CCCLIII.—*Beryllium Dialkyls.*

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IN continuation of studies on organoberyllium halides (Gilman, *J. Amer. Chem. Soc.*, 1925, **45**, 2693; see also Durand, *Compt. rend.*, 1926, **182**, 1162) it was necessary to prepare some beryllium dialkyls for comparative purposes, inasmuch as the two classes of compounds appear to be interconvertible.

Cahours (*Ann. Chim. Phys.*, 1860, **58**, 22) claimed to have prepared beryllium diethyl by heating the metal with ethyl iodide in a sealed tube. Later (*Compt. rend.*, 1873, **76**, 1383. Cahours's work on beryllium dialkyls has been discussed by Frankland, J., 1861, **13**, 181, 194) he reported the preparation of beryllium diethyl and beryllium dipropyl by heating the metal with the corresponding mercury dialkyls in a sealed tube at 130°. It is highly probable that Cahours's work on beryllium diethyl is incorrect. His beryllium diethyl was distilled in an atmosphere of carbon dioxide and boiled

at 185—188°. We have found that beryllium diethyl not only reacts with carbon dioxide, but also boils at a much higher temperature range (with decomposition) than that reported by Cahours. Furthermore, we had no success in the preparation of beryllium diethyl and beryllium di-n-butyl from the mercury dialkyls as recommended by Cahours. Incidentally, Cahours incorrectly described magnesium diethyl as a liquid, inasmuch as it is a solid (Gilman and Schulze, *J. Amer. Chem. Soc.*, 1927, **49**, 2328).

Lavroff (*J. Russ. Phys. Chem. Soc.*, 1884, **16**, 93 ; *Bull. Soc. chim.*, 1884, **41**, 548) very briefly mentioned the preparation of beryllium dimethyl by the action of beryllium on mercury dimethyl in a sealed tube at 130°. We have found no further mention of his work. Despite the very meagre detail in his preliminary communication, it is quite probable that he did have beryllium dimethyl.

Krause and Wendt (*Ber.*, 1923, **56**, 467, footnote 2) state that beryllium dialkyls may be prepared by the reaction between beryllium chloride and an excess of Grignard reagent.

EXPERIMENTAL.

Several unsuccessful attempts were made to prepare beryllium diethyl and beryllium di-n-butyl from finely crushed beryllium and equivalent quantities of the corresponding mercury dialkyls. No evidence of reaction was obtained when the mixtures were kept in sealed tubes for 3 weeks at room temperature ; when they were heated for 3 weeks at 90°, some free mercury was formed, and heating for 15 hours at 130°, 175°, 200°, and 225° apparently induced only decomposition of the mercury dialkyls ; in no case was there evidence of the formation of beryllium dialkyls.

Beryllium diphenyl and beryllium di-p-tolyl may be readily prepared by heating beryllium with equivalent quantities of mercury diphenyl and mercury di-p-tolyl and a trace of mercuric chloride in sealed tubes at 225° for 6 hours.

In the experiments with mercury dialkyls, no mercuric chloride was added. Other studies (Gilman and Schulze, *loc. cit.*) have shown that mercuric chloride is an almost indispensable catalyst in the preparation of some metallic dialkyls, like magnesium diethyl. No attempt was made to prepare beryllium dimethyl from beryllium and mercury dimethyl. It is quite reasonable to assume that traces of some mercuric halide were contained in the materials used by Lavroff. The beryllium used in the present studies was obtained from the Beryllium Corporation of America and contained more than 99·5% of beryllium.

It is possible to prepare beryllium dialkyls by heating beryllium with the appropriate alkyl halides, an alkylberyllium halide being

an intermediate product.   Here, again, mercuric chloride is a very helpful catalyst.

However, it appears that the most convenient method for the preparation of beryllium dialkyls is the reaction between anhydrous beryllium chloride and the appropriate Grignard reagent.   We have prepared beryllium dimethyl, diethyl, and di-n-butyl by this method.

Preparation of Beryllium Dialkyls.—Because of the highly hygroscopic nature of anhydrous beryllium chloride and the ready decomposability of beryllium alkyls and the Grignard reagent by air, all operations were carried out in pure dry hydrogen or nitrogen, admitted through the tube A.   Anhydrous beryllium chloride (8 g.; 0·1 g.-mol.) is dissolved in 50 c.c. of anhydrous ether, cooled by running water.   The filtered oily solution, which may be either colourless or pale yellow and separates into a lower layer of beryllium chloride etherate and an upper layer consisting largely of ether, falls directly into 75 c.c. of 4M-magnesium methyl iodide (0·3 g.-mol.) contained in a 250 c.c. flask, B, the Grignard solution being gently shaken during addition.   There is little heat of reaction if the beryllium chloride solution is pure and anhydrous.   The formation of white clouds on the surface of the reaction mixture is indicative of the presence of air or oxygen.

