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ORGANO-ALUMINUM COMPOUNDS

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This invention relates to ogano-aluminum compounds and more particularly relates to an improved method for reducing organo-aluminum halides to form organo-aluminum compounds containing a greater proportion of organic substituents.

Organo-aluminum compounds have been reduced heretofore by reaction with reducing metals such as sodium and magnesium. More specifically, monoorgano-aluminum dihalides have been reduced in this manner to form diorgano-aluminum monohalides or triorgano compounds. Similarly, diorgano-aluminum halides have been reacted in this manner to form triorgano-aluminum compounds. Also mixtures of the diorgano-aluminum monohalides and monoorgano-aluminum dihalides have been reacted with reducing metals to form organo-aluminum compounds containing a higher proportion of organic substituents. These methods of the prior art have had a number of disadvantages. For example, these reducing reactions are strongly exothermic and, as a result, proper control of the reaction is extremely difficult. Also, when sodium, for example, is employed as the reducing metal, it is necessary that the sodium be completely reacted for safety reasons, since otherwise the operator must dispose of this highly reactive metal at the end of the preparation. Another disadvantage is that the reducing metal employed in the reaction must be broken up into a finely divided state if it is to react completely in the preparation. For these reasons, there has been a need for a simple, safe and effective method for reducing organo-aluminum compounds, particularly since these reduced organo-aluminum compounds are finding increasing use as catalysts for carrying out chemical reactions.

A novel and improved method has now been found for converting organo-aluminum halides to organo-aluminum compounds containing a higher proportion of organic substituents. More specifically, the improved method of the present invention comprises reacting an organo-aluminum halide with the reducing metal in the form of an amalgam, preferably in the form of a liquid amalgam. It has been found that this improved method promotes a readily controllable reaction which can be carried out safely without danger to the operator. The present method also has the advantage that it can be carried out conveniently on either a batch or continuous basis. The use of liquid amalgam is particularly convenient.

The reducing metals useful in the method of the present invention are preferably alkali metals such as, for example, sodium, potassium and lithium. If desired, alkaline earth metals such as calcium, strontium and barium may also be employed. The amalgams are prepared simply by mixing the reducing metal with mercury. Generally it will be preferable to mix the maximum amount of reducing metal with mercury which will still provide an amalgam which will be liquid at the temperature of reaction and preferably which is also liquid at room temperature. Lesser amounts of the reducing metal may be employed if desired, although this will necessitate the use of greater amounts of amalgam in the

reaction with the organo-aluminum halides. The maximum amount of the reducing metal which may be incorporated in the amalgam and still provide a liquid amalgam will depend upon the particular metal selected. For example, when using sodium metal, liquid amalgams containing up to about 1.5 weight percent, based on total amalgam, can be employed. At concentrations much above about 1.5 weight percent of sodium, the amalgam is a solid at the temperature of reaction with the organo-aluminum halides and thus suffers the disadvantage of failing to provide effective contacting between the sodium and the organo-aluminum halide. Concentrations as low as about 0.1 weight percent or lower of the reducing metal may be employed if desired. It will be understood, of course, that amalgams containing mixtures of two or more reducing metals may be employed in the present method if desired. The presence of the mercury in the reaction mixture does not interfere with the present reaction as it is inert.

The organo-aluminum halides which may be reduced in accordance with the improved method of the present invention include (1) diorgano-aluminum monohalides having the formula

$$R_2AlX$$

and (2) monoorgano-aluminum dihalides having the formula

$$RAlX_2$$

and (3) mixtures of diorgano-aluminum monohalides and monoorgano-aluminum dihalides. In the above formulas, R represents an organic group, preferably a hydrocarbon group. It will be understood that the R radicals may represent different organic groups. Generally the R radicals will contain about 1 to 20 carbon atoms, preferably about 1 to 12 carbon atoms. The present invention is particularly effective when the R radicals are alkyl groups containing 1 to 12 carbon atoms. It has been found that excellent results have been obtained when R represents an ethyl group. R may also represent various other organic groups such as, for example, aryl (e. g. phenyl), aralkyl and alkaryl groups. In the above formulas, X represents a halogen atom. The present method is particularly effective with organo-aluminum halides wherein X represents a bromine, iodine and especially a chlorine atom. It will be understood that two halogen atoms in the dihalides may be different halogens. Specific examples of diorgano-aluminum monohalides useful in the present invention include diethyl aluminum chloride, dimethyl aluminum chloride, diethyl aluminum bromide, dimethyl aluminum bromide, diethyl aluminum iodide, dimethyl aluminum iodide, dipropyl aluminum chloride, dibutyl aluminum bromide, methyl ethyl aluminum chloride, diphenyl aluminum bromide, phenyl ethyl aluminum chloride, etc. Specific examples of monoorgano-aluminum dihalides which may be employed in the present invention include ethyl aluminum dichloride, ethyl aluminum dibromide, ethyl aluminum diiodide, methyl aluminum dichloride, butyl aluminum dibromide, propyl aluminum diiodide, ethyl aluminum chloride bromide, phenyl aluminum dichloride, etc.

