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METHOD OF PREPARING ORGANO
BERYLLIUM HALIDES

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The present invention relates to pure organic beryllium compounds and to a method of preparing the same. More particularly, our invention relates to the preparation of compounds of the type BeRR_1 in which R is a low molecular weight alkyl radical and R_1 is a halogen or R.

The methods known from the literature for preparing beryllium dialkyls are based on reactions between metal beryllium and mercury dialkyls or between beryllium dihalides and Grignard reagents. These processes, however, are impracticable on a commercial scale due to the toxicity of alkyl mercury compounds and/or because of the requirement of employing large amounts of ether (in the reaction between beryllium dihalides and Grignard reagents).

With regard to the preparation of beryllium alkyl halides, the processes known from the literature involve reacting metal beryllium with alkyl halides or beryllium dihalides with beryllium dialkyls. Such processes lead to very low yields because these reactions take place only with difficulty.

We have now surprisingly found that beryllium alkyl halides can be readily obtained in good yields by treating beryllium dihalides with approximately equimolar amounts of aluminium trialkyls according to an improvement in the process described in Italian patent application prov. filing No. 8,056/60 (Milan). The beryllium alkyl halides thus formed can be easily separated from the dialkyl aluminum monohalides that have been formed.

Particularly suitable beryllium halides include beryllium chloride or bromide. Suitable aluminum trialkyls include aluminum triethyl, aluminum tripropyl and aluminum triisobutyl, and the like.

The reaction between beryllium halides and aluminum trialkyls leads to an equilibrium and therefore beryllium dialkyls are also formed. The higher the amount of reacted aluminum trialkyl, the higher is the amount of beryllium dialkyl formed. By operating the amounts of beryllium dihalides and of aluminum trialkyls in molar ratios of about 1:1, i.e., from about 0.9:1 to 1.1:1, essentially beryllium alkyl halides are obtained. The aluminum dialkyl monohalide thus formed can be separated, according to our invention, by vacuum distillation or by extraction at room temperature with a suitable solvent, preferably a low boiling aliphatic hydrocarbon solvent. The relatively non-volatile beryllium alkyl halides, which are virtually insoluble in the solvent at room temperature, remain as a residue.

The beryllium alkyl halide can be purified by removing any beryllium dihalides which may be present by extraction with hydrocarbon solvents at their boiling point, followed by cooling to very low temperatures whereupon the beryllium alkyl halide precipitates. The hydrocarbon solvent should preferably be an aromatic solvent.

The solvent used in the extraction must be of sufficient volatility that it can be removed by evaporation from the beryllium alkyl halide, and must at the same time exhibit a very low freezing point, so as to permit strong cooling. A solvent which was found to be particularly suitable is toluene, for it solidifies at a very low temperature and yet is sufficiently volatile.

By the aforementioned process beryllium alkyl halides

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can be prepared and purified with the obtaining of good yields.

We have also surprisingly found that from the beryllium alkyl halides thus prepared, pure beryllium dialkyls can be obtained with good yields by reacting such beryllium alkyl halides with a hydride of a metal which is more electropositive than beryllium, and then adding a suitable olefin which is transformed to the corresponding alkyl. That is, the beryllium alkyl halide reacts with the metal hydride to form a halide of such metal and a beryllium alkyl hydride, which beryllium alkyl hydride, by the addition of an olefin, is transformed into beryllium dialkyl.

Suitable olefins which can be added to the beryllium alkyl-hydride according to our invention are those olefins which will react to form a low molecular weight alkyl radical and include ethylene, propylene, butylene, isobutylene, etc.

The dehalogenation reaction is preferably carried out in the presence of a solvent or dispersant. Thus, if ethyl ether is used, the beryllium alkyl halide is completely dissolved. In contrast, if a hydrocarbon is used, e.g., toluene, heptane, or the like, only a portion of the beryllium alkyl halide goes into solution and reacts with the metal hydride to form the beryllium alkyl hydride; the beryllium alkyl hydride is formed, further amounts of beryllium alkyl halide go into solution, until finally all of it has been completely dehalogenated.

The course of the dehalogenation can be controlled by withdrawing samples of clear liquid and analyzing the halogen present. The dehalogenation reaction according to our invention is carried out at a temperature of from about 60 to 150° C., and more preferably from about 80 to 120° C.

The olefin is easily added to the alkyl beryllium hydride by operating preferably under a positive pressure. The addition reaction with the olefin, e.g., ethylene, is carried out at a temperature of from about 50 to 80° C., while maintaining a constant pressure of from about 6 to 8 atmospheres in the system.

The presence of a halide of the metal which is more electropositive than beryllium does not disturb the addition reaction of the olefin. For instance, by using NaH as the dehalogenating agent, NaCl is formed which is insoluble in ethers and hydrocarbons and precipitates as a finely divided powder. Upon addition of the olefin, a beryllium dialkyl is formed which is completely soluble both in ethers and hydrocarbons. By filtration, centrifuging, or the like, the powdered halide of the metal (the hydride of which was used as the dehalogenating agent) is readily separated.

The ether or hydrocarbon solution of beryllium dialkyl can be used as it is or the solvent can be removed by evaporation under a moderate vacuum. The beryllium dialkyl is then distilled under a high vacuum. In such instance there is no need to separate the more electropositive metal halide, for even in its presence one can first remove the solvent and then distill the beryllium dialkyl under a high vacuum.

If the halogenation has been carried out in the presence of an ether, there is formed a beryllium dialkyl etherate. This etherate is, however, by distillation under a high vacuum, decomposed to produce a beryllium dialkyl which is virtually free of ether.

