed, e.g., methyl chloride and ethyl bromide, to produce mixtures of tetramethyl lead and tetraethyl lead, along with mixed tetraalkyl leads wherein methyl and ethyl groups are present in the same molecule.

There may also be employed, as both an alkylating agent and a current-carrier, methyl diethylsulfonium iodide which is readily prepared in situ in acetonitrile by mixing methyl iodide with diethyl sulfide, whereby mixtures of methyl and ethyl lead compounds are produced.

Example 6

A. The method of Example 1A is followed. The catholyte consists of

171 g. acetonitrile (225 ml.)
5 g. $(CH_3)_4NBr$ (0.15 mole/kg. catholyte)
45.5 g. CH_3I (1.44 mole/kg. catholyte)

The anolyte is Na_2CO_3 in water as given.

B. Procedure A above is repeated except that 2.54 g. (3 ml.) of dimethyl sulfide replaces the tetramethylammonium bromide current-carrier, apparently reacting with some of the methyl iodide to yield trimethylsulfonium iodide as the current-carrier.

YIELDS OF TETRAMETHYL LEAD, PERCENT

Method	A	B
Based on lead	61	86
Based on current	64	85

Example 7

In the apparatus of Example 1 are placed a catholyte consisting of 250 ml. N,N-dimethylformamide, 22 ml. allyl chloride and 5.5 g. lithium chloride (corresponding to 1.03 moles of allyl chloride and 0.50 mole of lithium chloride per kg. of catholyte), and an anolyte solution of 28 g. sodium carbonate in 250 ml. water. Electrolysis is carried out for 4.5 hours at a current density of 0.012 amp./sq. cm. and a temperature of about 30° C. thoughout the run. The organolead content of the catholyte corresponds to a 65% yield based on lead and calculated as tetraalkyl lead.

Example 8

Example 1A is repeated with an arsenic cathode and a catholyte solution of 5 g. tetraethylammonium bromide and 10 ml. benzyl bromide in 200 ml. acetonitrile, corresponding to 0.48 mole of benzyl bromide and 0.14 mole of Et_4NBr per kg. of catholyte. The electrolysis is conducted under a nitrogen atmosphere for about 4 hours at 3–9 volts, 0.05–0.5 ampere (current density=0.001–0.01 amp./sq. cm.), and 25–35° C. The resulting catholyte is concentrated to a small volume at reduced pressure, and the residue washed with water and then ethyl ether to give tetrabenzylarsonium bromide in a yield of about 9% based on the arsenic. This product apparently results from the reaction of benzyl bromide with the tribenzyl arsenic product of the electrolysis.

When cathodes of bismuth and antimony are employed in the above procedure, they are similarly observed to dissolve during electrolysis. From the catholytes organobismuth and organoantimony derivatives may be obtained.

Example 9

Example 1A is repeated with a cathode of tin instead of lead, to form tetraethyl tin in a yield of about 72% based on the tin, determined by bromide titration of the product.

Similarly other alkylating agents may be employed, for example n-butyl bromide to produce tetra-n-butyl tin.

It will be apparent from the preceding examples that the method of this invention, wherein reductive alkylation is effected in a non-hydroxylic catholyte, is applicable to the production of organo derivatives of metals of groups IVA and VA of the Periodic Table, the organo derivatives being those wherein at least one hydrocarbon radical is directly attached through a saturated carbon atom to said metal.

It will be understood that the preceding examples have been given for illustrative purposes solely, and that this invention is not limited to the specific embodiments described therein. On the other hand, it will be readily apparent to those skilled in the art that, subject to the limitations set forth in the general description, many variations can be made in the materials, proportions, conditions, techniques and apparatus employed without departing from the spirit or scope of this invention.

