Organic and Biological Chemistry

Concerning the Redistribution of Beryllium Alkyls and Aryls with Beryllium Halides in Diethyl Ether[1]

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Abstract: Dimethyl-, diethyl-, and diphenylberyllium were found to redistribute rapidly with $BeCl_2$ and $BeBr_2$ in diethyl ether contrary to earlier reports. The redistribution was determined by a combination of selective precipitation, molecular association, and low-temperature nmr techniques. The composition of a mixture of $R_2Be + BeX_2$ in diethyl ether solution is represented by the equilibrium $R_2Be + BeX_2 \rightleftharpoons RBeX$. This equilibrium lies predominantly if not entirely to the right for the compounds studied. The reasons for earlier work indicating no exchange results appear to have been found.

Redistribution of dialkyl and diaryl organometallic compounds of groups IIA and IIB with their corresponding halides has been the subject of much investigation for several years. In general, these systems are characterized by equilibrium 1 in ether solvents, where R

$$R_2M + MX_2 \rightleftharpoons 2RMX \qquad (1)$$

= alkyl, aryl and X = halogen. Of necessity, associated forms of the species indicated must be included in any discussion; however, they are not indicated here for simplicity. The problem basically is whether or not this equilibrium lies to the right, the left, or whether an equilibrium involving alkyl exchange exists at all. Only recently have unambiguous and definitive results been reported for magnesium[4-9] and zinc[10,11] in tetrahydrofuran and diethyl ether. The mercury alkyls and aryls have long been known to redistribute with the corresponding halides, the reactions being an important synthetic method for preparation of organomercury halides. Definitive data for the cadmium case is lacking, although some work has been done indicating both nonexchange[12] and exchange.[13]

For the beryllium system, previous work,[14] utilizing radioactive ^{7}Be in an exchange study between $(C_6H_5)_2Be$ and $^7BeBr_2$ showed that no exchange of the label occurs, $^7BeBr_2$ being recovered without loss of activity after precipitation from solution using 1,4-dioxane. On the other hand, Head, *et al.*,[15] reported the isolation of a volatile white solid from the reaction of $(t\text{-Bu})_2Be \cdot Et_2O$ and $BeCl_2$ which had the empirical formula $t\text{-}C_4H_9\text{-}BeCl \cdot (C_2H_5)_2O$. However, this empirical formula is not inconsistent with the no exchange results reported above since the compound could be dimeric, $(t\text{-}C_4H_9)_2Be \cdot BeCl_2 \cdot 2(C_2H_5)_2O$. Bell and Coates,[16] in the preparation of CH_3BeH from $(CH_3)_2Be$, $BeBr_2$, and LiH, may have generated CH_3BeBr as an intermediate, since BeH_2 is insoluble in Et_2O. However, reaction intermediates other than CH_3BeBr could explain the results and a dimeric or polymeric product $[(CH_3)_2Be \cdot BeH_2]_n$ is consistent with no exchange results.

In view of the fact that the alkyls and aryls of Mg, Zn, Hg, and possibly Cd, exhibit redistribution with their halides in ether solvents, it seemed to us very likely that a reinvestigation of the beryllium case might be warranted, since this system would be expected to behave similarly.

Experimental Section

Note: Beryllium and its compounds are extremely toxic. Any work with these materials should be conducted according to the established[17] safe-handling procedures.

Reagents. Beryllium was obtained from the Brush Beryllium Co., Elmore, Ohio, as high purity electrorefined flake. Impurities (in parts per million) are listed as follows: BeO (0.3%); C, 140; B, −1; Al, 13; Cr, 80; Fe, 30; Mg, 20; Mn, 6; Ni, −8; Na, 110; Ca, −85; Cu, 30; Si, 40; Zn, −55; Cl, 1900; Be, balance. The metal was used as obtained, after drying in a current of warm, dry nitrogen.

Dimethylmercury, diethylmercury, and diphenylmercury were obtained from Metallomer Labs. The entire sample of diethylmercury obtained from the above source was distilled at 157–158° (756 mm) and found to contain no contaminating impurity. Dimethylmercury and diphenylmercury were used without further purification.

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Bromine was Matheson Coleman and Bell ACS reagent grade, used without further purification. Chlorine was Matheson high purity also used without further purification.

n-C_4H_9Li as a 1.6 *M* solution in hexane was obtained from Foote Mineral Co. The reagent was standardized for C-bound Li and transferred volumetrically.

C_6H_5I was Eastman reagent, distilled before use at reduced pressure. Solvents were all reagent grade: $(C_2H_5)_2O$ was distilled from $LiAlH_4$ and 1,4-dioxane from $NaAlH_4$ immediately prior to use. Benzene was also distilled from $NaAlH_4$ at atmospheric pressure.

