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PREPARATION OF ORGANIC LEAD
COMPOUNDS

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This invention relates to organometallic compounds and more particularly concerns improvements in an electrolytic process for preparing tetra-alkyl lead compounds such as tetraethyl lead or tetramethyl lead.

Tetraethyl lead, and now tetramethyl lead, are important organometallic compounds of commerce. It has heretofore been discovered that tetra-alkyl lead compounds such as these may be prepared by electrolyzing an alkyl Grignard reagent, e.g. ethyl magnesium chloride, using a lead anode. By this procedure, alkyl groups on the Grignard reagent are transferred to the lead anode, forming tetra-alkyl lead and giving magnesium chloride as a byproduct. This electrolytic process is vastly superior to purely chemical processes by reason of the low investment and raw materials costs.

Unfortunately, certain processing difficulties are inherent in this electrolytic process. One of the most serious of these is the fact that electrolytic conductivity decreases substantially during electrolysis, often dropping to less than half of the original value. Decreased conductivity, or its correlative opposite, higher resistance, lowers the obtainable current density at constant voltage. Not only does this decrease electrolytic cell capacity but it imposes higher power requirements and also produces undesirable heating effects due to I^2R loss. It is accordingly a major object of the present invention to provide an improved electrolytic tetra-alkyl lead process wherein electrolyte conductivity is maintained at a high level.

Briefly, according to the invention, electrolysis of an electrolyte comprising an alkyl Grignard reagent, excess alkyl halide, and an ether, with a lead anode, is effected with an ether mixture comprising, in conjoint presence, a dialkyl ether of an ethylene glycol having at least two carbon atoms in each alkyl group and not more than two ethylene groups in the glycol portion, and tetrahydrofuran.

Thus the invention is based in part on the discovery that tetrahydrofuran markedly increases the conductivity of Grignard-containing electrolyte, frequently by a factor of 3 to 5 fold.

The inventive ether mixture preferably comprises from about 98 to about 40 percent by weight of a dialkyl ether of an ethylene glycol and from about 2 to about 60 percent by weight of tetrahydrofuran. A more optimum range is from about 90 to about 60% of dialkyl ether of an ethylene glycol and about 10–40 percent by weight of tetrahydrofuran. It has been found that, under some conditions, too high a tetrahydrofuran concentration may lead to the deposition of solid magnesium halide etherate which may make electrolysis rather difficult, and accordingly it is desirable but not essential to operate within the foregoing broad range.

The dialkyl ethers of ethylene glycols employed herein are the dialkyl ethers of ethylene glycols having at least two carbon atoms in each alkyl group and not more than two ethylene groups in the glycol portion. Thus the ethers have the formula $R-O-(C_2H_4-O)_n-R$, where the R's are the same or different alkyl groups, each having at least two and suitably up to about 12 carbon atoms per group. "n" is either one or two. Ethers outside of the foregoing definition tend to form a magnesium chloride etherate which precipitates from the electrolyte, thereby fouling equipment. Examples of

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suitable ethers for use herein include the "Carbitols," wherein "n" is one, and the "Cellosolves," wherein "n" is two. Specific ethers are diethyl Cellosolve, dibutyl Cellosolve, diethyl Carbitol, dibutyl Carbitol, and diethyl hexyl Carbitol.

The alkyl Grignard reagents are chosen to produce the desired tetra-alkyl lead compound. For example, an ethyl Grignard will afford tetraethyl lead while a methyl Grignard will produce tetramethyl lead. The alkyl lead compounds having from 1 to about 4 carbon atoms per alkyl group are most effectively produced by the electrolytic process. By employing mixed Grignard reagents, such as a mixture of ethyl Grignard and methyl Grignard, a mixed tetra-alkyl compound may be prepared; thus dimethyl diethyl lead may be obtained. The halide portion of the alkyl Grignard reagent may be the chloride, the bromide, or, less desirably, the iodide.

It has heretofore been found that the presence of excess alkyl halide in the electrolyte is of major advantage. Alkyl halide concentrations of, say 1–50 weight percent of the total electrolyte, react with magnesium metal which will otherwise plate out on the cathode and short the electrodes; it assists in maintaining a high level of electrolyte conductivity; it reduces side reactions; and it appears to provide a current efficiency well in excess of the theoretical. With respect to the last-mentioned point, this perhaps is due to the formation of a dialkyl lead compound electrolytically, which may then react with alkyl Grignard reagent chemically to form tetra-alkyl lead, requiring only two faradays per mol. Ordinarily the alkyl halide will correspond with the alkyl Grignard reagent; for example, ethyl chloride would normally be used with ethyl magnesium chloride.

Grignard reagents are well known and no discussion of their preparation is necessary.

Conditions in the electrolytic cell advantageously include a temperature within the range of about 20 to about 100° C., preferably 40–70° C., and optimally about 45–60° C. Anode and cathode current densities are each preferably within the range of about 0.2 to about 35 amperes per square foot. Cell pressures may range from atmospheric to high superatmospheric—up to 300 p.s.i.g. or even higher. Alkyl Grignard concentrations before the onset of electrolysis are advantageously within the range of about 1.5–3.5 Normal, and electrolysis may be continued until the electrolyte contains as little as 0.3 Normal Grignard, or even less.

