United States Patent Office 2,989,558 Patented June 20, 1961

2,989,558

MANUFACTURE OF ORGANOLEAD COMPOUNDS

Sidney M. Blitzer and Tillmon H. Pearson, Baton Rouge, La., assignors to Ethyl Corporation, New York, N.Y., a corporation of Delaware

No Drawing. Filed Nov. 3, 1958, Ser. No. 771,211
2 Claims. (Cl. 265—437)

This invention relates to a process for the manufacture of organolead compounds. In particular, this invention is directed to an improvement in a process for the manufacture of tetraethyllead from lead oxides and sulfides.

It is an object of this invention to provide a process for the manufacture of organolead compounds which overcomes objections to the present commercial process and provides an improvement over those processes which have been proposed more recently. Particularly, it is an object of the invention to increase the conversion of lead to tetraethyllead above that obtained in present commercial practice without requiring the use of metallic sodium, metallic lead, alkyl halogen compounds, or lead halides.

The above objects of this invention are accomplished by slowly adding a non-lead organometallic compound over a period of at least about 10 minutes to a lead chalkogen, that is lead oxide or sulfide. It has been found that for some unexplained reason the sequence of addition of the reactants is important to the achievement of high yields regardless of how the remainder of the reaction is conducted. Likewise, a slow mode of addition is particularly advantageous despite the amount of non-lead organometallic compound which is fed. In a preferred operation, the feed time of the non-lead organometallic compound to the lead chalkogen is at least 30 minutes. When the reverse mode of addition is employed regardless of how much longer the mixture is further reacted, there is a lower yield obtained than when conducting the operations according to the present invention. As will be brought out further in more detail hereinafter, the temperature, pressure and other conditions of the reaction are subject to considerable latitude without defeating the advantages and purposes achieved by the particular mode of the reaction described above.

In general, the metalloorganic reactants of the present invention have the general formula M^1Ry or M^2M^1Ry, where M^1 and M^2 are metals other than lead, R is an organic radical, and in particular a hydrocarbon radical, and y is an integer from 1 to 4, inclusive. It is not intended that the above formulae limit the reactants in the choice of the groups R, as non-lead metalloorganic compounds containing a plurality of hydrocarbon radicals, R, can be successfully employed in this invention.

In the preferred embodiment of this process the organic radicals are hydrocarbons and particularly are non-aromatic or aromatic radicals. Among the non-aromatic radicals we can employ alkyl, hydrocarbon substituted alkyl radicals, or alkenyl radicals. In general, we prefer the lower alkyl radicals and alkenyl radicals having up to and including about eight carbon atoms. Among the aromatic radicals which can be employed in the above reaction are included phenyl and hydrocarbon substituted phenyl radicals having up to and including 10 carbon atoms. Thus, the compounds M^1Ry and M^2M^1Ry may be considered alkylating or arylating agents with respect to the lead in the inorganic lead compound.

Among the preferred non-lead metals to be employed in the process of this invention are the alkali metals; i.e., lithium, sodium, and potassium; the alkaline earth metals, i.e., beryllium, magnesium, calcium, strontium, and barium; the Group II–B metals, zinc and cadmium; the Group III–A metals, boron, aluminum, gallium, and indium; and combinations thereof. In such combination,

each metal is only attached to the other and carbon. A preferred embodiment is the combination of bi-metal metalloorganic compounds comprising monovalent and trivalent metallo elements.

Illustrative of the alkylating or arylating agents which can be employed are methyl sodium, methyl potassium, methyl lithium, dimethyl magnesium, dimethyl calcium, dimethyl zinc, dimethyl cadmium, trimethyl aluminum, sodium zinc tetramethyl, magnesium aluminum tetramethyl, potassium aluminum tetramethyl, ethyl sodium, ethyl potassium, ethyl lithium, vinyl lithium, diethyl magnesium, diethyl calcium, diethyl zinc, diethyl cadmium, triethyl aluminum, vinyl sodium, trivinyl aluminum, sodium boro tetraethyl, lithium aluminum tetraethyl, potassium aluminum tetraethyl, propyl sodium, propyl potassium, propyl lithium, dipropyl magnesium, dipropyl calcium, dipropyl zinc, dipropyl cadmium, tripropyl aluminum, sodium gallium tetrapropyl, lithium aluminum tetrapropyl, aluminum boro tetraethyl, octyl sodium, octyl potassium, octyl lithium, dioctyl magnesium, dioctyl calcium, dioctyl zinc, dioctyl cadmium, sodium aluminum tetraoctyl, potassium aluminum tetraoctyl, phenyl sodium, phenyl potassium, phenyl lithium, diphenyl magnesium, titanium tetraethyl, diphenyl zinc, diphenyl cadmium, triphenyl aluminum, lithium aluminum tetraphenyl, tolyl sodium, tolyl potassium, tolyl lithium, ditolyl calcium, ditolyl zinc, zirconium tetramethyl, tritolyl aluminum, lithium aluminum tetratolyl, potassium aluminum tetratolyl, naphthyl sodium, naphthyl potassium, naphthyl lithium, dinaphthyl magnesium, sodium aluminum tetranaphthyl, lithium aluminum tetranaphthyl, and the like.

