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MANUFACTURE OF ORGANOLEAD COMPOUNDS

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This invention relates to a process for the manufacture of organolead compounds. In particular, this invention is directed to an improved process for the manufacture of tetraethyllead.

The process employed in present commercial practice for the manufacture of tetraethyllead has been in use for a number of years and, in general, is satisfactory. However, it has certain disadvantages which are overcome by practicing our invention. It proceeds by reacting a sodium-lead alloy, of composition controlled to correspond substantially to NaPb, with ethyl chloride according to the following equation:



With the highest yields obtained thereby only about 22 percent of the lead present in the NaPb alloy is converted to tetraethyllead. Under conditions of best operation of this process, no one heretofore, as far as we are aware, has been able to increase this yield of tetraethyllead by even a few percent, due to the inherent limitation in yield as is apparent from the consideration of the above equation. It should be noted that in this reaction at least 75 percent of the lead originally employed is not alkylated. Thus in this reaction, large quantities of lead must be recovered and reprocessed to NaPb alloy in order to make it economical. A further disadvantage of such a large quantity of unreacted lead is that valuable reaction space in the reaction vessel is occupied by materials which are essentially inert for the manufacture of tetraethyllead under present conditions and mode of operation.

Other processes for the production of organolead compounds, and in particular tetraethyllead, have been devised to consume the lead produced in the above equation. While such processes are satisfactory from the standpoint of lead consumption, they suffer an additional drawback in common with the present commercial process in that they require organo halide as the ethylating agent. One such process is that described in U. S. Patent 2,535,190 wherein lead as, for example, that produced in the commercial process, is treated with metallic magnesium and ethyl chloride in the presence of a catalyst, preferably an alkyl ether. Thus, in this process as well as the present commercial process, the tetraethyllead manufacturing operation is restricted by the necessary balance between the metallic sodium required and the organic chlorine in the ethyl chloride.

The classical Grignard synthesis for organolead compounds has been known for many years. Although proceeding readily, it has not been used commercially because of unfavorable economics. This process comprises reaction of an organomagnesium halide with a lead halide. Unfortunately, the lead halide is expensive and no known means for replacing it with an economical substitute has been shown heretofore.

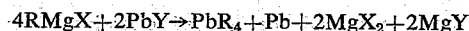
It is therefore an object of this invention to provide a process for the manufacture of organolead compounds which overcomes the above objections to the present commercial process and those processes which have been

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proposed earlier as well as more recently as an improvement there over. 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, or alkyl halogen compounds.

These and other objects of this invention are accomplished by reacting an inorganic lead chalkogen compound with an organomagnesium halide. In accordance with this invention, it has been discovered that to produce organolead compounds it is unnecessary to start with a lead alloy, a lead halide, or in fact to employ metallic lead at all.

The process of the present invention can best be understood by considering the chemical equation involved. In general, the process proceeds according to the equation



where R is an organic radical, X is a halogen of atomic weight greater than 35, and Y is a chalkogen, that is sulfur or oxygen. A satisfactory form of the lead to be employed in the process of this invention is the common lead ore, galena, or lead sulfide. An additional satisfactory source of lead for the present invention is lead oxide. Other lead oxides and sulfides can also be employed. In the preferred embodiment of this process the organic radicals are hydrocarbons and particularly are non-aromatic or aromatic. Among the non-aromatic radicals we can employ alkyl or hydrocarbon substituted alkyl radicals. In general, we prefer the lower alkyl radicals having up to about eight carbon atoms. Among the aromatic radicals which can be employed in the above reaction are included phenyl and hydrocarbon substituted phenyl radicals such as the alkaryl radicals. In general, aromatic radicals having up to 10 carbon atoms are satisfactory. Thus, the compounds RMgX may be considered alkylating or arylating agents with respect to the lead in the lead chalkogen compound represented by PbY.

Of greatest current importance from a commercial standpoint is the manufacture of tetraethyllead by the process of this invention. This embodiment can be illustrated by reference to the following equation representing the preferred embodiment.