Procedure. All operations were conducted in an atmosphere of dry, oxygen-free nitrogen. Transfers of reagents were made in a nitrogen-filled drybox equipped with a special recirculating system to remove oxygen (manganese oxide) and moisture (Drierite and Dry Ice–acetone traps). Glassware was heated and dried under a N_2 flush immediately before use.

Beryllium Halides. Preparation of beryllium halides by direct combination of halide and metal in $(C_2H_5)_2O$ was found to yield significant quantities of halogenated solvent as a by-product. $BeBr_2$ prepared in this manner becomes badly discolored on standing (dark brown) and gas chromatographic analysis of the hydrolysate confirms the presence of numerous impurities. Also, nmr spectra of solutions of this crude halide exhibit complexity of the ether bands attributable to the presence of halogenated solvent. Recrystallization and discarding the supernatant liquor was not completely effective in removing these contaminants after three recrystallizations of the $BeBr_2$.

Beryllium chloride and bromide in very pure form were prepared by direction reaction of the elements.[18] The reaction was carried out in a reactor and collecting vessel which consisted of a Pyrex glass reacting tube connected to a 250-ml, round-bottomed flask *via* a narrow neck, which was sealed with a torch at the completion of the reaction. Cl_2 or Br_2 in a slow nitrogen stream was passed over 0.25 g of Be flake in the reactor tube. The tube and beryllium were heated with a grid burner and the product, formed as a white, microcrystalline smoke, was swept through the restriction into the collecting volume where it collected as a fluffy deposit. A second burner serves to keep the product moving swiftly and prevents plugging at the restriction. The receiving flask must be vented adequately and a plug of glass wool in the neck of the flask prevents loss of the finely divided product. After the reaction subsides and little product continues to be formed, the halogen supply is cut off and the apparatus is allowed to cool under the slow flush of dry nitrogen. All connections were standard taper glass. The use of larger quantities of Be metal results in correspondingly larger quantities of voluminous product and a larger receiver must be used.

Ethereal solutions of the halides were prepared by adding the anhydrous halide, in small quantities, to cold $(C_2H_5)_2O$. Vigorous reaction occurs presumably due to release of the heat of solvation. The resulting solutions are clear and colorless and two-phase if the solubility limit is exceeded. Gas chromatography and nmr indicate the absence of any impurities and the solutions appear to be stable when stored wrapped with aluminum foil and tightly sealed. The Be:Cl ratio of $BeCl_2$ in ether solution was found by elemental analysis to be 1:2.04 and the Be:Br ratio of an ether solution of $BeBr_2$ was found to be 1:1.96.

Beryllium-7 Metal. ^7Be metal was obtained by bombardment in the Berkley 88-in. cyclotron of a 1-g sample of Be metal by 30-MeV deuterons for approximately 100 μA hr. We are indebted to Drs. B. G. Harvey and Ruth Larimer of the Lawrence Radiation Laboratory, University of California, Berkeley, Calif., for the samples.

Dimethylberyllium. After a modification of the method of Burg and Schlesinger,[19] 2.5 g of beryllium flake was placed in a 100-ml, round-bottomed flask fitted with a small water-cooled condenser and vented to a dry N_2 line. A small Teflon-coated stirring bar and 15 ml of $(CH_3)_2Hg$ were added and the mixture was refluxed, with stirring, at 110° in an oil bath. After 168 hr the Be was heavily amalgamated, white crystals of $(CH_3)_2Be$ were evident, and the reaction had apparently stopped. In a subsequent synthesis, it was found that the addition of a crystal of $(CH_3)_2Be$ and a small drop of Hg to the reaction mixture shortened the reaction time to 90 hr. Residual $(CH_3)_2Hg$ is removed at reduced pressure and 100° and the product vacuum sublimed at 130° for 12–20 hr. The sublimate is crystalline and is gray due to included elemental Hg. This material is dissolved in $(C_2H_5)_2O$ with little noticeable heat of solvation to give a clear, colorless solution, stable in tightly sealed flasks in the drybox. The nmr spectrum of this solution at 35° exhibits a sharp singlet at 70 cps upfield from internal TMS, in addition to the well-defined solvent bands. No change in the nmr was noticeable on prolonged storage, nor in a sample exposed briefly to the air to ascertain the effects of slight oxidation. Solutions of $(CH_3)_2Be$ are extremely reactive and fume vigorously in air. A qualitative test for residual Hg in the reagent was negative using ferrocyanide and 2,2′-dipyridyl. Standard solutions of $(CH_3)_2Be$ in diethyl ether were prepared by addition of the beryllium compound slowly to a solution of cold diethyl ether and analyzing the solution for beryllium. The analysis was made for grams of beryllium per gram of solution.