In addition to the normal hydrocarbon derivatives indicated heretofore, branched chain isomers can be employed. Likewise a mixture of two or more compounds M^1Ry and M^2M^1Ry can be employed, and if employed along with a redistribution catalyst there is produced a mixture of organolead compounds containing a multiplicity of hydrocarbon radicals. Likewise, when the Groups R are dissimilar, mixed organolead compounds result.

Among the preferred lead salts employed in this invention are galena, litharge, massicotite, and chemically prepared lead oxide and sulfide.

By the process of this invention, as much as 50 percent of the lead in the foregoing lead compounds is directly converted to organolead or in particular, in a commercial embodiment, to tetraethyllead. The remaining portion of the lead is in a highly active form as lead metal and is ideally suited for employment in the commercial process employing sodium-lead alloy or in that which proposes the reaction of metallic lead with an alkylating agent in the presence of magnesium and a catalyst. Conversely, the lead so produced by this invention can be recycled economically to the present process by conversion to the appropriate lead salt.

Our invention is adaptable to the production of organolead compounds generally, such as tetraethyllead, tetramethyllead, dimethyldiethyllead, tetravinyllead, tetraphenyllead, triethylphenyllead and tetrapropyllead. Nevertheless, for convenience in describing our invention hereafter, specific reference may be made to tetraethyllead, the most widely known because of its use as an antiknock agent. Whenever, in the following description, this material is referred to, it is to be understood that other organolead compounds or mixtures can be made by our process. While this invention is adapted to employ broadly the stable metalloorganic compounds defined heretofore, for convenience specific reference may be made hereinafter to employ aluminum triethyl as the preferred embodiment in manufacturing the important antiknock material, tetraethyllead.

Generally, the process of this invention is conducted as follows. Into a reaction vessel, preferably a stirred autoclave, is placed the desired quantity of an inert liquid carrier such as, for example, a hydrocarbon of medium boiling range. The lead oxide or sulfide, in finely divided solid form, is introduced through a hopper containing a plug cock into the autoclave while agitating to create a suspension thereof in the inert carrier. A suspension or solution of the non-lead organometallic compound in an inert liquid carrier is then fed to the reactor over a period of at least 10 minutes. The autoclave is sealed and moderate heat is applied while continuing the agitation. Thereupon, an exothermic reaction ensues and upon reaching the desired reaction temperature, cooling is provided through a jacket in the autoclave. After completion of the reaction, the organolead compound produced is in solution in the carrier liquid and the other products, namely the non-lead oxide or sulfide and metallic lead can be removed by filtration and the organolead compound removed from the carrier by distillation. An alternate and successful method of recovery comprises discharging the autoclave contents into a vessel containing water and recovering the organolead by steam distillation therefrom.

It has been indicated that the process of the present invention is conducted in the presence of an inert carrier liquid. Hydrocarbons of appropriate boiling point with respect to the organolead compound produced are satisfactory and can be chosen so as to provide a solution of the product suitable for other applications or so that they can be readily removed by distillation at a temperature at which the organolead compound will not decompose. Other inert carrier liquids are satisfactory and where the product is a liquid such as, for example, in the manufacture of tetraethyllead, the organolead compound itself can be employed as a carrier liquid. In such an operation, economics are effected by obviating the necessity of recovery by other means than merely filtration of the co-produced solids. Another class of carrier liquids comprises the liquid ethers, amines and liquid ammonia. The principal criterion of choice therefore, of a carrier, is the physical characteristic of the organolead compound produced, and the inertness of the liquid to the organometallic reactant. Certain of the aforementioned reactant carriers, while inert to the reactants, exhibit a beneficial effect on the reaction which may be considered catalytic in nature and contribute to the ease of reaction and rapidity of arriving at completion of the reaction at relatively lower temperatures and pressures. Aromatic hydrocarbons are well suited for this purpose.

