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CONCERNING THE PURITY OF MAGNESIUM AND BERYLLIUM ALKYLS AND HALIDES PREPARED BY DIFFERENT METHODS

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SUMMARY

Methods for preparing pure magnesium and beryllium alkyls, aryls and halides have been investigated and evaluated. Some previously reported methods were found to produce impure products whereas one method for each class of compounds above was found that produced an unusually pure product. The latter methods are recommended for the preparation of these classes of compounds when high purity products are necessary such as in molecular association or kinetic studies.

INTRODUCTION

The composition of Grignard reagents has been the object of considerable discussion since their discovery in 1900 and even more so in recent years. Reports in this area dealing with the association of Grignard reagents, magnesium halides and magnesium alkyls[1] and the exchange reactions that occur when magnesium halides and magnesium alkyls are mixed in various solvents, have been published[2]. More recently the redistribution behavior of dialkylberyllium/beryllium halide systems[3] have been reported. Since impurities can drastically alter association measurements as well as promote exchange in systems of this type, it became apparent that to insure reliability of results, it would be necessary to investigate in some detail the preparation of these reagents in a pure form.

Magnesium halides have been prepared directly from the elements with or without solvent[4,5]; from the reaction of magnesium with ethylene halides in ether[6]; and from the reaction of mercuric halides with magnesium[7]. Magnesium alkyls are normally prepared from Grignard reagents by dioxane precipitation of the magnesium halide from solution leaving in solution the R_2Mg compound[8]; by the reaction of magnesium with mercury alkyls in ether[9]; and as indicated in a recent publication by the reaction of a Grignard reagent with organolithium compounds in ether/hydrocarbon mixtures[10]. Beryllium alkyls have been prepared mainly by the reaction of mercury alkyls with beryllium metal[11,12] and by the reaction of Grignard reagents with beryllium halides[13,14]. Beryllium halides have been prepared mainly by the addition of halogen to beryllium metal at 500°**, and by the addition of halogen to

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beryllium in ether[15]. We have examined carefully all of the above methods and in addition have investigated new routes to some of the above classes of compounds in an attempt to determine the best method of preparing a very pure reagent. Results of this evaluation indicate that some methods, with minor modifications in reported procedures, have been found to be excellent for the preparation of a pure product whereas other methods have been found to produce quite impure products.

RESULTS AND DISCUSSION

Magnesium halides

The methods normally used for the preparation of magnesium halides are indicated by the following equations:

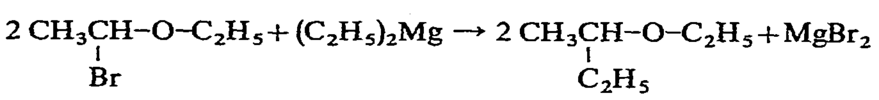
$$Mg+X_2 \rightarrow MgX_2 \qquad (1)$$

$$Mg+XCH_2CH_2X \rightarrow MgX_2+C_2H_4 \qquad (2)$$

$$Mg+HgX_2 \rightarrow MgX_2+Hg \qquad (3)$$

In the preparation directly from the elements in ether solvent at room temperature, halogenated ethers have been found to be a gross impurity. The concentration of these impurities can be minimized by carrying out the reaction at 0° to $-5°$, however, vapor phase chromatography of the solution obtained on hydrolysis of the resulting solid (obtained by removing the ether solvent *in vacuo*) indicates that the product is still contaminated with halogenated ethers. The solid magnesium halides prior to hydrolysis were faintly colored. Repeated recrystallizations from cold ether produced a pure white solid that gave a colorless solution when redissolved in diethyl ether. Magnesium bromide had to be recrystallized five times and magnesium iodide three times to achieve these results. A portion of this final solution when hydrolyzed and checked by VPC showed that no volatile impurities remained. The Mg/Br ratio was found to be exactly 1/2 and the solid analyzed as a monoetherate $[MgBr_2 \cdot O(C_2H_5)_2]$.