Diphenylberyllium. Attempted preparation of diphenylberyllium from beryllium flake and $(C_6H_5)_2Hg$, in a manner similar to the preparation of $(CH_3)_2Be$, proved unsatisfactory in the absence of a catalyst at 150°. The addition of a pea-sized piece of $HgCl_2$ after 48 hr was followed by the amalgamation of the Be metal to some extent; however, after 288 hr reaction time followed by extraction of the product with *o*-xylene,[14] very little product was isolated.

$(C_6H_5)_2Be$ was successfully synthesized by the reaction of C_6H_5Li with $BeCl_5$ in $(C_2H_5)_2O$. Ethereal C_6H_5Li was synthesized in a very pure form using a modification of the procedure of Schlosser and Ladenburger.[20] In a 2-l. flask, 178.6 mmol of C_6H_5Li in $(C_2H_5)_2O$ was added to 89.3 mmol of $BeCl_2$ in $(C_2H_5)_2O$ giving a reaction volume of 1236 ml. A white precipitate of LiCl formed immediately. The mixture was stirred for 40 hr at 25°. LiCl was removed by filtration through a coarse frit, and a clear colorless solution was obtained. The completion of reaction was indicated by Cl analysis of the resulting solution. Analysis for residual Cl indicated a concentration of 2.4×10^{-3} *M*. The nmr spectrum of the product is clearly different from that of C_6H_5Li, in that the observed complex bands lie closer to the benzene resonance and the *o*-H resonance is broadened into a wide band.

Diethylberyllium. In a typical synthesis, 0.2 mol of $(C_2H_5)_2Hg$ and 0.2 mol of Be were combined in a flask fitted with a condenser. Approximately 0.05–0.1 g of $HgCl_2$ was added as catalyst, and the mixture heated at 125° for 36 hr. At the end of this time a mercury pool had formed and the reaction appeared to be complete. The product was purified by vacuum distillation at 60° (150 μ) (lit. 63° (300 μ)). The distilled $(C_2H_5)_2Be$ was stored as the neat liquid. A qualitative test for residual mercury using 2,2′-dipyridyl was negative. A 4-ml sample of $(C_2H_5)_2{}^7Be$ prepared by this method produced 8.5×10^5 dps.

Dehydration of $BeCl_2$. Be metal (1 g) was dissolved in dilute aqueous HCl and then the liquid was evaporated to yield the solid white hydrate of $BeCl_2$. The hydrate was refluxed with freshly distilled $SOCl_2$ for 20 min and then excess $SOCl_2$ was removed at reduced pressure. Analysis of the solid white product gave the result Be:Cl 1.07:1.0.

Analytical Procedures. Halide analyses were performed by the Volhard method. Beryllium was determined using an empirical titrimetric procedure.[21] According to this procedure, Be is precipitated from aqueous solution at pH 8.5, using NaOH. Excess NaF is added to form the weakly ionized BeF_2, liberating hydroxyl ions which are titrated with H_2SO_4 to the phenolphthalein end point. The measured released alkalinity is proportional to the amount of Be present.

Precipitation Studies. 1,4-Dioxane, freshly distilled from $NaAlH_4$, was added to ethereal solutions of $(CH_3)_2Be$, $BeBr_2$, and equimolar mixtures of $(CH_3)_2Be$, $(C_2H_5)_2Be$, and $(C_6H_5)_2Be$ with $BeCl_2$ and $BeBr_2$. $BeBr_2$ yielded an insoluble dioxanate instantly. $(CH_3)_2Be$ gave a slow-forming precipitate which was soluble in excess $(C_2H_5)_2O$. In the case of the mixtures, a measured quantity (syringe) of 1,4-dioxane was added per millimole of Be present in the solution, and the mixture was stirred for at least 3 hr. All mixtures produced slow-forming white precipitates. For the methyl and phenyl systems, the precipitate was isolated by filtration through a medium frit glass sintered funnel. The filtrates and precipitates were analyzed for beryllium and halogen after hydrolysis of the samples.

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[18] We are indebted to Professor G. E. Coates, University of Durham, Durham, England, for calling this method of preparation of $BeCl_2$ to our attention. This method was also used for the preparation of $BeBr_2$. See also, G. B. Wood and A. Brenner, *J. Electrochem. Soc.*, **104**, 24 (1957).

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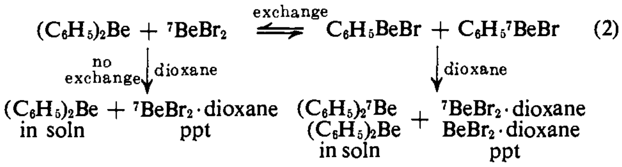
Molecular Association Measurements. The apparent molecular weights of the species present in this work were determined ebullioscopically in Et_2O at 760 mm, using a modified Cottrell boiling point elevation apparatus. Temperature changes were observed using a Beckman differential thermometer and the pressure was measured using a precision Wallace–Tiernan monometer. Solvent loss was prevented by using recirculated ice–water in the condenser of the apparatus. Solvent and samples were introduced by weight through a septum on the apparatus from carefully weighed and sealed syringes. Details of the operation of this apparatus with organometallic systems are in press.[22] Results are presented as (apparent molecular weight)/(formula weight) = i.