The excess of ether is removed by stopping the circulation of water in the condenser, C, until the oil-bath attains a temperature of 150°.   The water is then turned on slowly in order to prevent a too sudden contraction (due to the condensation of ether) that might draw air into the condenser and receiving flask.   Distillation is continued at 150—200° for 6 to 15 hours, so long as an ethereal solution of beryllium dimethyl collects in the receiving flask, D. Heat radiating from the oil-bath is sufficient to keep the temperature of the receiver above the boiling point of ether and thereby prevent the condensation of more ether than is necessary to hold the beryllium dimethyl in solution.   The distillation may be continued overnight, as it requires no attention.   Should the ether be driven out
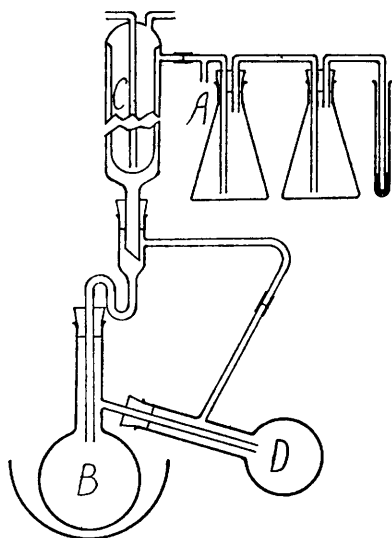
completely from the distilling flask, *B*, so that no more ether vapour circulates, it is necessary merely to heat the receiver gently to return the ether to flask *B*. Such heating should be moderate, otherwise some of the beryllium dimethyl will be driven back into *B* and so extend the time of recovery of the compound.

The ethereal solution of beryllium dimethyl obtained in this manner is clear and colourless (when care has been taken to exclude air), and it may be used directly in a study of the reactions of the compound. When not in use, it is kept preferably in sealed glass containers. Pure, ether-free beryllium dimethyl is obtained by heating the distillate. At about 100—125°, most of the ether is expelled and the whole solution suddenly turns to a mass of white needles containing some ether, which may be removed by heating to 200°. At 200° (external temperature), the compound commences to sublime rapidly, and part of it solidifies in the capillary when a constricted test-tube is used for the collection of ether-free samples. However, the capillary can be kept open prior to sealing by applying a small luminous flame. A repetition of this process of distillation in a sealed U-tube arrangement originally filled with ether vapour makes it possible to obtain material free from oxide or methoxide by alternately heating and cooling each part of the U-tube. The samples used for analysis were prepared in this manner.

3·5 G. (90% yield) of beryllium dimethyl were obtained from 0·1 g.-mol. of beryllium chloride; with 0·3 g.-mol., the yield was 84·7%.

Beryllium diethyl and di-*n*-butyl were prepared in essentially the same way as beryllium dimethyl. However, it is possible to distil beryllium diethyl and di-*n*-butyl directly in a vacuum. Because of the higher vapour pressure of beryllium di-*n*-butyl, it would probably be more advantageous to use a vacuum distillation rather than the ether distillation or ether sublimation process used for the dimethyl compound.

Analysis of Beryllium Dimethyl.—After being weighed, one of the sealed tubes, containing beryllium dimethyl prepared by distillation at 200°, was broken in a vessel filled with dry ether, and the volume of methane liberated on the addition of water and then dilute hydrochloric acid was measured in a special eudiometer containing concentrated sulphuric acid. An aliquot portion of the evolved gas, when exploded with a measured volume of oxygen, was shown to consist of pure methane.

The beryllium was analysed as beryllium oxide after careful removal of the glass, which was weighed to determine the weight of beryllium dimethyl originally present in the sealed container [0·1501 g. of beryllium dimethyl gave 173·2 c.c. (corr.) of methane

and 23·33% of beryllium. Calc. : 171·4 c.c. and 23·25%. 0·1771 G. gave 200·7 c.c. of methane. Calc. : 202·2 c.c.].

Properties of Beryllium Dialkyls.—Beryllium dimethyl crystallises from hot concentrated ethereal solution in snow-white needles (see Preparation). It is also deposited in the same form when it sublimes, without melting, at about 200°. The method of preparation is based on its high volatility in ether, and these ethereal solutions fume strongly when exposed to the atmosphere. When suddenly overheated, it undergoes partial decomposition, leaving a brown or grey mirror.

Beryllium diethyl is a colourless liquid, b. p. 93—95°/4 mm. and 110°/15 mm. It distils between 180° and 240° at atmospheric pressure with considerable decomposition. The compound is only distilled with difficulty because of its pronounced tendency to become superheated and then break suddenly into foam. This may be due to the decomposition of an etherate. A part of the purest material solidified, in a carbon dioxide–ether freezing mixture, to white crystals which on warming melted at −13° to −11°.