It is interesting to note that in previous exchange studies involving dialkylmagnesium/magnesium halide systems[4,16] magnesium halides were prepared in some cases by the addition of halogen to magnesium, in diethyl ether. This study shows that halogenated ethers were present and could have entered into reaction with the dialkylmagnesium compound as shown by eqn. (4).



$$2\,CH_3\underset{\substack{|\\ Br}}{CH}{-}O{-}C_2H_5+(C_2H_5)_2Mg \rightarrow 2\,CH_3\underset{\substack{|\\ C_2H_5}}{CH}{-}O{-}C_2H_5+MgBr_2 \qquad (4)$$

The second method involving preparation from magnesium and ethylene halide also did not produce a clear colorless solution. When a portion of the reaction mixture was hydrolyzed and examined by VPC, impurities were again shown to be present. It was also observed in these preparations that once the colorless solution was finally obtained, particularly in the case of the iodides, it was sensitive to light and with time became colored. However, if a small piece of magnesium was allowed to remain in the mixture, the solutions appeared to be more stable. Evidently halogen was being liberated in some photochemical reaction and a small piece of magnesium would react with it to prevent the increase in concentration of halogen and halogenated ether. The Mg/Br ratio of $MgBr_2$ prepared by this method was 1/1.8 once again indicating an impure product.

Several attempts were made to prepare magnesium bromide and iodide by the reaction of bromine or iodine vapor on magnesium metal at 700° in a vycor tube. As the halogen vapor was passed over the molten magnesium in a stream of nitrogen or argon, the reaction proceeded readily at the interface to produce a gray mixture of magnesium halide and unreacted magnesium. After cooling, the solid mixture was impervious to ethereal solvents and extraction of the magnesium halide was difficult. The overall yield by this method was very low in spite of a determined effort to develop this method.

The final method evaluated did prove to be the most satisfactory method of preparing magnesium halides. The reaction of mercuric halides with magnesium in refluxing diethyl ether and tetrahydrofuran produced colorless solutions which were filtered to remove unreacted magnesium and mercury in the form of an amalgam. VPC analysis of a hydrolyzed portion of this solution did not indicate the presence of any impurity. An excess of magnesium was used and a check for mercury remaining in the solution after the reaction was complete, proved negative. When the solvent was removed *in vacuo* a white solid was obtained. Complete analysis indicated a pure product. This method is considered to be the method of choice for preparing magnesium halides.

Magnesium alkyls

Magnesium alkyls can be prepared in the manner indicated by the following equations:

$$2\,\mathrm{RMgX} + 2\ \mathrm{Dioxane} \rightarrow \mathrm{R_2Mg} + \mathrm{MgX_2}\cdot 2\ \mathrm{Dioxane} \tag{5}$$

$$\mathrm{RMgX} + \mathrm{RLi} \xrightarrow{5\%\ \mathrm{ether/hydrocarbon}} \mathrm{R_2Mg} + \mathrm{LiX} \tag{6}$$

$$\mathrm{R_2Hg} + \mathrm{Mg} \rightarrow \mathrm{R_2Mg} + \mathrm{Hg} \tag{7}$$

The dioxane precipitation method is well documented in the literature and is straightforward. Precipitation of the magnesium halide is essentially quantitative when a 5–10% excess of dioxane is used. The principle limitation of this method is that some of the excess dioxane becomes complexed to the resulting dialkylmagnesium compound and is difficult to remove, even when the solid etherate (dioxanate) is placed under vacuum and heated in order to effect desolvation[17]. Furthermore, in the case of branched chain alkyls, elimination to give magnesium hydride will readily occur at temperatures close to those required for desolvation. When the final product, the unsolvated magnesium alkyl, must be put into another solvent for ebullioscopic molecular weight determination, the residual traces of previous solvents then constitute an intolerable impurity which due to its volatility would invalidate ebullioscopic association studies. This factor also becomes quite critical if dialkylmagnesium compounds of unusual purity are needed for kinetic studies.

The preparation of dialkylmagnesium compounds recently reported by Eastham and Kamienski[10], involving the use of organolithium reagents in an ether/hydrocarbon solution would be satisfactory for most cases where the alkyl chain is of sufficient length to insure solubility. The authors reported that the addition of hydrocarbon and removal of ether, both in a continuous manner, to the lithium halide-free dialkylmagnesium resulted in the removal of all but 0.01% of the dimethyl ether. In addition the yields were essentially quantitative.