From the foregoing description, it will be apparent that this invention provides a new and improved method for preparing organometal compounds by electrolytic processes. It employs relatively cheap and readily available starting materials and produces greatly improved yields of the desired organometal compounds. The process is simple and economical to operate, is readily controlled, and avoids many of the hazards and difficulties involved in other processes for making such organometal compounds, such as the alkyllead compounds. Accordingly, it will be apparent that this invention constitutes a valuable advance in and contribution to the art.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. The process for preparing organometal compounds having hydrocarbon radicals bonded directly to a metal selected from the group consisting of lead, tin, arsenic, antimony and bismuth, which comprises electrolyzing, at a cathode of the selected metal, a solution of an alkylating agent in a normally liquid, initially non-hydroxylic catholyte which, exclusive of the alkylating agent, has a higher reduction potential than the alkylating agent employing at least 0.01 mole of alkylating agent per kilogram of solution, said alkylating agent being at least one member of the group consisting of (a) esters of the formula RX wherein X is an anion whose conjugate acid, HX, has a molecular weight greater than 20 and a pKa in water of less than about 6 and R is a hydrocarbon radical of 1 to 10 carbon atoms having a saturated carbon atom attached to X and (b) onium salts of the formula G_nQY wherein G_nQ is an onium cation in which Q is an element selected from groups VA and VIA of the Periodic Table, *n* is an integer of 3 to 4, G is a hydrocarbon radical at least one of which is R as defined above, and Y is salt-forming anion, which onium salts are weakly acidic to weakly basic, their water solutions having a pH between 5 and 10, said catholyte containing a current-carrier in an amount sufficient to provide a conductivity of at least 0.0005 ohm^{-1} cm.$^{-1}$, said current-carrier being a dissolved current-carrying salt which, in water, has a pH in the range of 5 to 10; and recovering an organometal compound from said solution.

2. The process for preparing organometal compounds having hydrocarbon radicals bonded directly to a metal selected from the group consisting of lead, tin, arsenic, antimony and bismuth, which comprises electrolyzing, at a cathode of the selected metal, a solution of an alkylating agent in a normally liquid, initially non-hydroxylic catholyte which, exclusive of the alkylating agent, has a higher reduction potential than the alkylating agent, employing from about 0.01 to about 8.7 moles of alkylating agent per kilogram of solution, said alkylating agent being at least one ester of the formula RX wherein X is an anion whose conjugate acid, HX, has a molecular weight greater than 20 and a pKa in water of less than about 6 and R is a hydrocarbon radical of 1 to 10 carbon atoms having a saturated carbon atom attached to X, said catholyte containing a current-carrier in an amount sufficient to provide a conductivity of at least 0.0005 ohm^{-1} cm.$^{-1}$, said current-carrier being a dissolved current-carrying salt which, in water, has a pH in the range of 5 to 10; and recovering an organometal compound from said solution.

3. The process for preparing organometal compounds having hydrocarbon radicals bonded directly to a metal selected from the group consisting of lead, tin, arsenic, antimony and bismuth, which comprises electrolyzing, at a cathode of the selected metal in an electrolytic cell in which the catholyte is separated from the anolyte by a membrane permeable to an electric current, a solution of an alkylating agent in a normally liquid, initially non-hydroxylic catholyte which, exclusive of the alkylating agent, has a higher reduction potential than the alkylating agent, employing from about 0.01 to about 8.7 moles of alkylating agent per kilogram of solution, said alkylating agent being at least one member of the group consisting of (a) esters of the formula RX wherein X is an anion whose conjugate acid, HX, has a molecular weight greater than 20 and a pKa in water of less than about 6 and R is a hydrocarbon radical of 1 to 10 carbon atoms having a saturated carbon atom attached to X and (b) onium salts of the formula G_nQY wherein G_nQ is an onium cation in which Q is an element selected from groups VA and VIA of the Periodic Table, *n* is an integer of 3 to 4, G is a hydrocarbon radical at least one of which is R as defined above, and Y is a salt-forming anion, which onium salts are weakly acidic to weakly basic, their water solutions having a pH between 5 and 10, said catholyte containing a current-carrier in an amount sufficient to provide a conductivity of at least 0.0005 ohm^{-1} cm.$^{-1}$, said current-carrier being a dissolved current-carrying salt which, in water, has a pH in the range of 5 to 10; and recovering an organometal compound from said solution.

