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Zelinskii Institute of Organic Chemistry,
Academy of Sciences of the USSR

ORGANIC COMPOUNDS OF BERYLLIUM, CALCIUM, STRONTIUM, AND BARIUM

G.A.Balueva and S.T.Ioffe

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INTRODUCTION

The immense part played by magnesium compounds in modern organic chemistry is well known. The number of papers on methods of obtaining organomagnesium compounds, their structure, properties, and especially their use in organic synthesis is continually increasing and has reached many thousands[1]. Such intensive development of the chemistry of these compounds is explained by their extraordinarily high reactivity, which enables numerous derivatives of the most varied classes of compounds to be readily obtained.

In contrast to magnesium, the remaining elements of its subgroup received little attention, and it is only recently that the chemistry of the organic compounds of beryllium, calcium, barium, and strontium has begun to be developed. It therefore seems useful to make a short survey of the present position in this field, especially as its literature is scattered among various journals, which are often not readily available. The review by Jones and Gilman[2] considers very briefly only methods for obtaining these organometallic compounds, and the review published by Novoselova *et al.*[3] in 1958 deals only with organic compounds of beryllium.

The present review examines only compounds containing a carbon–metal bond. Thus it is not concerned with salts of organic acids, metal alkoxides, or similar compounds, nor with many complex compounds.

Since there are only a small number of publications we divide the review according to the metals. Each section includes methods of preparation, physical and chemical properties, and also (where information is available) the fields of application of the organometallic compounds.

The organic compounds of both subgroups of metals in Group II show a clear connection between reactivity and change in electronegativity of the elements[4].

Ba Sr Ca Mg Be Zn Cd Hg

← electropositive more reactive

→ electronegative less reactive

organic derivatives

Organic compounds of the more electropositive elements — calcium, strontium, and barium — are quite like those of lithium and sodium in their ability to add to ethylenic bonds and in metallations, although in general they are some somewhat less reactive. Beryllium, like magnesium, forms organic compounds which are essentially covalent in structure and are relatively reactive, although inferior to organomagnesium compounds in this respect.

ORGANIC COMPOUNDS OF BERYLLIUM

Formally, the chemistry of organoberyllium compounds is entitled to celebrate its centenary, since the earliest publications date from 1860–1861. However, this work was not fully confirmed subsequently, and it can hardly be doubted that the pioneers of the organic chemistry of beryllium were not dealing with individual compounds.

Interest in the chemistry of beryllium has grown especially during the past 10–15 years. This is due both to general progress in the chemistry of organometallic compounds and to the importance which beryllium has acquired in modern technology: its uses in the form of the especially heat-resistant beryllium bronzes, and in the production of atomic energy[5] as radium–beryllium neutron sources and also as moderators in nuclear reactors[6], are well known. The heat and corrosion resistance of beryllium are important in the construction of nuclear reactors. However, the brittleness of metallic beryllium and its oxide restrict their application.

Modern technology requires in many instances extremely pure metals. In this respect the organic chemistry of beryllium may be of interest even to metallurgists, since conversion of a metal into an organic compound may provide a method of purifying the metal.

Beryllium compounds are toxic, the resulting poisoning being known as "berylliosis". In the acute form the symptoms are similar to those of chlorine poisoning. Chronic forms of beryllium poisoning have been described, in which the characteristic signs of the illness develop over several years[6].

The number of organic compounds of beryllium known to date is small. They can all be included in one of two classes of compounds, symmetrical beryllium dialkyls or diaryls R_2Be, and mixed organoberyllium compounds RBeX, where X represents a halogen or an amino-group; unsymmetrical compounds RBeR′ have not yet been described.

The observation by Cahours[7] of the reaction of beryllium with ethyl iodide on being heated in a sealed tube must probably be regarded as the first mention of the formation of an organoberyllium compound. Under these conditions a solid product was formed, which on distillation gave a liquid that vigorously decomposed water with the evolution of a flammable gas. Frankland[8] in his review points out the analogy between this reaction and the action of aluminium on ethyl iodide, but emphasised that formation of diethylberyllium was not confirmed by analysis.

It was shown much later that reaction of metallic beryllium with alkyl halides leads not to beryllium dialkyls but to mixed organoberyllium compounds RBeHal.[9]

At the present time the following methods are available for obtaining organoberyllium compounds.