When conducting this process in the presence of a liquid carrier as above, the amount of carrier should be proportioned so as to provide adequate heat removal facilities. In general, the load on the heat transfer medium is proportional to the concentration or relative proportion of the reactants and carrier. In a batch operation it is preferred to employ the liquid diluent in the proportion of as much as 1,000 parts per part of organometallic reactant. In an operation providing the maximum heat transfer medium, a more concentrated reaction mixture can be employed wherein as little as equal parts by weight of carrier and organometallic reactant are employed. In general, it has been found that a more concentrated reaction mixture provides a rapid reaction and, provided adequate heat removal means are provided, this is an advantage as the organolead product is subjected to the elevated reaction temperature for the shortest practical time thereby minimizing thermal decomposition or undesirable side reactions.

The organometallic compounds employed as the reactants of this invention can be prepared by methods well known in the art. For example, the alkali metal compounds can be prepared by reaction of the alkali metal with an organomercury compound. Thus lithium ethyl is prepared by reaction of metallic lithium with diethyl mercury. The organoalkaline earth reactants can be produced by reacting the metal with an organic halide. Thus, diethyl magnesium is prepared by reacting ethyl chloride with magnesium turnings in the presence of diethyl ether, followed by addition of dioxane, thereby creating a separate liquid phase containing diethyl magnesium, halide-free, in a mixture of diethyl ether and dioxane. Group III–A organo compounds can be produced by reaction of the Group III–A halide with an alkali metal organo compound. Thus aluminum triethyl is produced by reaction of lithium ethyl and aluminum trichloride. The Group II–B reactants can be prepared by direct reaction of the metal and an organic halide. Thus, zinc diethyl is produced by reacting a zinc-copper couple with ethyl chloride and distilling diethyl zinc from the reaction mixture. The mixed metal organics are typified by lithium aluminum tetraethyl which can be prepared by reaction of lithium hydride and aluminum chloride to first form lithium aluminum hydride, which is then alkylated with ethylene. Many of the organometallic compounds have recently been described as being derivable by direct alkylation of the corresponding metal hydride. Compounds so produced are likewise satisfactory in the process of this invention, and indeed are sometimes preferred.

This invention can be further understood by the following detailed working example of one method of practicing this invention as directed to the manufacture of tetraethyllead.

Example I

To an autoclave equipped with internal agitation, external heating means and external cooling means was added 95.5 parts of finely divided lead oxide and 39 parts of toluene. This mixture was agitated and heated to the reflux temperature. Then a solution of 12.2 parts of triethylaluminum in 21.7 parts of toluene was slowly added to the reactor over a total period of 1½ hours. The mixture was then refluxed for an additional 2¼ hours. At the end of this period the reaction mixture was cooled to room temperature, and analyzed. A tetraethyllead yield of 59 percent was obtained.

Similar results are obtained when the time of adding the triethylaluminum to the lead oxide is reduced to 10 minutes.

By way of comparison, the above procedure was repeated essentially as described with exception that about one third the amount of lead oxide and triethylaluminum respectively were employed and a reverse mode of addition was employed whereby the lead oxide was added to a refluxing solution of triethylaluminum over a period of 15 minutes. The resulting mixture was then refluxed for an additional 3½ hours and tetraethyllead recovered as described above. The yield of tetraethyllead was only 49 percent. Thus, an 18 percent reduction in tetraethyllead yield was obtained.

Example II

Employing the procedure of Example I, 1½ parts of triethylaluminum are fed over a period of 15 minutes to a slurry of 3.0 parts of lead oxide of particle size of less than ¼ inch in 87 parts of toluene. The temperature is maintained at 80 to 85° C. for 3 hours. The reaction mixture is then cooled to room temperature and filtered to remove the solid constituents. The filtrate is washed with an equal volume of water and the organic layer is transferred to a still for removal by vacuum distillation of the toluene and recovery of tetraethyllead from the mixture. Tetraethyllead is obtained in higher yield than when the reverse mode of addition is employed.