4. The process for preparing organometal compounds having hydrocarbon radicals bonded directly to a metal selected from the class consisting of lead, tin, arsenic, antimony and bismuth, which comprises electrolyzing, at a cathode of the selected metal in an electrolytic cell in which the catholyte is separated from the anolyte by an ion-permeable membrane, a solution of an alkylating agent in a normally liquid, initially non-hydroxylic catholyte which, exclusive of the alkylating agent, has a higher reduction potential than the alkylating agent, employing from about 0.01 to about 8.7 moles of alkylating agent per kilogram of solution, said alkylating agent being at least one ester of the formula RX wherein X is an anion whose conjugate acid, HX, has a molecular weight greater than 20 and a pKa in water of less than about 6 and R is a hydrocarbon radical of 1 to 10 carbon atoms having a saturated carbon atom attached to X, said catholyte containing a current-carrier in an amount sufficient to provide a conductivity of at least 0.0005 ohm^{-1} cm.$^{-1}$, said current-carrier being a dissolved current-carrying salt which, in water, has a pH in the range of 5 to 10; and recovering an organometal compound from said solution.

5. The process for preparing organolead compounds having hydrocarbon radicals bonded directly to lead, which comprises electrolyzing, at a lead cathode in an electrolytic cell in which the catholyte is separated from the anolyte by an ion-permeable membrane, a solution of an alkylating agent in a normally liquid, initially non-hydroxylic catholyte which, exclusive of the alkylating agent, has a higher reduction potential than the alkylating agent, employing from about 0.01 to about 8.7 moles of alkylating agent per kilogram of solution, said alkylating agent being at least one member of the group consisting of (a) esters of the formula RX wherein X is an anion whose conjugate acid, HX, has a molecular weight greater than 20 and a pKa in water of less than about 6 and R is a hydrocarbon radical of 1 to 10 carbon atoms having a saturated carbon atom attached to X and (b) onium salts of the formula G_nQY wherein G_nQ is an onium cation in which Q is an element selected from groups VA and VIA of the Periodic Table, *n* is an integer of 3 to 4, G is a hydrocarbon radical at least one of which is R is defined above, and Y is a salt-forming anion, which onium salts are weakly acidic to weakly basic, their water solutions having a pH betwen 5 and 10, said catholyte containing a current-carrier in an amount sufficient to provide a conductivity of at least 0.0005 ohm^{-1} cm.$^{-1}$, said current-carrier being a dissolved current-carrying salt which, in water, has a pH in the range of 5 to 10; and recovering an organolead compound from said solution.

6. The process for preparing organolead compounds having hydrocarbon radicals bonded directly to lead, which comprises electrolyzing, at a lead cathode in an electrolytic cell in which the catholyte is separated from the anolyte by an ion-permeable membrane, a solution of an alkylating agent in a normally liquid, initially non-hydroxylic catholyte which, exclusive of the alkylating agent, has a higher reduction potential than the alkylating agent, employing from about 0.01 to about 8.7 moles of alkylating agent per kilogram of solution, said alkylating agent being at least one ester of the formula RX wherein X is an anion whose conjugate acid, HX, has a molecular weight greater than 20 and a pKa in water of less than about 6 and R is a hydrocarbon radical of 1 to 10 carbon

atoms having a saturated carbon atom attached to X, said catholyte containing a current-carrier in an amount sufficient to provide a conductivity of at least 0.0005 ohm^{-1} cm.^{-1}, said current-carrier being a dissolved current-carrying salt which, in water, has a pH in the range of 5 to 10; and recovering an organolead compound from said solution.

7. The process for preparing organolead compounds having hydrocarbon radicals bonded directly to lead, which comprises electrolyzing, at a lead cathode in an electrolytic cell in which the catholyte is separated from the anolyte by an ion-permeable membrane, a solution of an alkylating agent in a normally liquid, initially non-hydroxylic catholyte which, exclusive of the alkylating agent, has a higher reduction potential than the alkylating agent, employing from about 0.01 to about 8.7 moles of alkylating agent per kilogram of solution, said alkylating agent being at least one ester of the formula RX wherein X is a halogen atom having an atomic number of at least 17 and R is a hydrocarbon radical of 1 to 5 carbon atoms having a saturated carbon atom attached to X, said catholyte containing a current-carrier in an amount sufficient to provide a conductivity of at least 0.0005 ohm^{-1} cm.^{-1}, said current-carrier being a dissolved current-carrying salt which, in water, has a pH in the range of 5 to 10; and recovering an organolead compound from said solution.