1. Reaction of metallic beryllium with dialkyl[10–12] or diaryl[13] derivatives of mercury in a sealed tube heated to 130°–150° (with the dialkyls) or 225° (with the diaryls). In order to obtain a purer product, it is advisable to remove the resulting metallic mercury with gold foil[14]. Traces of mercuric chloride act as catalyst in the preparation of beryllium diaryls[13].
2. Beryllium dialkyls are readily obtained by a Grignard reaction, by the interaction of anhydrous beryllium chloride or bromide with the corresponding alkylmagnesium halide[13,15]. The process must be carried out in anhydrous ether in an atmosphere of dry nitrogen or hydrogen. A disadvantage of this method is that the substance is isolated in the form of an addition compound with ether, from which it is very difficult to remove the ether. Therefore all workers who have used this method describe in detail procedures for obtaining the purest products; their methods will be noted in describing the preparation of individual beryllium dialkyls.

A related method is the synthesis of diphenylberyllium by the reaction of beryllium chloride with phenyllithium in ethereal solution[16].

Apart from these two main methods of synthesis, dialkylberyllium compounds are formed when alkylberyllium halides are cautiously heated[9], and also by the interaction of free methyl or ethyl radicals with metallic beryllium[17].

In the early 1930s a method was patented[18] for obtaining organoberyllium compounds by fusing beryllium oxide with carbon compounds which do not contain oxygen (saturated and unsaturated, and also cyclic and acyclic, hydrocarbons, nitro-compounds, primary and secondary amines, etc.). The reaction can be carried out in an inert organic solvent; metal oxides or salts of inorganic acids can be used as catalysts. In the case of benzene, the reaction is written as follows

$$2C_6H_6+BeO \rightarrow Be(C_6H_5)_2+H_2O.$$

No confirmatory results have appeared during recent years, and one agrees with Novoselova[3], who stresses that this mode of synthesis seems very improbable owing to the extreme sensitivity of organoberyllium compounds to moisture.

Comparatively recently a patent has been granted for the preparation of organoberyllium compounds of general formula BeR_2 by the addition of alkenes to BeH_2. The resulting compounds, containing a carbon–beryllium bond, can be used as catalysts for the polymerisation of alkenes and as intermediates. Thus diethylberyllium at 100° for 82 h adds to 2-methylpent-1-ene $C_3H_7.C(CH_3):CH_2$ to form the dialkylberyllium $C_3H_7.C(CH_3)(C_2H_5).CH_2.Be.C_2H_5$.[19]

The preparation of beryllium analogues of Grignard reagents, alkylberyllium halides, is difficult. All these compounds, like the magnesium derivatives, are extremely reactive, and are not isolated as pure substances, so that their formation can be demonstrated only indirectly, on the basis of various reactions.

In Gilman and Schulze's method[9] alkylberyllium halides are obtained by the prolonged heating (at 150°), in a sealed

tube, of finely divided metallic beryllium with the corresponding alkyl or aryl halide in the presence of ether and a catalyst ($HgCl_2$, free bromine, $BeCl_2$).

At room temperature dimethylberyllium is a solid, the remaining beryllium dialkyls being liquids which can be distilled *in vacuo*. They are soluble in most organic solvents and are associated in solution, the extent of association depending on the nature of the solvent and the time during which the solution has been allowed to stand[20].

The organic compounds of beryllium are quite reactive, in this respect approaching lithium derivatives in several reactions, and magnesium derivatives in some cases.

Beryllium dialkyls are extremely sensitive to moisture, some of them reacting extremely vigorously, even explosively, with water; hydrolysis results in the formation of the corresponding hydrocarbons. Beryllium dialkyls react with hydrogen peroxide in ether solution to form beryllium peroxide[21]. Reaction with phenyl isocyanate in ethereal solution yields the corresponding anilides[13].

In their reaction with ethylene[22,23] beryllium dialkyls resemble more closely aluminium and lithium compounds than those of magnesium, since the last do not show the stepwise addition of the alkene characteristic of the alkyl derivatives of the other three metals:

$$RM + CH_2{=}CH_2 \rightarrow RCH_2CH_2M \qquad (M = \text{metal})$$

$$RCH_2CH_2M \xrightarrow{C_2H_4} R(CH_2CH_2)_2M \xrightarrow{C_2H_4} R(CH_2CH_2)_3M.$$

Ziegler mentions in his review[22] that the beryllium dialkyls react with the higher alkenes, but these reactions have not been investigated in greater detail.

Reactions of beryllium derivatives resulting in the formation of hydrides have been quite fully studied; beryllium hydride is obtained in particular by the pyrolysis of beryllium dialkyls.

The considerable electronic unsaturation of the beryllium dialkyls readily leads to the formation of coordination compounds with electron-donating substances[24]. This electron deficit, caused by the fact that the total number of electrons is less than double the number of bonds present[25], also explains the strong association of organoberyllium compounds and the ease of formation of spiro-compounds, like the complexes described by Bähr and Thiele[26].