Illustrative of the alkylating or arylating agents which we can employ are methyl magnesium bromide, methyl magnesium chloride, ethyl magnesium iodide, ethyl magnesium bromide, propyl magnesium bromide, butyl magnesium bromide, amyl magnesium bromide, and amyl magnesium chloride, and the like up to about octyl magnesium halides; phenyl magnesium bromide, benzyl magnesium chloride, tolyl magnesium iodide, phenethyl magnesium chloride, phenethyl magnesium bromide, butylphenyl magnesium bromide, diethylphenyl magnesium chloride and the like. In addition to the normal alkyl magnesium halides indicated heretofore, the branched chain isomers can be employed. Likewise, a mixture of two or more compounds RMgX can be employed along with a redistribution catalyst to produce organolead compounds containing a multiplicity of hydrocarbon radicals. Thus, by employing a mixture of methyl magnesium chloride and ethyl magnesium chloride and conducting the reaction in the presence of a small quantity of catalyst such as aluminum chloride, the product comprises a mixture of tetramethyllead, trimethylethyllead, dimethyldiethyllead, methyltriethyllead, and tetraethyllead in an equilibrium proportion.

By the process of this invention, as much as 50 percent of the lead in the foregoing lead salts 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, tetraphenyllead, triethylphenyllead and tetrapropyllead. Nevertheless, for convenience in describing our invention hereafter, specific reference will 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.

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 appropriate lead salt, for example lead oxide in finely divided solid form is introduced through a hopper containing a plugcock into the autoclave while agitating to create a suspension of the lead oxide in the inert liquid carrier. A solution of the organo magnesium halide in a suitable diluent such as for example, an ether is introduced into the autoclave. The connection to the hopper is thereupon closed, the autoclave sealed, and moderate heat is applied while continuing the agitation. Reaction commences as the temperature is increased. Thereupon, an exothermic reaction ensues and upon reaching the desired reaction temperature, cooling is provided through a jacket in the autoclave. In contrast to other processes for the manufacture of tetraethyllead, when this invention is employed it is not necessary to provide expensive and complex reflux equipment as, by proper choice of the carrier liquid, the reaction can be conducted in a closed system. Thus, tetraethyllead can be produced without the copresence of ethyl chloride in the closed vessel. This greatly facilitates control of the reaction and prevents the existence of an otherwise hazardous operation. After completion of the reaction, the organolead compound produced is in solution in the carrier liquid and the other products, namely the magnesium salt and metallic lead can be removed by filtration and the organolead compound removed from the carrier by distillation.

The operation described above can be varied and it is not intended that this invention be limited to this specific sequence of addition. For example, the organo magnesium halide solution can be admitted to the reactor first and then the finely divided lead salt added thereto with agitation. In this instance the ether solution will serve as the inert carrier or an additional inert carrier can be added. Other modifications will be evident.

While the above operations were discussed in connection with a batch operation, they can be successfully adapted to a continuous process. In addition to applying the above operations to a continuous process, other modifications of a continuous process can be made, such as first mixing together all the reaction materials and then passing them continuously through a suitable reaction zone.

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 manu-

facture of tetraethyllead, the organolead compound itself can be employed as a carrier liquid. In such an operation, economies are effected by obviating the necessity of recovery by other means than merely filtration of the co-produced solids. The ethers can also be employed as the inert carrier. Usually that ether employed as diluent in the preparation of the organomagnesium halide is used. Typical of this class of ethers is diethyl ether. In general, lower alkyl ethers having from one to six carbon atoms in each alkyl group can be employed. Typical of such ethers are dimethyl ether, methylethyl ether, dibutyl ether and dihexyl ether. Another preferred class of solvents comprises the polyethers, such as the dialkyl ethers of glycols, including dimethyl ether of ethylene glycol, dimethyl ether of diethylene glycol, and the dialkyl ethers of the polyglycols, such as the dimethyl ether of polyethylene glycol. A still further class of ether solvents comprises the cyclic ethers, such as dioxane and tetrahydrofuran. Another class of carrier liquids comprises the liquid 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 organomagnesium halide 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.

In general, 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 a continuous operation or 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 organomagnesium compounds employed in the process of this invention can be prepared by methods well known in the art. For example, reaction of thin magnesium turnings with an ethyl bromide in the presence of an ether produces ethyl magnesium bromide. Corresponding reactions between magnesium and other halides of the desired organic group are employed for other embodiments of the present invention. It is not intended, however, that the scope of this invention be limited to any particular method of producing the hydrocarbon carrying reactant.