Beryllium di-*n*-butyl is a clear, colourless liquid having a mercaptan-like odour. The boiling point, 170°/25 mm., was determined with a rather small quantity of material and so may not be taken with too much credence.

Both beryllium dimethyl and diethyl are spontaneously inflammable in the air, and especially so in a humid atmosphere. Even concentrated ethereal solutions are inflammable spontaneously in the presence of moist air. The compounds burn with luminous flames, evolving dense white fumes of beryllium oxide. Their very high sensitivity to oxygen made it difficult, at first, to purify the hydrogen or nitrogen to such an extent that it would not give a white cloud of beryllium oxide when passed over the ethereal solutions of the dialkyls. For this reason, a magnesium phenyl bromide solution was inserted in the drying and purifying train in order to remove a residuum of oxygen. Beryllium di-*n*-butyl is not spontaneously inflammable when exposed to the air. But it does oxidise rapidly, when so exposed, with the evolution of heat. Very probably, beryllium butyloxide is a product of such oxidation, inasmuch as the odour of *n*-butyl alcohol becomes quite pronounced after a short air exposure.

The reaction of the dialkyls with water is violent, and in the presence of small amounts of water the materials frequently inflame. Methane and ethane are evolved when the corresponding dialkyls are decomposed by water.

Beryllium dimethyl in the solid state inflames when treated with carbon dioxide. With an ethereal solution, however, the reaction

is quite mild and acetic acid is formed. An ethereal solution of beryllium diethyl reacts with carbon dioxide to give triethylcarbinol.

Phenylcarbimide in ethereal solution reacts with extreme violence with the three dialkyls studied. In each case, a white solid separated at first, and then dissolved in the excess of beryllium dialkyl. The expected anilides were obtained, the valeranilide as an oil. This anilide is known to crystallise with difficulty, so that its identity has not been confirmed, as was done with the other two anilides, by a mixed-melting point determination with an authentic specimen. Aceto-α-naphthalide was obtained from beryllium dimethyl and α-naphthylcarbimide.

The three dialkyls give an immediate positive colour reaction with Michler's ketone according to the test described by Gilman and Schulze (*J. Amer. Chem. Soc.*, 1925, **47**, 2002) for RMgX and some other organometallic compounds. The blue instead of green colour given by beryllium di-*n*-butyl indicates that this dialkyl probably reduced the ketone to Michler's hydrol (*loc. cit.*).

Beryllium dimethyl with benzophenone gave diphenylmethylcarbinol, which was identified as αα-diphenylethylene. Beryllium diethyl, on the other hand, reduced benzophenone to benzhydrol. In the latter reaction, a bright orange-red colour was present transitorily at the junction of the two liquids. This may be indicative of the intermediate formation of a free radical.

Beryllium dimethyl with benzoyl chloride gave phenyldimethylcarbinol, and this was identified by the formation of *iso*propenylbenzene when the carbinol was distilled. The reaction product was probably free from acetophenone as indicated by a test with semicarbazide.

The beryllium dialkyls appear to have high solvent characteristics, for all the intermediate reaction products dissolved in an excess of the dialkyl. Equally striking is the fact that beryllium diethyl dissolved the beryllium oxide and ethoxide formed by partial decomposition of the dialkyl, as well as the brown or grey mirror formed by the high-temperature decomposition of the dialkyl.

Beryllium dimethyl and diethyl react vigorously with iodine. When 1·343 g. of beryllium dimethyl were treated with 1 equiv. (4·353 g.) of iodine, the solution still contained some dialkyl, as was evidenced by the fuming on air exposure and by a slight positive test (Gilman and Schulze, *loc. cit.*). After standing for several days in a cork-stoppered flask, the solution no longer fumed and gave a negative test. Very probably beryllium methyl iodide was formed as a result of the iodine reaction, because the solution gave acetanilide on treatment with phenylcarbimide, and when heated it fumed and gave a positive test. These are among the criteria

included for the characterisation of beryllium alkyl halides (Gilman and Schulze, *J. Amer. Chem. Soc.*, 1927, **49**, Nov.).

Beryllium diethyl reacts with an excess of an ethereal solution of beryllium chloride to give a solution with the characteristics of beryllium ethyl chloride. In view of these latter experiments, the following equilibrium is probable under certain conditions :

$$BeR_2 + BeX_2 \rightleftharpoons 2RBeX.$$
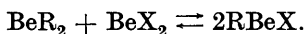
In general, the beryllium alkyl halides are less active than the beryllium dialkyls, and the beryllium dialkyls are at least equal in activity to the Grignard reagents.

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