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PROCESS FOR ISOMERIZING SECONDARY ALKYL ALUMINUM COMPOUNDS

Walter P. Barie, Jr., Pittsburgh, Herbert B. Fernald, Glenshaw, and Bernard H. Gwynn, Richland Township, Allegheny County, Pa., assignors to Gulf Research & Development Company, Pittsburgh, Pa., a corporation of Delaware

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This invention relates to a process for isomerizing secondary alkyl aluminum compounds to primary alkyl aluminum compounds.

Secondary aluminum alkyls are known and can be obtained, for example, by the direct reaction of aluminum, an olefinic hydrocarbon and hydrogen. It is also known that such aluminum alkyls can be successively oxidized and hydrolyzed to the corresponding alcohols. Since, in general, primary alcohols are more desirable commercially than secondary alcohols it would be advantageous to convert the secondary alkyl aluminum compounds to primary alkyl aluminum compounds prior to oxidation and hydrolysis in order to assure the production of the desirable primary alcohols.

We have found that secondary alkyl aluminum compounds can be converted to the corresponding primary alkyl aluminum compounds by heating the same at an elevated temperature and an elevated pressure in the presence of sodium.

The secondary alkyl aluminum compound which can be converted to the corresponding primary alkyl aluminum compound in accordance with our process is one having at least one secondary alkyl group having from three to 30 carbon atoms, preferably from three to 20 carbon atoms, directly attached to the aluminum. Examples of such secondary alkyl groups are isopropyl, sec-butyl, sec-pentyl, sec-hexyl, sec-heptyl, sec-octyl, sec-decyl, sec-dodecyl, sec-tetradecyl, sec-pentadecyl, sec-hexadecyl, etc. The remaining bonds on the aluminum, if not satisfied with the secondary alkyl groups defined above, can be satisfied with primary alkyl groups having two to 30, preferably from two to 20 carbon atoms, such as ethyl, propyl, pentyl, octyl, decyl, hexadecyl, etc.; aromatic groups such as phenyl, o-, m-, and p-tolyl, alkoxy, aryloxy or acetoxy groups or hydrogen. Examples of secondary alkyl aluminum compounds which can be isomerized in accordance with the process of this invention are triisopropylaluminum, tri-sec-butylaluminum, tri-sec-pentylaluminums such as tri-3-pentylaluminum, tri-sec-octylaluminums such as tri-4-octylaluminum, tri-sec-decylaluminums such as tri-2-decylaluminum, tri-sec-hexadecylaluminums such as tri-2-hexadecylaluminum, tri-sec-eicosylaluminums such as tri-8-eicosylaluminum, tri-sec-triacontylaluminums such as tri-3-triacontylaluminum, isopropyl-sec-butyl-3-pentylaluminum, di-2-pentylisobutylaluminum, di-2-heptylaluminum hydride, di-3-nonylphenylaluminum, sec-butyl-n-propylphenylaluminum, tris(1,4-dimethylpentyl)aluminum, diisopropyl-ethoxyaluminum, di-2-pentylphenoxyaluminum, di-2-pentyl-acetoxyaluminum, etc.

In carrying out the isomerization reaction of this invention, we first admix with the secondary alkyl aluminum compound defined above a controlled amount of sodium in finely-divided form. In general, about 0.001 to about five percent by weight of sodium, relative to the secondary alkyl aluminum compound, with the sodium having an average particle diameter of about five to about 50 microns, is satisfactory.

In the practice of the defined process the presence of a liquid phase is desirable, and for this purpose any liquid solvent inert to the charge or the product obtained or which does not adversely affect the course of the reaction

can be employed. Suitable inert solvents are the saturated aliphatic hydrocarbons, such as the pentanes, hexane, cyclohexane, heptane, octane and the like, the aromatic hydrocarbons, such as benzene, toluene and the xylenes and any mixtures thereof.

It is absolutely necessary in order to obtain any significant amount of isomerization that the mixture obtained thus far be subjected to elevated temperatures and elevated pressures. The temperature thus must be about 150° to about 250° C., preferably about 175° to about 225° C., and the pressure about 1500 to about 3500, preferably about 2000 to about 3000 pounds per square inch gauge. The pressure can be obtained in any suitable manner, for example, by pressuring the reaction system with an inert gas such as hydrogen, nitrogen, helium, neon, argon, etc. The reaction time in general must be about one to about ten, preferably about one to about five, hours.

Upon completion of the reaction, as hereinabove set forth, the desired primary alkyl aluminum compound can be recovered from the reaction product, which also contains the solvent and any unconverted secondary alkyl aluminum compound, in any suitable manner. Thus the product can be subjected to distillation in any conventional manner. The solvent will come off first, followed by the branched alkyl aluminum and the primary alkyl aluminum in that order. The primary alkyl aluminum compound so recovered can be employed as such as catalyst, subjected to oxidation and hydrolysis to obtain desired alcohol or for any desired purpose.

The process of this invention can further be illustrated by reference to the following examples.