The present invention is also applicable to organo-aluminum sesquihalides which are mixtures of diorgano-aluminum monohalides and monoorgano-aluminum dihalides. These sesquichlorides may be prepared in accordance with the following chemical equation:

$$3RX+2Al \rightarrow R_2AlX+RAlX_2$$

wherein R and X have their aforementioned definitions. This reaction is conveniently carried out at a temperature of about 40° to 140° C. for about 0.5 to 10 hours. The resultant organo-aluminum sesquihalide may be fractionally distilled to yield as separate products, the diorgano-aluminum halide and the monoaluminum dihalide.

Specific examples of these organo-aluminum sesquihalides include ethyl aluminum sesquichloride, ethyl aluminum sesquibromide, ethyl aluminum sesquiiodide, methyl aluminum sesquichloride, etc. Other mixtures of the monohalides and dihalides in any proportions may also be employed in this invention.

The present method is carried out simply by contacting the reducing metal in the form of a liquid amalgam with the organo-aluminum halide which is to be reduced. Preferably the reaction is carried out with stirring to thereby provide effective contact between the reducing metal and the organo-aluminum halide. The proportions of the reducing metal and the organo-aluminum halide are dependent upon (1) the particular organo-aluminum halide which is to be reduced, i. e., whether it is a diorgano-aluminum monohalide or a monoorgano-aluminum dihalide and (2) the desired organo-aluminum product. More particularly, the present reaction is carried out in accordance with the following general chemical equations (wherein for simplicity the reducing metal is shown as sodium metal):

(1) $2RAlX_2+3Na\rightarrow R_2AlX+3NaX+Al$

(2) $3R_2AlX+3Na\rightarrow 2R_3Al+3NaX+Al$

(3) $3RAlX_2+6Na\rightarrow R_3Al+6NaX+2Al$

Thus in carrying out the present method, approximately stoichiometric proportions of the reactants will be employed and the particular stoichiometric proportions will depend upon the organo-aluminum halide to be reduced and the organo-aluminum compound to be formed as indicated by the above chemical equations. The aluminum metal which is a byproduct of the reaction is produced in a finely divided form which does not interfere with the reaction.

Generally the present reducing reaction will be carried out at a temperature in the range of about 80° to 180° C., preferably in the range of about 100° to 160° C. It is particularly preferred when reducing a monorgano-aluminum dihalide to a diorgano-aluminum monohalide to employ temperatures in the range of about 100° to 140° C., e. g., 120° C. It is also particularly preferred when reducing a diorgano-aluminum monohalide to a triorgano-aluminum to employ reaction temperatures in the range of about 140° to 160° C., e. g., 150° C. The time required to effect the desired reduction will generally be in the range of about 0.1 to 10 hours, usually in the range of about 0.5 to 5 hours. Quite effective results have been obtained employing a reaction time in the range of about 1 to 3 hours. Generally it will be convenient to carry out the present reaction at atmospheric pressure although if desired somewhat higher or lower pressures may be used. Also, if desired, the reducing metal may be added incrementally during the reaction. The incrementally-added reducing metal reacts almost instantaneously with the mercury present on mixing to form an amalgam rather than participating in the organo-aluminum halide reduction. The incremental addition of the reducing metal can be employed with particular advantage when the present invention is employed in a continuous process.

After the reaction is completed, the resultant organo-aluminum product (i. e., the diorgano-aluminum monohalide formed from a monoorgano-aluminum dihalide; or the triorgano-aluminum formed from monoorgano-aluminum dihalide and/or diorgano-aluminum monohalide) may be separated from the reaction mixture. This may be accomplished, for example, by vacuum distillation or by extraction using an organic solvent. Vacuum distillation is usually preferred and generally will be carried out at a pressure in the range of about 0.1 to 150, preferably about 1 to 100, mm. of Hg. Preferably the temperature during vacuum distillation is maintained in the range of about 30° to 200° C., more preferably in the range of about 70° to 160° C. In the alternative extraction method, the organo-aluminum product is extracted using an organic solvent such as an ether or a hydrocarbon.