Similarly, when trimethyl aluminum, tripropyl aluminum, triphenyl aluminum, tribenzyl aluminum, triethyl aluminum, and tributyl aluminum are employed in the process of Example I, satisfactory yields of tetramethyllead, tetrapropyllead, tetraphenyllead, tetrabenzyllead,

tetraethyllead, and tetrabutyllead are produced, respectively. Likewise, when trimethyl boron, tripropyl gallium, triphenyl indium, tribenzyl gallium, triethyl boron, and tributyl indium are employed in the process of Example I, satisfactory yields of tetramethyllead, tetrapropyllead, tetraphenyllead, tetrabenzyllead, tetraethyllead, and tetrabutyllead are produced, respectively.

In general, the reaction of this process is completed within a relatively short period at elevated temperatures, but a somewhat longer time is required at lower temperatures. In general, a reaction time of between about one-half to twenty hours is employed, after addition of the reactants. In particular, in the manufacture of tetraethyllead with triethylaluminum and lead sulfide, we prefer to employ a reaction time of about ten hours or less.

The pressure employed in the reaction vessel is not critical and is usually the autogenous pressure created by the carrier liquid at the temperature employed. Since organolead compounds are relatively toxic, it is desirable to employ a closed vessel in conducting this reaction which may create an elevated pressure if low boiling carrier liquids are employed.

The temperature required to initiate the self-sustaining reaction of this invention varies with the organolead compound being produced. In general, with the lower alkyl or alkenyl lead compounds such as tetramethyllead, it is preferred to employ temperatures in the range of 25° to 150° C. With aryllead compounds, for example tetraphenyllead, it is preferred to operate in the range of 50° to 150° C.

While it was indicated above that, in general, a catalyst is not required for the practice of this invention, certain materials do exhibit a catalytic effect upon the reaction and, in many instances, their inclusion in the reaction provides a smoother operation. Typical of such materials are heavy metal iodides as well as iodine itself, organic iodides, certain ketones such as acetone and methyl ethyl ketone, and ethers, amines, and aromatic solvents as indicated heretofore.

The following detailed examples serve to illustrate additional specific embodiments of the present invention. However, the invention is not intended to be limited thereto.

Example III

The equipment employed is the same as that in Example I. The autoclave is flushed with nitrogen, then 50 parts of benzene are added thereto, agitation is commenced and 3.5 parts of lead oxide are added into the autoclave. A suspension of 1.82 parts of ethyl potassium in 100 parts of benzene is added to this mixture over a period of about 30 minutes while continuously being agitated. The reactor is then heated to about 80° C. initiating the exothermic reaction. The heat is removed and external cooling is commenced in order to maintain the temperature between 90° and 100° C. The pressure which develops in the system during the reaction is about 20 pounds per square inch gage. At the end of four hours reaction period, the reaction mixture is cooled to room temperature. To the reaction mixture is added sufficient isopropanol, about 28 parts, in order to destroy excess ethyl potassium. The resulting mixture is filtered to remove the solid constituents. The solids are processed for recovery of the lead value. The filtrate is washed as described in Example II and the organic layer is processed for recovery of the tetraethyllead. Based on the lead converted to organolead, a nearly quantitative yield of tetraethyllead is produced.

In place of the benzene employed in the foregoing and other examples as an inert carrier liquid, equally good results are obtained when toluene, xylene, triethyl amine, or diphenyl are employed. In addition to the ingredients specified in the foregoing example, thermal stabilizers may be employed, such as for example naphthalene and styrene to permit operation of the reaction at still higher temperatures without concomitant decomposition of the tetraethyllead so produced.

Example IV

Amyl sodium is reacted with lead sulfide in substantially stoichiometric amounts essentially as described in Example III to produce tetraamyllead in high yield. The amyl sodium and lead sulfide are suspended in a C_{10}—C_{12} hydrocarbon petroleum fraction as the inert diluent thus permitting operation at atmospheric pressure.

Example V

The procedure of Example III is conducted essentially as described with the exception that phenyl sodium is reacted with lead oxide employing benzene as a diluent. The reaction is conducted for a period of five hours with the temperature maintained between 110° and 120° C. Tetraphenyllead is obtained in high yield.

Example VI

When benzyl sodium is reacted with lead oxide in substantially stoichiometric amounts, essentially as described in Example III, tetrabenzyllead is obtained in high yield. The reaction is conducted for a period of eight hours at a temperature of 110° to 115° C.

The following example will demonstrate another embodiment wherein the tetraethyllead is used as the inert carrier.