Example I

Into a one-gallon autoclave, equipped with a stirrer having a speed of 710 revolutions per minute, there was placed 81 grams of atomized aluminum having an average particle size of 9 microns, 105.7 grams of heptane solvent, 643 grams of pentene-2, 4.5 grams of sodium dispersion in white oil (the sodium having an average particle size of 12 microns and amounting to 1.57 grams) and one percent aluminum octanoate in white oil. The contents of the autoclave were pressured to 1800 pounds per square inch gauge with hydrogen. Upon application of heat the temperature rose to about 182° to 198° C. and the pressure to about 2800 pounds per square inch gauge. This temperature and pressure (by the addition of hydrogen as needed during the reaction) was maintained throughout the reaction period of 10 hours. The contents of the autoclave were then cooled to room temperature, depressured, filtered through a sintered glass filter and the heptane removed therefrom by heating at a temperature of 40° C. under vacuum. In order to determine the amount of primary alkyl aluminum and secondary alkyl aluminum in the product remaining 49.3 grams of the product was initially treated with 32.9 grams of octanol-1. This was done in order to destroy any aluminum-hydrogen bonds remaining on the aluminum alkyls present and avoid the formation of water in the subsequent oxidation and hydrolysis reaction. In cases wherein an aluminum-hydrogen bond existed, the treatment with octanol-1 resulted in a dipentyl aluminum alkoxide. The product obtained at this point was thereafter oxidized with oxygen at a temperature of about 30° C. and hydrolyzed with a 1:1 mixture of concentrated hydrochloric acid and water, with the temperature being maintained below 30° C. The resultant product contained two layers, an upper organic layer and a lower aqueous layer. The upper layer, which contained the alcohols, was separated from the lower layer by decantation. Gas chromatographic analysis showed the upper layer to contain 44.4 percent by weight of pentanol-1,

16.3 percent by weight of secondary pentanols and 39.3 percent by weight of octanol-1. The distribution of pentyl alcohols in the product was 73.2 weight percent pentanol-1 and 26.8 weight percent sec-pentanols. The pentanol-1/sec-pentanol ratio was 2.73.

Example II

86.1 grams of the product remaining, and which was not subjected to treatment with octanol-1 in Example I, was placed back in the autoclave with 132.0 grams of hexane solvent, one gram of a sodium dispersion similar to that employed in Example I and 65.0 grams of pentene-2. The olefin was employed in order to react with any aluminum-hydrogen bonds which were present on the aluminum alkyls. The contents of the autoclave were pressured to 2700 pounds per square inch gauge with 37.8 grams of hydrogen. The contents of the autoclave were then subjected to a temperature of 200° C. for four hours. It was noted during this reaction that the hydrogen was not consumed. The contents of the autoclave were then cooled to room temperature, depressured, filtered through a sintered glass filter and the heptane removed therefrom by heating at a temperature of 40° C. under a vacuum. The remainder of the contents of the autoclave were treated with octanol-1, oxidized and hydrolyzed in a manner similar to that employed in Example I. There was found 58.7 percent by weight of pentanol-1, four percent by weight of secondary pentanols and 37.3 percent by weight of octanol-1. The distribution of pentyl alcohols in the product was 93.8 weight percent pentanol-1 and 6.2 weight percent sec-pentanols. The pentanol-1/sec-pentanol ratio was 15.0.

Comparing the results obtained in Example II with those obtained in Example I, it can be seen that the process of this invention results in almost quantitative isomerization. The ratio of pentyl groups to secondary pentyl groups in Example I was 2.73, while in Example II it was 15.0, an increase of 12.27.

Obviously, many modifications and variations of the invention, as hereinabove set forth, can be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A process for converting a secondary alkyl aluminum compound to a primary alkyl aluminum compound which comprises subjecting said secondary alkyl aluminum compound to a temperature of about 150° to about 250° C. and a pressure of about 1500 to about 3500 pounds per square inch gauge in the presence of about 0.001 to about five percent by weight of a sodium dispersion, with the sodium having an average particle diameter of about five to about 50 microns.

2. A process for converting a secondary pentyl aluminum compound to a primary pentyl aluminum compound which comprises subjecting said secondary alkyl aluminum compound to a temperature of about 150° to about 250° C. and a pressure of about 1500 to about 3500 pounds per square inch gauge in the presence of about 0.001 to about five percent by weight of a sodium dispersion, with the sodium having an average particle diameter of about five to about 50 microns.

3. A process for converting a secondary alkyl aluminum compound to a primary alkyl aluminum compound which comprises subjecting said secondary alkyl aluminum compound to a temperature of about 150° to about 250° C. and a pressure of about 1500 to about 3500 pounds per square inch gauge in a hydrogen atmosphere in the presence of about 0.001 to about five percent by weight of a sodium dispersion, with the sodium having an average particle diameter of about five to about 50 microns.

4. A process for converting a secondary pentyl aluminum compound to a primary pentyl aluminum compound which comprises subjecting said secondary alkyl aluminum compound to a temperature of about 150° to about 250° C. and a pressure of about 1500 to about 3500 pounds per square inch gauge in a hydrogen atmosphere in the presence of about 0.001 to about five percent by weight of a sodium dispersion, with the sodium having an average particle diameter of about five to about 50 microns.

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