Thus the removal of solvated ethers from R_2Mg compounds has always been a little tedious. The solution to this problem would be to prepare these reagents in such a manner that no ether was ever present. Existing reports in the literature discuss the preparation of R_2Mg compounds from R_2Hg compounds, usually in ether solvent. Initial reports involved a sealed tube reaction at a temperature of 130° for the reaction of diethylmercury with magnesium using no solvent[18,19]. Gilman reported that no reaction took place at 130° unless a trace of mercuric chloride was added. In an attempt to promote reaction at 150° using no catalyst the seal tube exploded. Not only are sealed tube reactions inconvenient in most cases, but the product obtained from this procedure usually contains ether insoluble material which probably is RMgH or MgH_2 produced by olefin elimination at such high temperatures. We have found that sealed tubes are not necessary and that successful reaction can be obtained by mixing the reagents in a flask using no catalyst. A mixture of dimethylmercury and excess magnesium was found to react spontaneously at room temperature after a short induction period (15 min). The temperature of the reaction rose to about 60° in two hours and produced dimethylmagnesium in essentially 100% yield. The product is isolated by extracting the reaction mixture with the solvent of choice, leaving behind the insoluble mercury and excess magnesium metal. Diethylmercury behaved similarly at reaction temperatures of 60–90°. Diphenylmercury and -magnesium had to be heated to 150°, however, diphenylmagnesium was produced in 99.2% yield. Traces of unreacted dialkylmercury can be removed under vacuum prior to effecting solution (diphenylmercury can be sublimed from the reaction mixture). This modification produces ultra-pure solutions of magnesium alkyls in high yield under much milder conditions than had been previously reported. Analysis of the solutions for mercury were negative for all of the above preparations.

Since mercury alkyls were found to react so readily with magnesium metal, it was felt that lead alkyls might react just as well. Considering that tetramethyl- and tetraethyllead are available for about $1/lb compared to $350/lb for the corresponding mercury alkyls, such a preparation would be of obvious merit. The bulk of this experimentation was carried out using tetraethyllead and in a few cases tetramethyllead and tetraphenyllead. In some cases neat tetraethyllead was used and in others solvents such as ether, hexane and toluene were employed. Aluminum chloride, bismuth chloride, triethylbismuth, diethylmagnesium, diethylmercury and mercury were used as catalysts in a number of reactions. Temperatures ranging from 25–100° were investigated. Purified tetraethyllead decomposed readily in light to give lead deposits and reactions were carried out both in sunlight and in the dark. In some attempts high speed stirring was used to insure fresh surface on the magnesium for reaction sites. In no case did we observe that reaction took place to produce the desired dialkylmagnesium product.

In conclusion, then, pure $MgBr_2$ and $MgCl_2$ are best and most conveniently prepared from the corresponding mercury halide and excess magnesium metal in either diethyl ether or tetrahydrofuran. On the other hand pure magnesium alkyls and aryls are best and most conveniently prepared by the reaction of the corresponding mercury alkyl or aryl with excess magnesium in the absence of solvent. The product is then extracted with the solvent of choice. Both of the reactions to prepare MgX_2 and R_2Mg compounds proceed in essentially quantitative yield to produce an unusually pure product.

Beryllium halides

The methods normally used for the preparation of beryllium halides are indicated by the following equations.

$$Be+X_2 \xrightarrow{\text{Ether}} BeX_2 \tag{8}$$

$$Be+HCl \xrightarrow{H_2O} BeCl_2\cdot xH_2O \xrightarrow{SOCl_2} BeCl_2 \tag{9}$$

$$Be+X_2 \xrightarrow{\text{Hot tube}} BeX_2 \tag{10}$$

The preparation of beryllium bromide directly from the elements in diethyl ether was investigated first at the temperature of refluxing ether. Since bromine had been shown to produce halogenated ethers in the preparation of magnesium bromide from Mg and Br_2 in diethyl ether, it was not surprising to find that halogenated ethers were also produced in this preparation. Bromine was added slowly to beryllium metal covered with ether, and the solution was refluxed for eight hours. At the end of this time the solution was black, whereas a solution of pure beryllium bromide is colorless. In a second experiment the reaction was initiated at dry-ice temperature. After partial addition of bromine the reaction stopped and the bromine color intensified in solution. The mixture was warmed to 0° and finally to reflux temperature before the bromine color disappeared. The final solution was colorless after a total reflux time of two hours but darkened after standing for an additional thirty minutes.