Example VII

Ethyl sodium is prepared in the usual manner to result in a suspension comprising 8.30 parts of finely divided ethyl sodium in 260 parts n-hexane. To this suspension is added about 100 parts of tetraethyllead. The mixture is then heated to vaporize essentially all of the hexane therefrom. To a reactor is added about 50 parts of tetraethyllead and then 8.8 parts of finely divided lead sulfied are added thereto with agitation. The suspension of the ethyl sodium in tetraethyllead is then added to the reactor over a period of 40 minutes and it is sealed. The autoclave is heated to about 80° C. and then by means of cooling and heating, as necessary, the reaction temperature is maintained between 80° and 90° C. At the end of four hours the reaction mixture is cooled to room temperature, treated with alcohol, washed and filtered as in the above examples. The tetraethyllead prepared in this manner is recovered in high yield and high purity.

The above embodiment employing tetraethyllead as a carrier liquid is equally satisfactory when the ethylating agent employed is ethyl potassium, ethyl lithium, diethyl beryllium, diethyl magnesium, ethyl magnesium chloride, diethyl calcium, diethyl strontium, diethyl zinc, diethyl cadmium, triethyl aluminum, triethyl gallium, triethyl indium, sodium aluminum tetraethyl, potassium aluminum tetraethyl, lithium aluminum tetraethyl, and the like.

Example VIII

The procedure of Example II is followed with the exception that the temperature is maintained between about 116° and 123° C. and the total reaction period is 3¼ hours. 2.36 parts of diethyl zinc are reacted with 3.11 parts of lead sulfide of particle size less than ⅛ inch in 200 parts n-hexane. Tetraethyllead is recovered in nearly quantitative yields and high conversion. The unreacted lead sulfide is recycled to a second operation for further conversion to tetraethyllead.

Example IX

Tetrabutyllead is prepared when reacting 4.0 parts of di-n-butyl zinc with 5.0 parts of finely divided lead oxide in 150 parts cyclohexane at a temperature of 100° C. for three hours according to the procedure of Example I.

Similarly, when butyl zinc or dibutyl cadmium is reacted with lead sulfide as in the foregoing example, and

at a temperature between about 90° and 100° C., equally satisfactory results are obtained.

Example X

To the reactor of Example I is added 150 parts of petroleum ether and then 2.9 parts of finely divided lead oxide are added thereto with agitation. An atmosphere of nitrogen is then maintained in the reactor and 2.36 parts of diethyl zinc are added thereto over a period of 45 minutes. The reaction mixture is heated to a temperature of 140° C. and maintained at this temperature by alternate heating and cooling as required for a period of four hours. At the end of this period, the reaction mixture is cooled to room temperature and filtered to remove solids. The filtrate is washed with an equal volume of water. The organic layer is separated from the water and transferred to a still where, by fractional distillation under vacuum, the tetraethyllead is recovered from the petroleum ether.

Certain of the organozinc and cadmium compounds are solid. When employing the solid organo compounds, it is preferable to first dissolve them in a suitable solvent for ease of handling. Such a procedure is described by the following example.

Example XI

To the reactor are added 150 parts of xylene and then 2.5 parts of finely divided lead oxide are added with agitation. The reactor is then maintained under a dry nitrogen atmosphere for the remainder of the cycle. Diphenyl cadmium, 3.0 parts, are dissolved in 50 parts xylene under a nitrogen atmosphere. This solution is admitted to the reactor over a period of 30 minutes, the reaction mixture is heated to a temperature of 100° C. and maintained at this temperature by alternate heating and cooling, as required, for a period of six hours. The reaction mixture is then cooled to room temperature and filtered to remove the solids as in the preceding examples. The filtrate is washed with an equal volume of water and the organic layer is separated therefrom. Tetraphenyllead is recovered in high yield from the organic layer by vacuum distillation.

Example XII

Following the procedure of Example I, 1.5 parts of triethylaluminum are reacted with 3.11 parts of lead sulfide in 200 parts of n-hexane. The temperature employed is 0° to 120° C. and the reaction period is 2.5 hours. High conversion to tetraethyllead is obtained and unreacted lead sulfide is recycled for additional conversion.

In the above example, when n-hexane is replaced by 200 parts and 20 parts of toluene, the conversion at the latter concentration is nearly twice that at the former. Further reduction in the amount of toluene results in a corresponding increase in the yield of tetraethyllead.

Example XIII

Tetrahexyllead is prepared in high yield by feeding trihexyl aluminum to lead oxide over a period of 40 minutes in essentially stoichiometric amounts in the presence of cyclohexane at atmospheric pressure and at a temperature of 80° to 95° C. for three hours reaction time.