Preferred solvents are saturated aliphatic hydrocarbons containing about 5 to 10 carbon atoms. The saturated aliphatic hydrocarbon solvents are particularly preferred when recovering alkyl aluminum products from the reaction mixture. Preferably the organic solvent is relatively low boiling so that the organo-aluminum product may be recovered simply by evaporation or stripping off the solvent. Specific examples of organic solvents useful in the recovery of the organo-aluminum products include petroleum ether, a mixture of hexanes or heptanes, n-heptane, isooctane, benzene, toluene, diethyl ether, diisopropyl ether, di-n-butyl ether and the like.

The invention will be more fully understood by reference to the following examples. It is pointed out, however, that the examples are given for the purpose of illustration only and are not to be construed as limiting the scope of the present invention in any way. These examples illustrate the reduction of ethyl aluminum halide using sodium metal as the reducing metal in the form of a liquid amalgam in accordance with the present invention, the reaction resulting in the conversion of the alkyl aluminum halide to a more highly alkylated aluminum compound, or expressing in another way, resulting in the dehalogenation of the alkyl aluminum halide.

Example I

1 gram atomic weight (23 grams) of sodium was converted to a 1 weight percent of sodium amalgam by adding small pieces of the sodium metal to 5 pounds of mercury while stirring continuously in a flask protected by a nitrogen atmosphere. To this liquid sodium amalgam was added 106 grams of a mixture containing 82 weight percent diethyl aluminum chloride and 18 weight percent ethyl aluminum dichloride. The heat of reaction raised the temperature of the reaction mixture from room temperature to about 48° C. The mixture was further heated with stirring to about 120° C. and held there for about 1 hour and 25 minutes. The product was distilled directly from the reaction mixture at a pressure of 3 mm. of Hg and then redistilled at a pressure of about 3 mm. of Hg to give a final product yield of 66 grams. The product was found to contain about 68 weight percent of diethyl aluminum chloride and about 32 weight percent of triethyl aluminum.

Example II

Example I was repeated except that the reaction mixture was heated to 143–150° C. for about 1 hour and 40 minutes. A yield of 48 grams of product was obtained from the resultant reaction mixture by vacuum distillation at 80–83° C. at 3 mm. of Hg. This product contained about 96.7 weight percent of triethyl aluminum and about 3.3 weight percent of diethyl aluminum chloride.

EXAMPLE III

In this example, 173 grams of a mixture containing 82 weight percent of diethyl aluminum chloride and 18 weight percent of ethyl aluminum dichloride, and 91 grams of a mixture of 41 weight percent of diethyl aluminum bromide and 59 weight percent of ethyl aluminum dibromide, were added to a stirred amalgam containing about 1.2 weight percent of sodium (the liquid amalgam contained 54.4 grams of sodium metal). During the addition of the alkyl aluminum halide mixture, the temperature of the reaction mixture rose from 70° C. to 142° C. The temperature was maintained at 142–154° C. for a period of 2 hours and 10 minutes. A yield of 112 ml. of product was obtained from the reaction mixture by vacuum distillation at 80–83° C. at 3 mm. of Hg. This product contained about 1.6 weight percent of diethyl aluminum chloride and about 98.4 weight percent of triethyl aluminum.

EXAMPLE IV

In this example, 2.56 gram atoms (59 grams) of sodium were converted into the form of a liquid amalgam containing 1.3 weight percent of sodium metal by the

addition of pieces of sodium metal to 10 pounds of stirred mercury. To this liquid amalgam was added 270 grams of ethyl aluminum chloride mixture containing 84 weight percent of diethyl aluminum chloride and 16 weight percent of ethyl aluminum dichloride. The reaction mixture was heated at 150–160° C. for 2 hours and 10 minutes. Then, after cooling, 1.38 gram atoms (31.6 grams) of sodium metal was added to the "spent" amalgam in the reaction flask followed by the addition of 145 grams of fresh ethyl aluminum chloride (84 weight percent of diethyl aluminum chloride and 16 weight percent ethyl aluminum dichloride). The reaction mixture was then heated for 2 hours at 143–150° C., after which the product was distilled directly from the reaction flask and redistilled at about 80–83° C. at 3 mm. of Hg. A yield of 234 ml. of product was obtained which contained no detectable amount of ethyl aluminum halide.

EXAMPLE V

In this example, sodium metal was added to 10 pounds of mercury to make a liquid sodium amalgam containing 1.07 weight percent of sodium metal. To this liquid amalgam was added with stirring 251 grams of analytically pure diethyl aluminum chloride. The temperature of the liquid amalgam was 75° C. at the start of addition and at the end of 12 minutes, during which the entire amount of diethyl aluminum chloride was added, the temperature had dropped to 68° C. The resultant mixture was then heated to 150° C. and held there for about 2 hours. The product was distilled directly from the reaction mixture at a pressure of 3 mm. of Hg and then redistilled at a pressure of 3 mm. of Hg. The resultant product had a boiling point of 80–83.5° C. with 95 weight percent of the product distilling from 82 to 83.2° C. A nearly quantitative yield of aluminum triethyl was obtained which contained less than 0.5 weight percent of diethyl aluminum chloride.