The reaction of beryllium metal with hydrochloric acid followed by dehydration of the beryllium chloride in refluxing thionyl chloride has been reported in the literature[15]. This procedure was followed and the beryllium chloride produced was placed under vacuum for several hours to remove traces of any volatile materials produced. Analysis of the resulting solid gave a beryllium to halogen ratio of 1/1 instead of the expected 1/2. The method does not appear to be satisfactory for the preparation of anhydrous beryllium chloride. It has been suggested that attempted dehydration of $BeBr_2$ and $BeCl_2$ results in hydrolysis to produce beryllium oxychloride[20].

The third method involves the reaction of beryllium metal with halogen vapor in a hot tube reaction. Beryllium chloride and beryllium bromide were prepared as flocculent white solids. When cold ether was added to the solid beryllium halides, the heat of solvation was sufficent to boil the solution. However, when the solid was spooned into cold ether in a dry box, clear colorless solutions of pure beryllium halides could be obtained. Analysis of a hydrolyzed portion of this solution by vapor phase chromatography did not indicate the presence of any impurities. Elemental analysis showed a beryllium/halogen ratio of exactly 1/2 for both $BeBr_2$ and $BeCl_2$. This method is the method of choice for the preparation of very pure beryllium halides.

Beryllium alkyls

Several methods are again available for the preparation of beryllium alkyls, as indicated by the following equations.

$$Be + R_2Hg \rightarrow R_2Be + Hg \tag{11}$$

$$BeX_2 + 2\,RMgX \rightarrow R_2Be + 2\,MgX_2 \tag{12}$$

$$BeX_2 + 2\,RLi \rightarrow R_2Be + 2\,LiX \tag{13}$$

Dimethylberyllium could best be prepared in high yield by the reaction of beryllium metal with dimethylmercury. The reaction was carried out at 110° with a reaction time of 90 hours to produce the desired beryllium compound leaving a pool of mercury in the bottom of the flask. In a second experiment it was found that the reaction could be catalyzed by the addition of a crystal of dimethylberyllium and a drop of mercury to the reaction mixture, prior to placing the flask on the oil bath. The resulting dimethylberyllium was sublimed from the reaction mixture at 130° and then dissolved in diethyl ether to produce a clear colorless solution. Elemental analysis of the product showed the absence of Hg and an NMR spectrum showed one clean singlet 70 cps upfield from TMS to be expected for pure $(CH_3)_2Be$.

Diethylberyllium was prepared by both the Grignard method and by the reaction of diethylmercury with beryllium metal. Using the Grignard method the same problems encountered in the preparation of magnesium alkyls arise. The resulting dialkylberyllium compound contained traces of ether which were difficult to remove completely. An alternative preparation from diethylmercury avoids this problem and the reaction was carried out easily at 120° in 48 hours using a trace of mercuric chloride as a catalyst. The latter method is preferred from a convenience standpoint. In either preparation the $(C_2H_5)_2Be$ product must be distilled under high vacuum such that the product is distilled below 50° in order to prevent olefin elimination.

Initial attempts to prepare diphenylberyllium proved fruitless. One report in the literature for the preparation of diphenylberyllium from $(C_6H_5)_2Hg$ and Be metal uses proportionately large quantites of mercuric chloride and beryllium bromide as a catalytic mixture[15]. The reaction is carried out in a sealed tube at 170° with a reaction time of 72 hours. Since the primary objective was to prepare diphenylberyllium uncontaminated by other materials we attempted this reaction using no catalyst at atmospheric pressure and 150°. The lower temperature was used since diphenylberyllium is reported[20] to decompose without melting at 160°. No reaction took place and the diphenylmercury sublimed from the reaction mixture. When a trace of mercuric chloride was added some reaction took place after 48 hours but the yield was low and unreacted diphenylmercury was recovered. The preparation was also attempted using the Grignard method. Unlike the previous case in which diethylberyllium could be distilled from the reaction mixture, diphenylberyllium was not obtained completely free of halogen.