Nmr Studies. Spectra were recorded on a Varian Associates, A60 (60 mc) spectrometer with variable-temperature probe. The probe was calibrated using the temperature-dependent resonance in CH_3OH.

Volumetrically prepared samples from standardized solutions were introduced into carefully dried nmr tubes in the drybox, and capped tightly. Comparison spectra using internal and external TMS were identical; the internal standard was preferred because of greater reliability of temperature equilibrium being attained by both sample and reference, and obvious operational simplicity. No evidence of sample–TMS reaction was observed.

Results and Discussion

Earlier studies concerned with redistribution in the system $R_2Be + BeX_2$ were centered around isotopic labeling[14] experiments. The exact system studied involved solution of diphenylberyllium with $^7BeBr_2$ in diethyl ether followed by precipitation of $BeBr_2$ from solution as the dioxanate. It was then determined



$$\begin{tikzcd}[column sep=large] (C_6H_5)_2Be + {}^7BeBr_2 \arrow[r, phantom, "\overset{\text{exchange}}{\rightleftharpoons}"] \arrow[d, "\text{dioxane}", "\text{no exchange}"'] & C_6H_5BeBr + C_6H_5{}^7BeBr \arrow[d, "\text{dioxane}"] & (2) \\ \underset{\text{in soln}}{(C_6H_5)_2Be} + \underset{\text{ppt}}{{}^7BeBr_2\cdot\text{dioxane}} & \underset{\text{in soln}}{\begin{matrix}(C_6H_5)_2{}^7Be\\(C_6H_5)_2Be\end{matrix}} + \underset{\text{ppt}}{\begin{matrix}{}^7BeBr_2\cdot\text{dioxane}\\BeBr_2\cdot\text{dioxane}\end{matrix}} & \end{tikzcd}$$

that no exchange had taken place in solution since the ^7Be label was not statistically distributed between the $(C_6H_5)_2Be$ and $BeBr_2$ after precipitation of the $BeBr_2$.

An attempt to repeat the prior isotopic labeling work led to a very unusual result. First of all, the system studied was $(C_2H_5)_2{}^7Be + BeBr_2$ rather than $(C_6H_5)_2Be + {}^7BeBr_2$. The reasons for this are the following: (1) $(C_2H_5)_2Be$ is a liquid which can be obtained very pure by vacuum distillation whereas $(C_6H_5)_2Be$ is a solid which, by the method of preparation reported, could not be obtained pure; (2) putting the isotope label in the R_2Be rather than the BeX_2 has several obvious advantages from a purity and convenience standpoint. It is of course very important that in such isotopic labeling studies that all starting materials be exceptionally pure since a trace impurity might catalyze or prevent redistribution and give misleading results. In this respect much care was given to the preparation of the starting materials used in this study. The $(C_2H_5)_2{}^7Be$ was prepared from distilled $(C_2H_5)Hg$ and electrorefined Be (99.7% pure) in admixture with ^7Be and the resulting product distilled prior to use. The $BeBr_2$ was prepared as a white crystalline solid from Be metal and Br_2 in a hot tube reaction and purified by sublimation prior to use.

On admixture of standard diethyl ether solutions of $(C_2H_5)_2{}^7Be$ and $BeBr_2$ followed by dioxane precipitation, it was surprising to find that no $BeBr_2$ but a product of empirical formula C_2H_5BeBr precipitated. Fractional precipitation of the product by adding incremental amounts of dioxane produced fractions of a white solid that in each case had a Be:Br ratio of 1:1. Such a result precludes the validity of an isotopic labeling experiment such that earlier reports could not be considered valid provided the $(C_6H_5)_2Be–BeBr_2$ system behaves in the same manner. The data to be presented later show that this is the case.

One other factor that appears to invalidate the earlier isotopic labeling study is concerned with the preparation of the $^7BeBr_2$. In the earlier study ^7Be was dissolved in aqueous HCl to form $^7BeCl_2 \cdot nH_2O$. The halide was then reported to undergo dehydration by refluxing with $SOCl_2$. The resulting product was then diluted with $BeBr_2$ (prepared from Be and Br_2 in diethyl ether) to form the reported $^7BeBr_2$. We have found that adding aqueous HCl to Be metal to form $BeCl_2 \cdot nH_2O$ proceeds readily; however, refluxing this with $SOCl_2$ does not produce anhydrous $BeCl_2$, but what appears to be beryllium oxychloride (Be:Cl ratio of product was found to be 1:1). The oxychloride is insoluble in diethyl ether and thus if the label actually was in the form of insoluble beryllium (7) oxychloride, solution with $(C_6H_5)_2Be$ was never effected and addition of dioxane simply resulted in the filtration of the insoluble beryllium (7) oxychloride (with precipitated $(C_6H_5BeBr)_n$) with all of the radioactive material appearing in the precipitate.