Beryllium dialkyls give an immediate positive reaction with Michler's ketone[13]; diaryl derivatives do not give satisfactory results with this colour reaction[27].

The compounds of mixed type, RBeX, are in general less reactive than the corresponding R_2Be derivatives[9]. They are decomposed by water with formation of the corresponding hydrocarbons. Their ethereal solutions do not fume in air, but if the ether is removed and the liquid residue heated, white fumes are evolved, probably of beryllium oxide. Cautious heating converts alkylberyllium halides into beryllium dialkyls. In contrast to the latter, which give an immediate colour reaction with Michler's ketone, the halides give a positive result only after 10–15 min.[9]

The elementary analysis for carbon and hydrogen in organoberyllium compounds is difficult because of their peculiar properties, and requires the application of special techniques[28].

Very little information is available on the practical applications of organic beryllium derivatives. According to the patent literature[29-31] organoberyllium compounds R_2Be, where R is an alkyl or an aryl group, may be used as initiators for the dimerisation and the polymerisation of individual alkenes and alkene mixtures. In particular, it is claimed that diethylberyllium, diphenylberyllium, and sodium triethylberyllate may be used to activate the dimerisation of propene[32]. The use of mixed catalysts of $(C_2H_5)_2Be$ and $TiCl_4$ for the polymerisation of propene has been patented. The molar ratios of these compounds determine the length of the induction period in the polymerisation[33].

In 1931 a method was patented for obtaining metallic beryllium from its organic compounds[18], and in 1957 Wood and Brenner[16] described the electrodeposition of beryllium and its alloys from solutions of its inorganic and organic compounds in various solvents. The best results (beryllium contents up to 95%) were obtained by electrolysis of a mixture of dimethylberyllium and beryllium chloride in ethereal solution. Solutions of diphenylberyllium are electrically conducting, but, in contrast to dimethylberyllium, the metal cannot be electrodeposited from them.

Dimethylberyllium $(CH_3)_2Be$

Dimethylberyllium was first obtained by Lavrov[11,12] in 1884, by the reaction of dimethylmercury and metallic beryllium. This method has recently been found[14] to give a high degree of purity (97%) and a quantitative yield. It has been used to prepare radioactive dimethylberyllium containing ^7Be.[34] Schulze[35] prepared dimethylberyllium by the reaction of beryllium with dimethylmercury containing traces of mercurous iodide. It has also been obtained by a Grignard reaction[13,35]. In order to obtain the compound free from ether, the distilled reaction product is heated at 100°–125°, when most of the ether is expelled and the whole of the solution is suddenly converted into a mass of white needles containing some ether, which can be removed by heating to 200°. At this limiting temperature the compound begins to sublime rapidly; the yield of dimethylberyllium is 85–90%.[13] In order to remove the ether more effectively, it is advisable to pass a current of dry nitrogen through the reactants[36]. Changes in the conditions of the Grignard reaction have no great effect on the yield of dimethylberyllium[16].

At room temperature dimethylberyllium is a solid. It crystallises from hot ether solution as snow-white crystals, and forms similar crystals on sublimation[13].

X-Ray structural analysis suggests[37,38] that dimethylberyllium has a chain structure in which the CH_3-groups are arranged tetrahedrally about the beryllium. The C–Be–C angle, 114°, is rather greater than the tetrahedral angle, while the Be–C–Be angle is 66°. The Be–C distance in the electron-deficient bond is 1.93 Å. This structure is consistent with the rule that electron-deficient bonds arise because metals having fewer valency electrons than low-energy orbitals utilise the latter for bond formation.

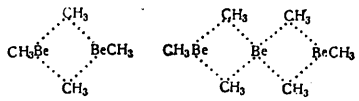
The body-centred orthorhombic unit cell of dimethylberyllium is characterised by the constants $a_0 = 6.13$, $b_0 = 11.53$, and $c_0 = 4.18$ Å, and is of the SiS_2 type[37,39].

Coates *et al.*[40] measured the vapour pressure and vapour density of dimethylberyllium and determined its degree of association and several physical constants. Above 200° the compound shows signs of thermal decomposition. The vapour pressure can be represented by the equation

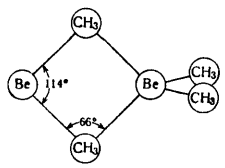
$\log p$ (mm) = 12.530 - 4771/T over the range 100°–155°, and by $\log p$ (mm) = 13.292 - 5100/T over the range 155°–180°. An equilibrium between monomer and dimer is established in the vapour; a certain amount of trimer is also present. At 180° the saturated vapour consists of 41% of monomer +44% of dimer +14% of trimer; at 160° the corresponding percentages are 27, 50, and 23%.