The final method investigated for the preparation of very pure diphenylberyllium proved to be the most satisfactory. Phenyllithium was prepared in hydrocarbon[21] and purified by washing with petroleum ether. The reaction of phenyllithium with beryllium chloride (prepared by the hot tube method) proceeded readily in ether with lithium chloride precipitating from the reaction mixture[22]. Elemental analysis of the product showed only a trace of Cl in the product and an NMR analysis was consistent with that expected for pure $(C_6H_5)_2Be$. The simplicity of this method aided by the insolubility of LiCl in diethyl ether makes this method the method of choice for the preparation of $(C_6H_5)_2Be$.

EXPERIMENTAL

All reactions were carried out under an inert atmosphere of nitrogen. The solvents used in this work were freshly distilled from either lithium aluminum hydride or sodium aluminum hydride depending on the boiling point of the particular solvent. All metallic salts obtained commercially were dried by heating under vacuum with a P_2O_5 trap to absorb water, even though the salts were labeled anhydrous. Tetraethyllead was purified by allowing it to stand over charcoal to remove the stabilizer, pumping under vacuum to remove traces of volatile materials present and finally dried again over molecular sieve. Dow triply sublimed magnesium and electrorefined beryllium flake (Brush Beryllium Company) were used in these studies. All manipulations were carried out in a nitrogen dry box or under nitrogen at the bench using syrings.

Preparation of magnesium halides

Magnesium bromide was prepared in diethyl ether using the following procedure. Magnesium metal (1.0 moles, 24.3 g) was placed in a flask equipped with a magnetic stirrer, dry ice condensor and two addition funnels. Bromine (0.5 moles, 7910 g) was placed in one funnel with 500 ml of freshly distilled diethyl ether in the other. Enough bromine was added to initiate the reaction with the ether covered magnesium. Then the remaining ether was added and the system maintained at 0° for the continued addition of bromine. After the reaction was complete, the solution was filtered and the solvent was removed *in vacuo*. A light tan product resulted which was recrystallized five times from cold ether to give pure white magnesium bromide. The addition of ether to the solid produced a clear, colorless solution. A portion taken for hydrolysis and subsequent VPC analysis showed that no impurities were present in the final solution. The Mg/Br ratio was found to be 1/1.96 and the solid analyzed as a monoetherate $[MgBr_2 \cdot O(C_2H_5)_2]$. Magnesium iodide was prepared in a similar manner with the iodine first dissolved in some of the ether. Subsequent analysis of the magnesium iodide gave a Mg/I ratio of 1/2.02.

Magnesium halides were prepared from the corresponding mercuric salts using an excess of magnesium. Magnesium chloride was prepared in tetrahydrofuran, magnesium bromide in tetrahydrofuran and diethyl ether, and magnesium iodide in diethyl ether. The procedure consisted of mixing the ether solution of mercuric halide and magnesium and maintaining the system under reflux for several hours. After completion of the reaction no mercury was found in the solution. The reaction mixtures were clear and no solvent by-products were found. An aliquot of magnesium bromide in ether was analyzed for magnesium and bromine and gave a Mg/Br ratio of 1/1.96. An aliquot of magnesium chloride in tetrahydrofuran was analyzed for magnesium and chlorine and gave a Mg/Cl ratio of 1/1.99. These analysis are indicative of the high degree of purity of magnesium halides produced, using this method of preparation.

Magnesium bromide was also prepared from ethylene bromide and magnesium in ether. The reaction proceeded readily with the evolution of ethylene, however the final solution was dark colored. Part of the ether was removed by vacuum distillation at room temperature and magnesium bromide crystallized in the flask. The crystals were removed by filtration and dried on a vacuum manifold. Analysis of the solid for magnesium and bromine gave a Mg/Br ratio of 1/1.85. Ethylene chloride did not react with magnesium in diethyl ether using the same reaction conditions.