8. The process for preparing organolead compounds having hydrocarbon radicals bonded directly to lead, which comprises electrolyzing, at a lead cathode in an electrolytic cell in which the catholyte is separated from the anolyte by an ion-permeable membrane, a solution of an alkylating agent in a normally liquid, initially non-hydroxylic catholyte which, exclusive of the alkylating agent, has a higher reduction potential than the alkylating agent, employing from about 0.01 to about 8.7 moles of alkylating agent per kilogram of solution, said alkylating agent being at least one ester of the formula RX wherein X is a halogen atom having an atomic number of at least 17 and R is an alkyl radical of 1 to 2 carbon atoms, said catholyte containing a current-carrier in an amount sufficient to provide a conductivity of at least 0.0005 ohm^{-1} cm.^{-1}, said current-carrier being a dissolved current-carrying salt which, in water, has a pH in the range of 5 to 10; and recovering an organolead compound from said solution.

9. The process for preparing tetraethyl lead which comprises electrolyzing, at a lead cathode in an electrolytic cell in which the catholyte is separated from the anolyte by an ion-permeable membrane, a solution of an ethyl halide in which the halogen has an atomic number of at least 17 in a normally liquid, initially non-hydroxylic catholyte which, exclusive of the ethyl halide, has a higher reduction potential than the ethyl halide, employing from about 0.01 to about 8.7 moles of ethyl halide per kilogram of solution, said catholyte containing a current-carrier in an amount sufficient to provide a conductivity of at least 0.0005 ohm^{-1} cm.^{-1}, said current-carrier being a dissolved current-carrying salt which, in water, has a pH in the range of 5 to 10; and recovering tetraethyl lead from said solution.

10. The process for preparing tetramethyl lead which comprises electrolyzing, at a lead cathode in an electrolytic cell in which the catholyte is separated from the anolyte by an ion-permeable membrane, a solution of a methyl halide in which the halogen has an atomic number of at least 17 in a normally liquid, initially non-hydroxylic catholyte which, exclusive of the methyl halide, has a higher reduction potential than the methyl halide, employing from about 0.01 to about 8.7 moles of methyl halide per kilogram of solution, said catholyte containing a current-carrier in an amount sufficient to provide a conductivity of at least 0.0005 ohm^{-1} cm.^{-1}, said current-carrier being a dissolved current-carrying salt which, in water, has a pH in the range of 5 to 10; and recovering tetramethyl lead from said solution.

11. The process for preparing an organolead compound in an electrolytic cell in which the catholyte is separated from the anolyte by an ion-permeable membrane, which comprises immersing a lead cathode in a non-hydroxylic catholyte in the cell, which catholyte consists essentially of a solution of (a) at least one ester of the formula RX wherein X is an anion whose conjugate acid, HX, has a molecular weight greater than 20 and a pKa of less than about 6 and R is a hydrocarbon radical of 1 to 10 carbon atoms having a saturated carbon atom attached to X, and (b) an onium salt of the formula G_nQY wherein G is a hydrocarbon radical of 1 to 10 carbon atoms having a saturated carbon atom attached to QY, *n* is an integer of 3 to 4, Q is an element selected from groups VA and VIA of the Periodic Table, and Y is a salt-forming anion, which onium salts are weakly acidic to weakly basic, their water solutions having a pH between 5 and 10, in a normally liquid, non-hydroxylic organic solvent which has a higher reduction potential than said ester, in the proportions of from about 0.1 to about 8.7 moles of said ester and from about 0.07 to about 0.5 mole of said onium salt per kilogram of catholyte, and passing an electric current of from about 4 to about 30 volts and of a current density of from about 0.01 to about 1 amp./sq. cm. through said cathode and said catholyte, and recovering an organolead compound from the catholyte.