The ability of tetrahydrofuran to increase electrolyte conductivity is quite remarkable, and no present mechanism is available to explain this property. Nonetheless when, for example, a 1.5 N ethyl magnesium chloride solution is made up in dibutyl Carbitol, the specific resistance is 15,000 ohm-centimeters, while an identical solution but containing only 5.4 weight percent tetrahydrofuran has a specific resistance of 9,800 ohm-centimeters. Similarly, a 1.5 Normal ethyl magnesium chloride solution containing 10.8 weight percent tetrahydrofuran has a specific resistance of 6,700 ohm-centimeters, and a 21.6% tetrahydrofuran solution has a specific resistance of 3,600 ohm-centimeters.

To more fully describe and to exemplify the present invention, the following illustrative embodiments are presented. It will be understood that these are for illustrative purposes only, and accordingly the conditions and quantities are not necessarily definitive with respect to scope or conditions.

Example I

This example illustrates the electrolysis of a methyl Grignard reagent in dibutyl Carbitol and tetrahydrofuran to produce tetramethyl lead.

To an electrolytic cell having three lead electrodes

spaced about one-eighth inch apart and each being a two inch by 3 inch rectangle, 190 grams of a 2.0 Normal methyl magnesium chloride solution in dibutyl Carbitol is added. The outer plates are connected together to serve as a cathode. Cell characteristics are determined by applying progressively increasing voltages across the electrodes and measuring the amperages.

To the electrolyte is added 21.4 grams of tetrahydrofuran. Again cell characteristics are determined, and the results are presented below. Keeping in mind that Grignard normality decreases upon dilution with tetrahydrofuran, the results are even more striking.

Original Solution		With Tetrahydrofuran	
Volts	Amps	Volts	Amps
4.4-----	0.032	4.5-----	0.20
7.8-----	0.08	7.7-----	0.36
9.1-----	0.10	9.0-----	0.42
12.2-----	0.143	12.4-----	0.50
14.0-----	0.173	14.0-----	0.67

Methyl chloride is added in three portions for a total of 30 grams. Electrolysis is commenced at an initial voltage of 15 volts and at a temperature of 30° C. The run is terminated when, after about 10 ampere hours, cell current falls to 0.02 ampere.

Unreacted methyl chloride is bled off and the cell contents are transferred to a flask. Two liquid layers separate out, a clear upper layer containing tetrahydrofuran, dibutyl Carbitol, and tetramethyl lead with only a trace of Grignard (0.01 Normal), and a dark viscous lower layer containing residual Grignard reagent, magnesium chloride etherate, and some tetramethyl lead, tetrahydrofuran, and dibutyl Carbitol. The upper phase contains 19 weight percent tetramethyl lead and represents roughly 50% of the total tetramethyl lead produced.

Both phases are hydrolyzed with ice and aqueous hydrochloric acid. The organic phase is steam distilled at about 100° C. The overhead distillate contains tetrahydrofuran as well as tetramethyl lead, and is repeatedly water washed to remove the tetrahydrofuran.

Tetramethyl lead is recovered in a yield of 19.1 grams, and remains water white after exposure to light for several weeks.

Example II

In this example a methyl Grignard reagent is electrolyzed with an ether mixture containing 40% tetrahydrofuran and 60% dibutyl Carbitol by weight.

One hundred seventy grams of a 1.8 Normal methyl magnesium chloride solution is placed in an electrolytic cell having 6 square inches of anode surface area and arranged as in the cell of Example I, except that electrode spacing is about $\frac{3}{32}$ inch.

The cell is charged with 21 grams of methyl chloride and electrolysis is commenced. At a temperature of 27° C. and a cell voltage of 6.3 volts the initial current flow is 1.58 amperes. After 2 hours the voltage is 8.5 and the amperage 1.4. Thereafter, current flow decreases

slowly as Grignard is converted to tetramethyl lead and magnesium chloride.

After 2 hours of electrolysis, an additional charge of 11 grams of methyl chloride is introduced, and electrolysis is continued for a total of 10.1 ampere hours.

The cell contents are then hydrolyzed with saturated aqueous ammonium chloride solution and the liquid phase which separates out is steam distilled. The overhead mixture of tetramethyl lead and tetrahydrofuran is washed repeatedly with aqueous sodium chloride.

Tetramethyl lead is recovered in a yield of 24.9 grams. By gas chromatography the product is shown to contain more than 95% tetramethyl lead by weight.

Thus while the invention has been described with reference to a particular embodiment thereof, it is evident that many alternatives, modifications, and variations will be apparent to those skilled in the art in light of the foregoing description. Accordingly it is intended to embrace all such alternatives, modifications, and variations as fall within the spirit and broad scope of the appended claims.

We claim:

1. In a process for preparing a tetra-alkyl lead compound by electrolyzing an electrolyte comprising an alkyl Grignard reagent, excess alkyl halide, and an ether, with a lead anode, the improvement characterized by superior electrolyte conductivity which comprises effecting said electrolysis in the presence of an ether mixture comprising, in conjoint presence, from about 98 to about 40% by weight of a dialkyl ether of an ethylene glycol having at least two carbon atoms in each alkyl group and not more than two ethylene groups in the glycol portion, and from about 2 to about 60% by weight of tetrahydrofuran.
2. Process of claim 1 wherein said tetra-alkyl lead compound is tetraethyl lead.
3. Process of claim 1 wherein said tetra-alkyl lead compound is tetramethyl lead.
4. Process of claim 1 wherein said ether mixture comprises from about 90 to about 60% of said dialkyl ether of an ethylene glycol and from about 10 to about 40% of tetrahydrofuran.
5. Process of claim 1 wherein said dialkyl ether of an ethylene glycol is dibutyl ether of diethylene glycol.
6. Process of claim 1 wherein said dialkyl ether of an ethylene glycol is ethyl hexyl ether of diethylene glycol.

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