The attempted preparation of magnesium bromide in a vycor reactor was carried out as follows. Magnesium (0.125 moles, 3.0 g) was placed in the reactor and heated to 650°. Bromine vapor was passed over the molten magnesium in a stream of argon. White powdery crystals of magnesium bromide were produced, however, extraction with ether proved difficult since much of the product was trapped in the melt after the system had cooled. Modifications of the apparatus and the procedure did not result in significant improvement.

Preparation of magnesium alkyls

Magnesium alkyls were prepared using the dioxane precipitation method. VPC analysis of the solution obtained after hydrolysis of the solid, desolvated dialkylmagnesium products under benzene, showed the presence of traces of ether and dioxane.

In a typical preparation of dialkylmagnesium compounds from the corresponding dialkylmercury, with no solvent present during the reaction, the following procedure was used. Dimethylmercury (0.435 moles, 100 g) was placed in a flask with magnesium (0.87 moles, 21.0 g). The flask was placed under a water-cooled condensor and maintained under a nitrogen atmosphere. The reaction was spontaneous, and the heat release ended after 1.5 h. The resulting solid was extracted with either diethyl ether, tetrahydrofuran or tetramethylethylenediamine. The standard test using 2,2-bipyridine was used to check the resulting solution for mercury and proved negative in all cases. Diethylmercury reacted with magnesium at a temperature of 60°, with the final temperature raised to 90° to insure complete reaction. Diphenylmercury was melted and the temperature maintained at 150° for 40 h for the preparation of diphenylmagnesium. A trace amount of diphenylmercury was observed in the condensor after the reaction had ceased and was not allowed to fall back into the reaction mixture. The yields were 98% or better for these experiments.

The attempted preparation of diethylmagnesium from tetraethyllead was carried out in the following manner. The general procedure was to put magnesium metal (at least 100% excess) in a flask equipped with a stirring apparatus and condensor. Tetraethyllead was then added along with solvent and catalyst if needed. All manipulations were carried out under nitrogen. The reaction mixtures were first shielded from light and if no reaction took place the mixture was exposed to light. Heat was provided by an oil bath. In some cases it was apparent that no reaction had taken place by visual observation. Where this was not possible the mixture was extracted and hydrolyzed, the water layer acidified and then checked for magnesium by titration with EDTA.

Preparation of beryllium halides

The preparation of beryllium halides directly from the elements in diethyl ether was carried out in a manner analogous to the preparation of magnesium halides directly from the elements in ether. The preparation of beryllium chloride from beryllium and hydrochloric acid was carried out using the procedure of Dessy[15]. In this case however the "beryllium halide" was isolated and the beryllium analysis carried out using the procedure of McClure and Banks[23]. The analysis for beryllium and chlorine gave a Be/Cl ratio of 1/1. The compound isolated was not pure beryllium chloride.

The preparation of beryllium bromide and beryllium chloride directly from the elements in a hot tube was carried out as follows, using an apparatus shown in Fig. 1. Beryllium flake (0.28 moles, 0.25 g) was placed in the side arm of the apparatus.

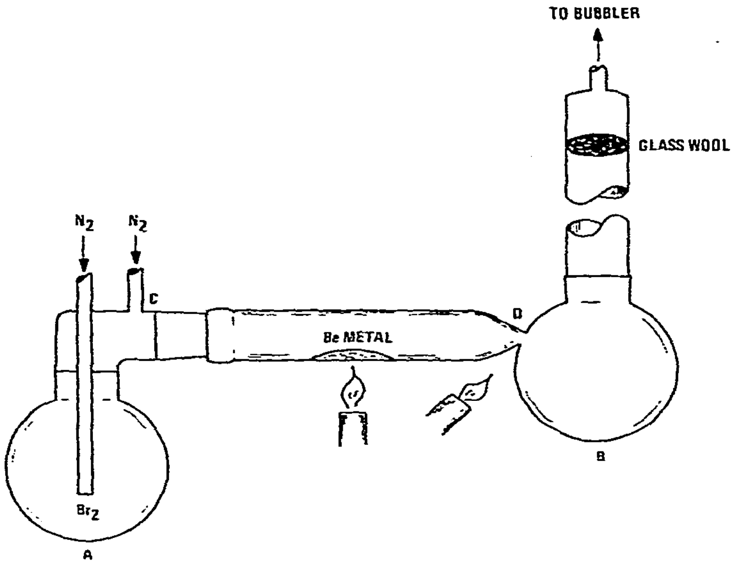


Fig. 1. Apparatus for preparing beryllium halides from beryllium metal and halogen.