A third complication of the earlier method used was the preparation of $BeBr_2$ used for the dilution of the labeled halide. In the earlier method bromine was added to Be in diethyl ether to form the diethyl ether soluble $BeBr_2$. In studying this reaction we have found that the diethyl ether is highly brominated (vpc analysis of hydrolyzed solution) during the course of this reaction although the resulting solution appears clear and colorless temporarily. Since a beryllium alkyl or aryl might be expected to react with an α-bromo ether, this factor also brings uncertainty into the earlier method used. Thus from the reasons presented above it appears clear that the earlier isotopic labeling experiment indicating no redistribution in the system $(C_6H_5)_2Be–BeBr_2$ is invalid.

Since a solution of $(C_2H_5)_2Be$ and $BeBr_2$ deposited solid fractions of empirical formula C_2H_5BeBr on fractional precipitation with dioxane, it is evident that redistribution in the system can be established if the product could be shown to be monomeric. It is also clear that redistribution might be detected by low-temperature nmr studies provided a separate signal for the R_2Be and RBeX compounds can be detected. In the ensuing discussions are presented the results of (1) selective precipitation studies of solutions of R_2Be and BeX_2 compounds using dioxane, (2) molecular association studies of R_2Be, BeX_2, and $R_2Be–BeX_2$ mixtures, and (3) low-temperature nmr studies of R_2Be and $R_2Be–BeX_2$ mixtures. These studies were carried out using $(CH_3)_2Be$, $(C_2H_5)_2Be$, and $(C_6H_5)_2Be$ as the alkyl or aryl beryllium compound and $BeCl_2$ and/or $BeBr_2$ as the beryllium halide in diethyl ether as the solvent.

Precipitation Studies. Table I summarizes the results of the addition of 1,4-dioxane to equimolar (1:1) mixtures of Me_2Be and Ph_2Be with $BeCl_2$ and $BeBr_2$ in $(C_2H_5)_2O$. It is clear from the data that a species of empirical formula RBeX is being precipitated as the dioxanate. From the experimental stoichiometry of

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[22] E. C. Ashby and F. Walker, *J. Chem. Educ.*, in press.

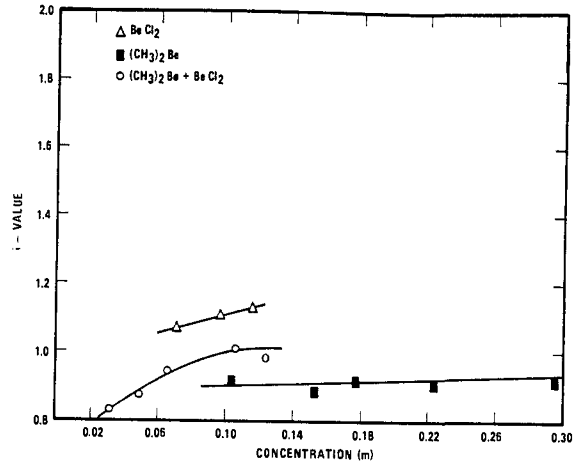


Figure 1. Association of $BeCl_2$, $(CH_3)_2Be$, and $(CH_3)_2Be + BeCl_2$ in diethyl ether.

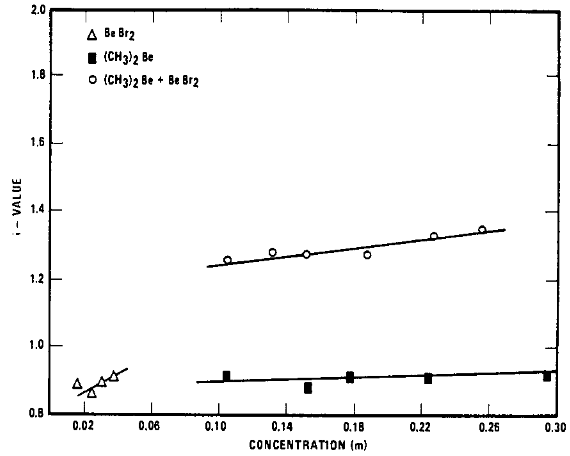


Figure 2. Association of $BeBr_2$, $(CH_3)_2Be$, and $(CH_3)_2Be + BeBr_2$ in diethyl ether.

the precipitation reaction, a monodioxanate is formed, and excess Be is found in the supernatant liquid.