At the end of the distillation there remains a powder consisting essentially of the more electropositive metal halide and containing small amounts of non-dehalogenated beryllium alkyl halide with small amounts of unreacted metal hydride.

When the desired end product is the beryllium dialkyl, it is not necessary to purify the beryllium alkyl halide

by extraction and crystallization since the dehalogenation reaction can be carried out on the raw product obtained by reaction of the beryllium dihalide with aluminum trialkyl, after distillation to remove the aluminum dialkyl halide obtained.

The following examples will further illustrate our invention without limiting the scope thereof. All parts are by weight unless otherwise indicated.

Example 1

106 g. of anhydrous powdered BeCl_2 (corresponding to 1.33 moles) are charged under nitrogen into a 1-liter three-necked flask provided with a central agitator and a distillation adapter. 165 g. of $\text{Al}(\text{C}_2\text{H}_5)_3$ (1.45 moles) are added dropwise thereto while agitating. When the addition is completed the flask is agitated for 30 minutes while heating on an oil bath to 100°C . The mixture is then distilled under a high vacuum (0.01 mm. Hg) by heating the oil bath from room temperature to a maximum of 120°C . 166 g. of distilled product are obtained, and the amounts of Al, Be and Cl contained therein are determined. The product shows 0.093 g. atoms of Be, 1.28 g. atoms of Al and 1.24 g. atoms of Cl.

The residue is first treated with anhydrous toluene at room temperature in order to remove the soluble aluminum product and, after filtration, is then treated with 300 ml. of anhydrous toluene at 110°C . The clear liquid is filtered at a temperature of about 110°C . and is then cooled to -70°C ., whereupon beryllium ethyl halide is thus precipitated. The solution is siphoned into the flask, the treatment at 110°C . is repeated and beryllium ethyl chloride is extracted at a temperature of about 110°C . and then precipitated at about -70°C . until it has been completely removed. The thus crystallized product is dried by heating under vacuum to a final residual pressure of 1 mm. Hg thus obtaining 70.5 g. of a white powder. The analysis of this product showed: Be=13%; Cl=47.8%; Al=nil.

Upon decomposition with ethylhexylalcohol a gas is evolved which, by analysis in a mass spectrograph, is shown to consist essentially of ethane.

The analysis of the dried product and of the evolved gas shows that the extracted product consists essentially of beryllium ethyl chloride (theoretical composition: Be=12.3%; Cl=48.5%).

Example 2

51 g. of anhydrous BeCl_2 (0.635 mole) are introduced, under pure nitrogen, into a 250 ml. flask provided with a distillation column and an agitation system. 74.5 g. of $\text{Al}(\text{C}_2\text{H}_5)_3$ (0.653 mole) are then introduced. The mixture is agitated and heated to 100°C . for 30 minutes. By successive vacuum distillation, 80.5 g. of product which, by analysis, shows 0.647 g. atoms of Al and 0.62 g. atoms of Cl, are obtained.

The residue, which consists essentially of $\text{C}_2\text{H}_5\text{BeCl}$, is dissolved in 150 ml. of anhydrous ether while agitating and is reacted with 30 g. of a 52.5% NaH dispersion in mineral oil (0.63 mole of NaH) in a 350 ml. shaking

autoclave kept under agitation at 120°C . for 15 hours. The autoclave is then cooled, connected with a bottle containing ethylene, and heated to 65°C . The olefin is continuously fed under a constant pressure of about 8 atmospheres for 6 hours. The product is discharged, the autoclave is carefully washed with anhydrous ether, and the whole is concentrated under vacuum to a final residual pressure of 1 mm. Hg and finally distilled under a high vacuum. The product distills at $56-58^\circ\text{C}$. (under 0.1 to 0.5 mm. Hg) and weighs 34.7 g. Analysis of this product shows: Be=8.22%; Al=nil. 0.318 g. atoms of Be are therefore present. Yield of organic Be=50%.

Variations can, of course, be made without departing from the spirit of our invention.

Having thus described our invention, what we desire to secure and claim by Letters Patent is:

1. A method of preparing pure organic beryllium compounds of the formula BeRX wherein R is alkyl and X is selected from the group consisting of chloride and bromide, this process comprising alkylating a beryllium dihalide wherein the halogen substituents are selected from the group consisting of chloride and bromide with an approximately equimolar quantity of a trialkyl aluminum, the molar ratio of said beryllium dihalide to said aluminum trialkyl being from about 0.9:1 to 1.1:1, to form BeRX and a dialkyl aluminum halide wherein the halide substituent is selected from the group consisting of chloride and bromide, and removing said dialkyl aluminum halide therefrom.

2. The method of claim 1 wherein said removal is effected by vacuum distilling off of said dialkyl aluminum halide.

3. The method of claim 1 wherein said removal is effected by extracting at room temperature said dialkyl aluminum halide with a low-boiling aliphatic hydrocarbon, then extracting the residue with an aromatic hydrocarbon at its boiling point, followed by cooling to thereby precipitate BeRX .

4. The method of claim 1 wherein R is ethyl.

5. The method of claim 1 wherein said alkylation is carried out at a temperature of from about 20 to 120°C .

6. The method of claim 3 wherein the aliphatic hydrocarbon solvent is heptane.

7. The method of claim 6 wherein the aromatic hydrocarbon is toluene.

8. The method of claim 1 wherein X is chloride.

9. The method of claim 1 wherein the aluminum trialkyl is triethyl aluminum.

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