Bromine was added to flask A and swept over the beryllium, previously heated to 500°, with a stream of nitrogen. The resulting beryllium bromide was collected in flask B (250 ml capacity) and filled the flask. The glass wool plug is necessary to prevent the loss of the fluffy solid throughout the ventilation system. Once the required amount of halogen had been introduced the passage from A was closed and nitrogen flow at C was maintained to sweep the system free of unreacted halogen. During the reaction time the constriction at D was kept hot to prevent the beryllium halide from causing a stoppage. At the completion of the reaction the constriction at D was sealed with a torch and the apparatus taken into the dry box where the solid was added to cold ether to effect solution. When chlorine was used instead of bromine, the gas was passed directly from a lecture bottle into the system through a three-way stopcock installed at point C and the reaction carried out in a similar manner. Aliquots of the ether solutions were hydrolyzed and analyzed for beryllium and halogen. The beryllium chloride solution gave a Be/Cl ratio of 1/2.04. The beryllium bromide solution gave a Be/Br ratio of 1/1.96.

Preparation of beryllium alkyls

Dimethylberyllium was prepared from dimethylmercury and beryllium metal in a manner similar to the preparation of dimethylmagnesium from dimethylmercury. A slight excess of beryllium was used and the reaction temperature was maintained at 110° for 90 h. At the end of this time traces of unreacted dimethylmercury were removed *in vacuo* and the product sublimed from the residual mercury at 130°. The sublimed dimethylberyllium was then dissolved in diethyl ether. A sample was taken and hydrolyzed, and the ether layer was examined by VPC. No impurities were found. Traces of mercury carried through in the sublimation of dimethylberyllium were found in the bottom of the flask* however, the solution itself gave a negative test for mercury. An NMR spectrum of the ether solution showed one clean singlet 70 cps upfield from TMS, as expected for pure dimethylberyllium.

Diethylberyllium was prepared from beryllium metal (0.15 mole, 1.35 g) and diethylmercury (0.16 mole, 42.0 g) using a mercuric chloride catalyst (0.05–0.10 g), in an apparatus consisting of a flask and condensor. The system was maintained at 125° for 48 h. At the completion of the reaction the sample was allowed to cool and the unreacted diethylmercury removed *in vacuo*. The flask was then connected to a distilling apparatus and the diethylberyllium vacuum distilled. The main fraction was collected at 61° at 0.15 mm. A report in the literature indicates that diethylberyllium boils at 63° at 0.3 mm[20]. If no catalyst was employed the reaction failed to proceed at 100° over a period of several days.

The attempted preparation of diphenylberyllium from diphenylmercury using no catalyst was unsuccessful. Diphenylmercury (0.1 mole, 35.0 g) was added to beryllium metal (0.11 mole, 1.0 g) in a flask and placed under a condensor. The system was maintained at 150° for 240 h, during which time no reaction took place, and diphenylmercury sublimed in the condensor. A trace of mercuric chloride was then added and the reaction conditions maintained for an additional 48 h. At this time the reaction was halted and much of the diphenylmercury was recovered unreacted.

A better preparation was found in which phenyllithium (178.6 moles) in diethyl ether was mixed with beryllium chloride (89.3 moles) in diethyl ether. The total volume was 1200 ml. The mixture was stirred for 40 h and lithium chloride separated as an insoluble precipitate, which was later filtered from the solution. Trace amounts of chloride were found in the solution resulting from the low solubility of lithium chloride in ether. The NMR spectrum of the ether solution of the product was consistent with that expected for pure diphenylberyllium.

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* Other workers observed this same result, having prepared the dimethylberyllium under slightly different reaction conditions[24].

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