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

The reactor employed comprises an autoclave with internal agitation, external heating means, and a means for cooling. Attached to the top thereof is provided a hopper for containing solid reactant having a plug cock by which the solid reactant is admitted into the autoclave. The autoclave is flushed with dry nitrogen. To the autoclave is added 165 parts of n-hexane. With agitation, 7.8 parts of lead oxide of particle size less than $\frac{1}{16}$ inch is admitted to the autoclave from the hopper. Thus a suspension of the lead oxide is formed. To this mixture

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is added a solution of 11.2 parts of ethyl magnesium bromide in 36 parts diethyl ether. The autoclave is then sealed. The resulting mixture is heated to about 114° C. Since the reaction is exothermic, the heat is then removed and the mixture is cooled to maintain a temperature between about 114° to 122° C. When the temperature drops, as the reaction proceeds, heat is again applied to maintain the temperature within the aforementioned range. At the end of 3 hours the agitation is stopped. The mixture is cooled to room temperature and the pressure in the system is released. It is then filtered to remove solids. The filtrate is washed with an equal volume of water and the organic layer transferred to a still for the removal by vacuum distillation of the ether and n-hexane and recovery of the tetraethyllead from the mixture. The conversion obtained was 13 percent.

Similarly, when methyl magnesium bromide, propyl magnesium chloride, phenyl magnesium iodide, benzyl magnesium bromide, ethyl magnesium iodide, and butyl magnesium chloride are employed in the process of the foregoing example, satisfactory yields of tetramethyllead, tetrapropyllead, tetraphenyllead, tetrabenzyl lead, 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. In particular, in the manufacture of tetraethyllead with ethyl magnesium bromide and lead sulfide or oxide, 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 lead compounds such as tetraethyllead, 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.

As the lead chalkogen reactants in this invention are solids, and generally a solvent therefore is not employed, it is preferred in order to provide a relatively rapid and controllable reaction to employ these reactants in finely divided form, or at least in the form of small granules.

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 and amines 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 II

The procedure of Example I is followed essentially as described with the exception that the reaction temperature is maintained between 114° and 118° C. for 3¼ hours. In this instance, 11.2 parts of ethyl magnesium bromide in 36 parts diethyl ether are reacted with 5.98 parts of finely divided lead sulfide in 165 parts of benzene. Tetraethyllead is obtained in high yield.

In place of the benzene employed in the foregoing example as an inert carrier liquid, equally good results are

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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 III

The autoclave of Example I is modified to include a reflux condenser. During the operation, an atmosphere of dry nitrogen is maintained in the reactor. Lead oxide is reacted with amyl magnesium chloride in essentially stoichiometric amounts in a C₆-C₈ hydrocarbon petroleum fraction at the reflux temperature for four hours thus permitting operation at atmospheric pressure. Tetraamyllead is recovered in high yield.

Similarly, when amyl magnesium bromide is reacted with lead sulfide as in the foregoing example, and at a temperature between about 90° to 100° C., equally satisfactory results are obtained.

Example IV

When reacting finely divided lead oxide with phenyl magnesium bromide in essentially stoichiometric amounts in cyclohexane at the reflux temperature for five hours, tetraphenyllead is obtained.

Example V

The procedure of Example III is repeated reacting finely divided lead oxide with benzyl magnesium bromide in excess of 0.1% of the theoretical. The reaction is conducted in di-n-butyl ether at the reflux temperature for sixteen hours. Tetrabenzyllead is obtained in high yield.

The following example demonstrates one embodiment of this invention wherein tetraethyllead is employed as a carrier.

Example VI

A similar solution of ethyl magnesium bromide as employed in Example I is prepared and 30 parts of tetraethyllead are added thereto. This mixture is subjected to distillation under vacuum wherein a substantial proportion of the diethyl ether is vaporized from the mixture to result in a mixture of ethyl magnesium bromide in tetraethyllead. The autoclave is charged with 150 parts of tetraethyllead and the finely divided lead oxide is added thereto. The procedure of Example I is then followed as described. Upon completion of the reaction and separation, tetraethyllead is recovered in high yield.

We claim:

1. A process for making hydrocarbon lead compounds which comprises reacting a hydrocarbon magnesium halide wherein the hydrocarbon radical has up to about 10 carbon atoms with a lead chalkogen wherein the chalkogen is selected from the group consisting of oxygen and sulfur.

2. A process for making alkyl lead compounds which comprises reacting an alkyl magnesium halide wherein the alkyl group contains less than about 8 carbon atoms with a lead chalkogen wherein the chalkogen is selected from the group consisting of oxygen and sulfur.

3. The process of claim 2 wherein the reaction is conducted at a temperature between about 25 to 150° C. in the presence of an essentially inert carrier liquid.

4. The process for the manufacture of tetraethyllead which comprises reacting ethyl magnesium bromide with lead oxide.

5. The process of claim 4 wherein the reaction is conducted at a temperature between about 25 to 150° C. in the presence of an essentially inert carrier liquid.

6. The process of claim 2 wherein the lead chalkogen is lead sulfide.

No references cited.