These results show clearly that BeX_2 is not being precipitated selectively, in an manner analogous to the behavior of MgX_2–R_2Mg mixtures toward dioxane. This discovery prohibits the use of dioxane precipitation to recover BeX_2 in the radioactive labeling experiments attempted by ourselves and others.[14] Similar findings have been reported[9] for the systems $(C_2H_5)_2Zn$–ZnI_2 in tetrahydrofuran and $(C_2H_5)_2O$, and $(C_2H_5)_2Zn$–$ZnBr_2$ in $(C_2H_5)_2O$. Here, the precipitate found using tetramethylethylenediamine (TMED) gave the empirical formula RZnX·TMED. However, it was also found that $(C_2H_5)_2Zn$–$ZnBr_2$ in THF precipitated, $ZnBr_2$·TMED.

Table I. Precipitation Studies. Addition of Dioxane to R_2Be–BX_2 Mixtures in Diethyl Ether

R_2Be–BeX_2 R	X	Initial Be:X ratio	Be present, mmol	Dioxane added, mmol	Be:X ratio Ppt	Be:X ratio Filtrate	Residual Be in soln, %
CH_3	Cl	1.02:1	3.3	1.65	1:1.16	1.29:1	50
CH_3	Br	1:1.02	4.6	2.3	1:1.05	1:1.04	50
C_6H_5	Br	1.04:1	2.6	1.3	1.06:1	1.04:1	50

When dioxane was added to a diethyl ether solution of $BeCl_2$ or $BeBr_2$ an immediate precipitate of the BeX_2·dioxanate was obtained. On the other hand when dioxane was added to a solution of $(CH_3)_2Be$ or $(C_6H_5)_2Be$ precipitation of the R_2Be·dioxanate was very slow and complete precipitation took place only after a large excess (three- to tenfold) of dioxane was added. In contrast, when dioxane was added to the R_2Be–BeX_2 mixtures precipitation was relatively slow. The results indicate that if the solution contained a mixture of R_2Be and BeX_2, the BeX_2 should have precipitated first and rapidly leaving behind the relatively soluble R_2Be especially under the conditions used when the Be:dioxane ratio was 2:1.

The precipitation data are consistent with equilibrium 1; however, the precipitation data alone do not distinguish between RBeX and $(RBeX)_2$. Since the dimer can be represented by the species R_2Be–BeX_2, it is necessary to know the molecular weight of the species in solution in order to resolve this ambiguity.

Molecular Weight Measurements. The ebullioscopically determined association data (*i* values) of the compounds and mixtures studied in diethyl ether at 36° are shown in Table II and plotted in Figures 1, 2, and 3.

Table II

R_2Be–BeX_2 (ratio)	Concn range, *m*	*i*
$(CH_3)_2Be$	0.152–0.428 0.104–0.381	0.88–0.94 0.92–0.97
$(CH_3)_2Be$–$BeBr_2$ (1:1)	0.056–0.255 0.081–0.201	1.01–0.35 1.01–1.22
$(CH_3)_2Be$–$BeCl_2$ (1:1)	0.031–0.123	0.83–0.99
$(C_6H_5)_2Be$	0.039–0.138	0.90–0.98
$(C_6H_5)_2Be$–$BeBr_2$ (1:1)	0.035–0.130	0.92–1.1
$BeCl_2$	0.040–0.115	0.91–1.1
$BeBr_2$	0.037	0.91

It is seen that over the concentration range studied, the species are monomeric when calculated as R_2Be, BeX_2, and RBeX. Also, the degree of molecular association is seen to increase slightly with increasing concentration, as expected. The association determinations were made in the same concentration range as the dioxane precipitation studies. The low solubility of $BeBr_2$ prevented study over a wider concentration range.

Together with the precipitation data, the molecular weights of the species in solution allow assignment of equilibrium 1 to be predominantly to the right, as the redistributed species RBeX. It must be recognized that the average molecular weight produced by the experiment excludes only associated species from equilibrium 1 and that removal of a 1:1 precipitate from the mixture implies that RBeX is present as the predominant species. If significant quantities of BeX_2 were present, the halide dioxanate would be expected to precipitate preferentially because of the preferential reaction of BeX_2 with dioxane compared to the other less acidic species in solution and because of the greater insolubility of BeX_2·dioxanate. Also, enhanced solubility of the beryllium halides in the presence of $(CH_3)_2Be$ and $(C_6H_5)_2Be$ demonstrates that appreciable interaction occurs; since the interaction is not association, it must be the result of redistribution.