Example XIV

Again employing the procedure of Example I, tetraphenyllead is obtained in high yield when triphenyl aluminum dissolved in benzene is reacted with lead sulfide in essentially stoichiometric quantities. The temperature employed is 75° to 83° C. for a period of 5½ hours.

Equally good results are obtained when the corresponding and other organo compounds of gallium, boron, and indium are employed in the above examples. For example, triethyl gallium, indium, or boron can be reacted with lead sulfide to produce tetraethyllead. Triphenyl gallium, indium, or boron, preferably dissolved in a suitable solvent such as benzene, can be reacted with lead oxide to produce tetraphenyllead. Other examples will be evident.

Example XV

When conducting the process essentially as described in Example I, with the exception that ethyl lithium is reacted with 4.78 parts of lead sulfide in 165 parts of n-hexane at a temperature between about 114° and 122° C. for three and one-fourth hours, tetraethyllead is obtained in high yield and purity.

Example XVI

When 4.0 parts of phenyl lithium in 50 parts benzene is reacted with 5.0 parts of finely divided lead oxide in 150 parts benzene according to the procedure in Example I, with the temperature at 130° to 135° C. for four hours, tetraphenyllead is obtained in high yield.

Example XVII

The procedure of Example I is employed essentially as described with the exception that lithium aluminum tetraethyl is fed to and reacted with 17.9 parts of finely divided lead oxide. Tetraethyllead is obtained in high yield and purity.

Example XVIII

Again conducting the process essentially as described in Example I, tetraethyllead is prepared in high purity and yield when reacting sodium aluminum tetraethyl with finely divided lead oxide at a temperature between 70° and 80° C. for a period of six hours.

Example XIX

Lithium aluminum tetra-(2-phenyl ethyl) is reacted with lead oxide in essentially stoichiometric amounts in accordance with the procedure of Example I to produce tetra-(2-phenylethyl) lead.

Example XX

The procedure of Example I is repeated essentially as described with the exception that the reaction is conducted at room temperature at atmosphere pressure for 15 hours, under a nitrogen atmosphere. In this instance, 1.48 parts of diethyl magnesium in 30 parts diethyl ether-dioxane mixture are reacted with 3.35 parts of finely divided lead oxide in 87 parts of toluene. Upon recovery of the product by distillation under vacuum, greater than 50 percent conversion to tetraethyllead is obtained.

Example XXI

Following the procedure of Example I, tetraethyllead is obtained in high yield when reacting 3.05 parts of diethyl beryllium in 30 parts of n-butyl ether with 9.5 parts of lead oxide in 100 parts of toluene at a temperature of 110° C. for six hours.

Example XXII

Employing the procedure of Example I, lead sulfide is reacted with diethyl calcium in essentially stoichiometric amount to produce tetraethyllead in high yield.

Example XXIII

Diamylbarium is reacted with lead oxide in stoichiometric amounts according to the procedure of Example I with the exception that the temperature employed is 120° to 130° C. for three hours, Tetraamyllead is obtained in high yield.

Equally good results are obtained when diamyl strontium is substituted for diamyl barium in the above example.

Example XXIV

When trivinyl aluminum is added and reacted with lead oxide according to the procedure to Example I, tetravinyllead is obtained in high yield.

A particularly advantageous and preferred method of utilizing the process of this invention as specifically directed to a commercial method of manufacturing tetraethyllead comprises starting with free metal and hydriding to produce the corresponding metal hydride as the

first stage. A second stage then comprises reacting said hydride with ethylene preferably in the presence of a liquid diluent suitable as a carrier for the ethyl metal, which is thereafter reacted with the lead sulfide in accordance with the foregoing description of the present invention.

We claim:

1. In a process wherein an organometallic compound of a metal selected from the group consisting of metals of Groups IA, IIA, IIB, IIIA and IVB of the periodic System of the Elements is reacted with a lead chalkogen selected from the group consisting of lead oxides and sulfides, the improvement which comprises adding said organometallic compound to the lead chalkogen over a period of at least about 10 minutes.

2. A process for the manufacture of tetraethyllead which comprises feeding triethylaluminum to a suspension of lead oxide in toluene over a period of at least one-half hour and then conducting the reaction at a temperature between about 25 to 150° C. until essentially complete.

References Cited in the file of this patent

UNITED STATES PATENTS

2,786,860	Ziegler et al.	Mar. 26, 1957
2,859,225	Blitzer et al.	Nov. 4, 1958

OTHER REFERENCES

Leeper et al.: Chemical Reviews, 54 108, February 1954.