12. The process for preparing tetraalkyl lead compounds in an electrolytic cell in which the catholyte is separated from the anolyte by an ion-permeable membrane, which comprises immersing a lead cathode in a non-hydroxylic catholyte in the cell, which catholyte consists essentially of a solution of (a) at least one alkyl halide of 1 to 5 carbon atoms in which the halogen has an atomic number of at least 17 and (b) an onium salt of the formula R_4NX wherein R is an alkyl radical of 1 to 10 carbon atoms and X is a halogen atom, in a normally liquid, non-hydroxylic organic solvent which has a higher reduction potential than the alkyl halide, in the proportions of from about 0.1 to about 8.7 moles of alkyl halide and from about 0.07 to about 0.5 mole of said onium salt per kilogram of catholyte, and passing an electric current of from about 4 to about 30 volts and of a current density of from about 0.01 to about 1 amp./sq. cm. through said cathode and said catholyte, and recovering at least one tetraalkyl lead from the catholyte.

13. The process for preparing tetraalkyl lead compounds in an electrolytic cell in which the catholyte is separated from the anolyte by an ion-permeable membrane, which comprises immersing a lead cathode in a non-hydroxylic catholyte in the cell, which catholyte consists essentially of a solution of (a) at least one alkyl halide of 1 to 2 carbon atoms in which the halogen has an atomic number of at least 17 and (b) an onium salt of the formula R_4NX wherein R is an alkyl radical of 1 to 10 carbon atoms and X is a halogen atom having an atomic number of at least 17, in a normally liquid, non-hydroxylic organic solvent which has a higher reduction potential than the alkyl halide, in proportions of from about 0.1 to about 8.7 moles of alkyl halide and from about 0.07 to about 0.5 mole of said onium salt per kilogram of catholyte, and passing an electric current of from about 4 to about 30 volts and of a current density of from about 0.01 to about 1 amp./sq. cm. through said cathode and said catholyte, and recovering at least one tetraalkyl lead from the catholyte.

14. The process for preparing tetraethyl lead in an electrolytic cell in which the catholyte is separated from the anolyte by an ion-permeable membrane, which comprises immersing a lead cathode in a non-hydroxylic catholyte in the cell, which catholyte consists essentially of a solution of (a) an ethyl halide in which the halogen has an atomic number of at least 17 and (b) an onium salt of the formula R_4NX wherein R is an ethyl radical and X is a halogen atom having an atomic number of at least 17, in a normally liquid, non-hydroxylic organic solvent which has a higher reduction potential than the ethyl halide, in the proportions of from about 0.1 to about 8.7 moles of ethyl halide and from about 0.07 to about 0.5 mole of said onium salt per kilogram of catholyte, and passing an electric current of from about 4 to about 30 volts and of a current density of from about 0.01 to about 1 amp./sq. cm. through said cathode and said catholyte, and recovering tetraethyl lead from the catholyte.

15. The process for preparing tetraethyl lead in an electrolytic cell in which the catholyte is separated from the anolyte by an ion-permeable membrane, which comprises immersing a lead cathode in a non-hydroxylic catholyte in the cell, which catholyte consists essentially of a solution of (a) ethyl bromide and (b) tetraethylammonium bromide in acetonitrile in the proportions of from about 1 to about 8.7 moles of ethyl bromide and from about 0.1 to about 0.5 mole of tetraethylammonium bromide per kilogram of catholyte, and passing an electric current of from about 6 to about 15 volts and of a current density of from about 0.02 to about 0.03 amp./sq. cm. through said cathode and said catholyte, and recovering tetraethyl lead from the catholyte.

16. The process for preparing tetraalkyl lead compounds in an electrolytic cell in which the catholyte is separated from the anolyte by an ion-permeable membrane, which comprises immersing a lead cathode in a non-hydroxylic catholyte in the cell, which catholyte consists essentially of a solution of (a) at least one alkyl halide of 1 to 2 carbon atoms in which the halogen has an atomic number of at least 17 and (b) an onium salt of the formula R_3SX wherein R is an alkyl radical of 1 to 10 carbon atoms and X is a halogen atom having an atomic number of at least 17, in a normally liquid, non-hydroxylic organic solvent which has a higher reduction potential than the alkyl halide, in proportions of from about 0.1 to about 8.7 moles of alkyl halide and from about 0.07 to about 0.5 mole of said onium salt per kilogram of catholyte, and passing an electric current of from about 4 to about 30 volts and of a current density of from about 0.01 to about 1 amp./sq. cm. through said cathode and said catholyte, and recovering at least one tetraalkyl lead from the catholyte.