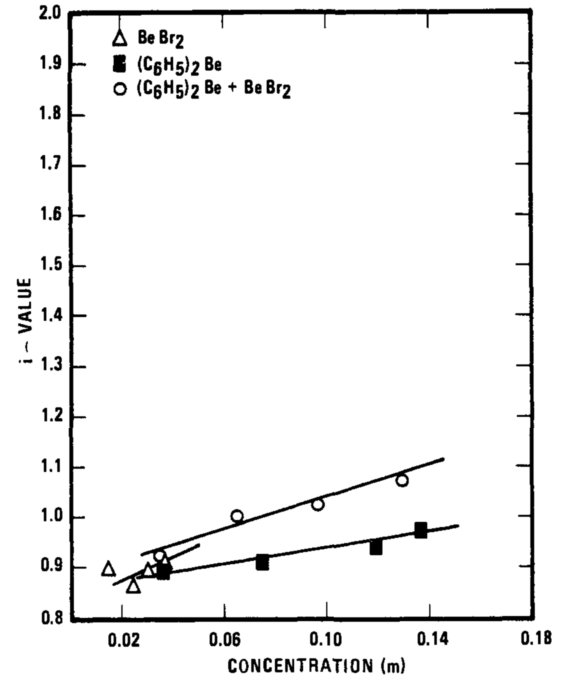


Figure 3. Association of $BeBr_2$, $(C_6H_5)_2Be$, and $(C_6H_5)_2Be$ + $BeBr_2$ in diethyl ether.

The precipitation of Zn Br_2·TMED discussed above suggests that in this case, equilibrium 3 may favor either

$$(C_2H_5)_2Zn + ZnBr_2 \rightleftharpoons 2C_2H_5ZnBr \qquad (3)$$

the mixture $R_2Zn + ZnX_2$, or the equilibrium may be facile enough, compared to complexation and precipitation, that the complexed halide is deposited preferentially. Similar arguments apply for organomagnesium systems. For these systems, the MgX_2·ligand adducts are the least soluble species which would be expected to precipitate on addition of a strong base (ligand).[23] When monomeric RMgX products precipitated instead, the conclusion was that the equilibrium lay entirely in the direction of the RMgX species. Factors which would be expected to determine the position of equilibria in these systems are solvent basicity, nature of halogen, and alkyl or aryl substituent.

Nmr Investigations. Tables III and IV summarize the data for low-temperature studies for $(CH_3)_2Be$–BeX_2 mixtures (X = Cl, Br) in $(C_2H_5)_2O$. The values in the table are the chemical shifts of the CH_3–Be resonance singlet, upfield from TMS, in cycles per second. The results for the system $(CH_3)_2Be$–$BeCl_2$ are plotted in Figure 4.

Table III. Chemical Shift of CH_3–Be Singlet Upfield from TMS in Cycles per Second for Mixtures of $(CH_3)_2Be$ and $BeBr_2$ in Diethyl Ether

	Ratio $(CH_3)_2Be$:$BeBr_2$			
T, °C	1:0	1:1	2:1	1:2
35	70.5	71	71	71
0	71	71	71.5	71
−15	71.5	72	72	72
−30	72.5	74	72.5	73
−45	74	73.5	73.5	74
−60	76	74.5	74.5	75
−75	78	75	75,79	75

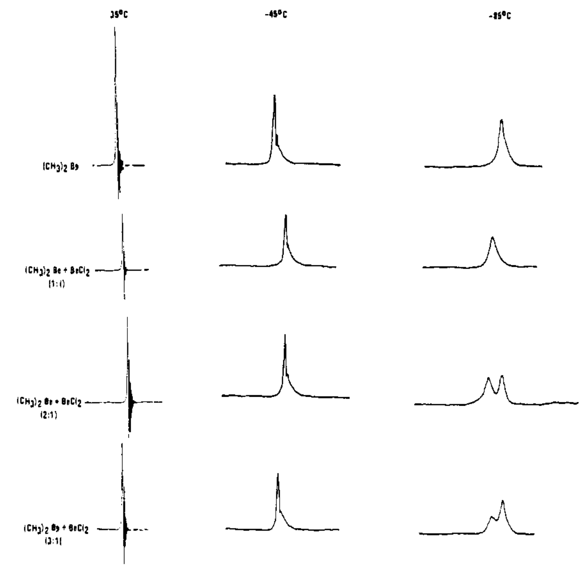
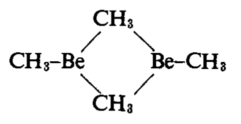


Figure 4. Nmr spectra of $(CH_3)_2Be$ and mixtures of $(CH_3)_2B$ + $BeCl_2$ in 1:1, 1:2, and 1:3 ratios in diethyl ether.