EXAMPLE VI

1 gram atomic weight (23 grams) of sodium metal was added to mercury to form a liquid amalgam containing 1 weight percent of sodium metal. This liquid amalgam was treated dropwise while stirring with 145 grams of ethyl aluminum sesquichloride (which contained 45 weight percent diethyl aluminum chloride and 55 weight percent ethyl aluminum dichloride). The heat of reaction carried the temperature from room temperature to about 58° C. The reaction was further heated and a mildly exothermic reaction took place, raising the temperature to 118° C. The final reaction temperature at the end of 45 minutes was 98° C. Distillation at a pressure of 3 mm. of Hg directly from the reaction mixture and redistillation gave 80 cc. of a product boiling at 69–80° C. The product analyzed as 93 weight percent diethyl aluminum chloride. The remainder of the distillate appeared to be aluminum triethyl.

What is claimed is:

1. In a method wherein an organo-aluminum halide containing a hydrocarbon radical of 1 to 12 carbon atoms selected from the group consisting of alkyl and phenyl groups is reduced with a reducing metal selected from the group consisting of alkali metals and alkaline earth metals, the improvement which comprises carrying out said reduction with a liquid amalgam of said reducing metal.

2. Method according to claim 1 wherein said reducing metal is sodium.

3. Method according to claim 1 wherein said organo-aluminum halide is a lower alkyl aluminum halide selected from the group consisting of chlorides, bromides and iodides.

4. Method according to claim 3 wherein said alkyl aluminum halide is an ethyl aluminum chloride.

5. Method according to claim 4 wherein said alkyl aluminum halide comprises ethyl aluminum dichloride.

6. Method according to claim 4 wherein said alkyl aluminum halide comprises diethyl aluminum chloride.

7. Method according to claim 4 wherein said alkyl aluminum halide comprises ethyl aluminum sesquichloride.

8. Method according to claim 1 wherein said organo-aluminum halide is a diphenyl aluminum halide.

9. In a method for reducing a C_1 to C_{12} alkyl aluminum chloride by reaction with sodium metal, the improvement which comprises carrying out said reaction with a liquid amalgam containing 0.1 to 1.5% by weight of said sodium metal.

10. An improved method for converting a C_1 to C_{12} alkyl aluminum halide to a more highly alkylated aluminum compound which comprises reacting said alkyl aluminum halide with a liquid amalgam containing 0.1 to 1.5% by weight of sodium at a temperature of about 80° to 180° C. for about 0.1 to 10 hours, and then separating the more highly alkylated aluminum compound from the reaction mixture.

11. Method according to claim 10 wherein said alkyl aluminum halide is an ethyl aluminum chloride.

12. Method according to claim 10 wherein said separation is carried out by vacuum distillation.

13. Method according to claim 10 wherein said separation is carried out by extracting the resultant more highly alkylated aluminum compound into an organic solvent.

14. An improved method for converting ethyl aluminum dichloride to diethyl aluminum chloride which comprises reacting ethyl aluminum dichloride with sodium metal in the molar ratio of about 2:3, at a temperature of about 100° to 160° C. for about 0.5 to 5 hours, said sodium metal being in the form of a liquid amalgam containing about 0.1 to 1.5% by weight of said sodium metal, and then separating the diethyl aluminum chloride from the resultant reaction mixture by vacuum distillation.

15. An improved method for converting diethyl aluminum chloride to triethyl aluminum which comprises reacting ethyl aluminum dichloride with sodium metal in the molar ratio of about 1:1, at a temperature of about 100° to 160° C. for about 0.5 to 5 hours, said sodium metal being in the form of a liquid amalgam containing about 0.1 to 1.5% by weight of said sodium metal, and then separating the triethyl aluminum from the resultant reaction mixture by vacuum distillation.

16. An improved method for converting ethyl aluminum dichloride to triethyl aluminum which comprises reacting ethyl aluminum dichloride with sodium metal in the molar ratio of about 1:2, at a temperature of about 100° to 160° C. for about 0.5 to 5 hours, said sodium metal being in the form of a liquid amalgam containing about 0.1 to 1.5% by weight of said sodium metal, and then separating the triethyl aluminum from the resultant reaction mixture by vacuum distillation.

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