17. The process for preparing tetraethyl lead in an electrolytic cell in which the catholyte is separated from the anolyte by an ion-permeable membrane, which comprises immersing a lead cathode in a non-hydroxylic catholyte in the cell, which catholyte consists essentially of a solution of (a) an ethyl halide in which the halogen has an atomic number of at least 17 and (b) an onium salt of the formula R_3SX wherein R is an ethyl radical and X is a halogen atom having an atomic number of at least 17, in a normally liquid, non-hydroxylic organic solvent which has a higher reduction potential than the ethyl halide, in the proportions of from about 0.1 to about 8.7 moles of ethyl halide and from about 0.07 to about 0.5 mole of said onium salt per kilogram of catholyte, and passing an electric current of from about 4 to about 30 volts and of a current density of from about 0.01 to about 1 amp./sq. cm. through said cathode and said catholyte, and recovering tetraethyl lead from the catholyte.

18. The process for preparing tetramethyl lead in an electrolytic cell in which the catholyte is separated from the anolyte by an ion-permeable membrane, which comprises immersing a lead cathode in a non- hydroxylic catholyte in the cell, which catholyte consists essentially of a solution of (a) a methyl halide in which the halogen has an atomic number of at least 17 and (b) an onium salt of the formula R_4NX wherein R is an alkyl radical of 1 to 2 carbon atoms and X is a halogen atom having an atomic number of at least 17, in a normally liquid, non-hydroxylic organic solvent which has a higher reduction potential than the methyl halide, in the proportions of from about 0.1 to about 8.7 moles of methyl halide and from about 0.07 to about 0.5 mole of said onium salt per kilogram of catholyte, and passing an electric current of from about 4 to about 30 volts and of a current density of from about 0.01 to about 1 amp./sq. cm. through said cathode and said catholyte, and recovering tetramethyl lead from the catholyte.

19. The process for preparing an organolead compound in an electrolytic cell in which the catholyte is separated from the anolyte by an ion-permeable membrane, which comprises immersing a lead cathode in a non-hydroxylic catholyte in the cell, which catholyte consists essentially of a solution of (a) at least one ester of the formula RX wherein X is an anion whose conjugate acid, HX, has a molecular weight greater than 20 and a pKa of less than about 6 and R is a hydrocarbon radical of 1 to 10 carbon atoms having a saturated carbon atom attached to X, and (b) a current-carrying dissolved salt which, in water, has a pH in the range of 5 to 10, in a normally liquid, non-hydroxylic organic solvent which has a higher reduction potential than said ester, in the proportions of from about 0.1 to about 8.7 moles of said ester and from about 0.07 to about 0.5 mole of said salt per kilogram of catholyte, and passing an electric current of from about 4 to about 30 volts and of a current density of from about 0.01 to about 1 amp./sq. cm. through said cathode and said catholyte, and recovering an organolead compound from the catholyte.

20. The process for preparing an organolead compound in an electrolytic cell in which the catholyte is separated from the anolyte by an ion-permeable membrane, which comprises immersing a lead cathode in a non-hydroxylic catholyte in the cell, which catholyte consists essentially of a solution of (a) at least one ester of the formula RX wherein X is an anion whose conjugate acid, HX, has a molecular weight greater than 20 and a pKa of less than about 6 and R is a hydrocarbon radical of 1 to 10 carbon atoms having a saturated carbon atom attached to X, and (b) a catholyte-soluble current-carrying halide of a metal of the group consisting of metals of groups IA and IIA of the Periodic Table, in a normally liquid, non-hydroxylic organic solvent which has a higher reduction potential than said ester, in the proportions of from about 0.1 to about 8.7 moles of said ester and from about 0.07 to about 0.5 mole of said metal halide per kilogram of catholyte, and passing an electric current of from about 4 to about 30 volts and of a current density of from about 0.01 to about 1 amp./sq. cm. through said cathode and said catholyte, and recovering an organolead compound from the catholyte.

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