The second column of Table III shows a low-temperature profile of $(CH_3)_2Be$ in diethyl ether. The position of the signal is markedly temperature dependent. The fact that only one signal is observed at −75° is indicative of the fact that $(CH_3)_2Be$ is not associated, otherwise two signals of equal intensity would have been observed—one signal for the two terminal methyls and one signal for the two bridging methyl groups.[24] When $(CH_3)_2Be$ and $BeBr_2$ were allowed to react in 1:1 ratio, only one signal was observed at −75°; however, it was at a position 3 cps different from that of $(CH_3)_2Be$ at the same temperature. Such a small difference is not very meaningful; however, the fourth column showing the results of the 2:1 ratio shows two signals at −75°. One signal is indicative of excess $(CH_3)_2Be$ and thus the other signal (present also at 1:1 ratio) is indicative of CH_3BeBr. The fact that $BeBr_2$ precipitated from the mixture at −75° in 1:2 ratio, while no precipitate occurred in 1:1 ratio, indicates once again that there is little association among the species in solution.

Table IV. Chemical Shift of CH_3–Be Singlet Upfield from TMS in Cycles per Second for Mixtures of $(CH_3)_2Be$ and $BeCl_2$ in Diethyl Ether

	Ratio $(CH_3)_2Be$:$BeCl_2$			
T, °C	1:0	1:1	2:1	3:1
35	70	75	72.5	72
0	70.5	76	74.5	73.5
−45	74.5	79	76	75.5
−85	86	82	81,86.5	81.58, 86.5



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(24) Such observations representing association have been made for $(CH_3)_3Al$ in benzene whereas in diethyl ether only one signal is observed since $(CH_3)_3Al$ is monomeric in this solvent.

The results of the $(CH_3)_2Be-BeCl_2$ nmr study are even more convincing (Table IV, Figure 4). At 35° only an average signal is observed for all of the mixtures due to the rapid exchange at this temperature. When $(CH_3)_2Be$ and $BeCl_2$ are in 1:1 ratio only one signal is observed at $-85°$ which is 4 cps different from $(CH_3)_2Be$ at the same temperature. Once again the convincing experiments are the nmr observations at 2:1 and 3:1 ratio. When $(CH_3)_2Be$ and $BeCl_2$ are in 2:1 ratio two signals are observed, one is characteristic of $(CH_3)_2Be$ and the other for what must be CH_3BeCl since the signals bear a 1:1 ratio. When $(CH_3)_2Be$ and $BeCl_2$ are added in 3:1 ratio the signal indicative of the excess $(CH_3)_2Be$ increases and the signal indicative of CH_3BeCl remains constant. Thus the nmr evidence alone appears conclusive to establish redistribution in the $(CH_3)_2Be-BeX_2$ systems.

The nmr spectra of similar mixtures of $(C_6H_5)_2Be-BeBr_2$ were also determined. The spectra obtained are qualitatively like those found for C_6H_5Li, $(C_6H_5)_2Mg$, and $(C_6H_5)_2Zn$.[25] The effect of replacing C_6H_5 by halogen was observed in slight upfield shifts of the bands, but the complexity of the AB_2C_2-type pattern made detailed and clear-cut analysis of the variable-temperature spectra beyond the scope of this paper.

The conclusion therefore is that the nmr evidence, in addition to selective precipitation and association studies, indicates strongly that rapid redistribution in the system $R_2Be-BeX_2$ where R = CH_3, C_2H_5, C_6H_5 and X = Cl, Br does take place.

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Charge-Transfer Complexes of Tetracyanoethylene with Acenaphthylene Photodimers. The ω Technique as an Approach to Transannular Interaction

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Abstract: The tetracyanoethylene charge-transfer complex of the *cis* photodimer of acenaphthylene shows a slight red shift in its two absorption bands relative to those of the *trans* isomer. The difference is greater for the higher energy band than for the lower one. ω-Technique calculations performed with an initially unsymmetrical positive ion afford a simple approach to the problem of transannular interaction and predict the observed behavior.

Electron donor–acceptor (EDA) complexes between aromatic compounds and Lewis acids have been studied extensively because of their sensitivity to relatively small steric and electronic changes in both donor and acceptor. For a series of methylated benzenes with tetracyanoethylene (TCNE), Merrifield and Phillips showed an increase in both the extent of complexation and the absorption wavelength for the complex with increased substitution.[2] The initial work of Mulliken[3] has resulted in several experimental and theoretical studies which have illustrated the relationship between the ionization potential of the donor, among other things, with both the free energy of formation and the energies of spectral transitions (E_{EDA}) of these complexes.[4] In particular, several workers have demonstrated a relationship between the energy of the highest occupied molecular orbital (HOMO) with E_{EDA}, using either simple Hückel[5] or more sophisticated calculations.[6]

Our interest in this topic involves the use of EDA complexes as measures of the extent of transannular interaction (TI). That such interaction results in significant differences in these complexes was shown by Cram in the paracyclophane series.[7] However, the problem of puckered rings encountered with these compounds renders them less than ideal, especially with regard to adaptation to π-electron calculations.[8]

We have investigated the behavior of the two acenaphthylene photodimers I and II, along with acenaphthene (III). In I, there is no puckering of the benzene rings

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