The heat of sublimation of dimethylberyllium is 23.5 kcal × × mole^{-1}, and the extrapolated sublimation point 217°. The heat of formation of the dimer from the monomer is 24 kcal × × mole^{-1}, and that of the trimer 45 kcal mole^{-1}. The entropy changes accompanying formation of the dimer and the trimer are 50 and 93 e.u. respectively[40].

The following structures have been suggested for the dimer and the trimer in the vapour state[40].



Dimethylberyllium is sparingly soluble in benzene, and is readily polymerised in solution. Polymerisation probably takes place by a chain mechanism, which can be represented as follows[20]: the dimer, having the structure



would add a further $(CH_3)_2Be$ molecule at the beryllium atom possessing an incomplete electron octet. The resulting trimer adds the next dimethylberyllium molecule, and polymerisation continues in this manner. The fact that true polymerisation is taking place follows from the observation that the molecular weight is independent of the concentration of dialkyiberyllium in solution.

From the net charge on the methyl group (-0.250) dimethylberyllium occupies an intermediate position between the methyl derivatives of magnesium and of aluminium[41].

Dimethylberyllium ignites spontaneously in air, especially in a moist atmosphere. It reacts with CO_2 in ether solution, yielding (after hydrolysis) acetic acid[13]; with phenyl isocyanate it forms the corresponding anilide, with 1-naphthyl isocyanate *N*-naphth-1-ylacetamide, with benzophenone 1,1-diphenylethanol, and with benzoyl chloride it yields 1-methyl-1-phenylethanol. Dimethylberyllium reacts vigorously with iodine, probably forming methylberyllium iodide[13].

Like the Grignard reagents, dimethylberyllium does not react with diphenylethylene or with diphenyl sulphone, but it does react with azobenzene[42]. The reaction was carried out in ethereal solution in a sealed tube at room temperature. After the reaction mixture had been allowed to stand for 7 days, analysis showed that two molecules of azobenzene had reacted with one molecule of dimethylberyllium, and the following equation was suggested

$$2C_6H_5N{=}NC_6H_5+(CH_3)_2Be \rightarrow \begin{matrix} C_6H_5N(CH_3)NC_6H_5 \\ | \\ Be \\ | \\ C_6H_5N(CH_3)NC_6H_5 \end{matrix}.$$

The reaction of dimethylberyllium with lithium tetrahydroaluminate in ethereal solution can be used to obtain beryllium hydride[36], but the product is contaminated with ether. In an attempt to prepare BeH_2 free from ether, the reaction was carried out with liquid $(CH_3)_2AlH$ in the absence of solvent. Although trimethylaluminium was formed, as indicated by the equation

$$2(CH_3)_2AlH+(CH_3)_2Be \rightarrow 2Al(CH_3)_3+BeH_2,$$

a product free from methyl groups was not obtained, perhaps owing to the intermediate occurrence of the reversible reaction:

$$(CH_3)_2AlH+(CH_3)_2Be \rightleftarrows CH_3BeH+Al(CH_3)_3.$$

Burg and Schlesinger showed[43] that dimethylberyllium reacts with diborane, the reaction taking place in several stages. Initially a vitreous mass is formed, containing a high percentage of methyl groups, which then changes into a mobile, non-volatile liquid. When this is further treated with diborane, an unstable solid is obtained which sublimes readily, and which analysis shows to correspond to the formula CH_3BeBH_4. This substance reacts vigorously with diborane yielding the final product, a volatile beryllium hydroborate BeB_2H_3 with a certain amount of a non-volatile substance, probably $(BeBH_5)_x$. In addition, trimethylboron and a methylated diborane are formed. These workers represent the overall reaction by the scheme

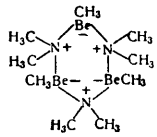
$$[Be(CH_3)_2]_x \xrightarrow{B_2H_6} (CH_3)BeBH_4 \xrightarrow{B_2H_6} HBeBH_4 \xrightarrow{B_2H_6} (BH_4)Be(BH_4),$$

with the reservation that it does not claim to represent the reaction mechanism or the structure of the products.

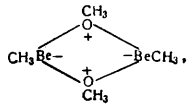
The considerable electron deficiency of dimethylberyllium results in its readily forming coordination complexes, as Coates and Huck[24] have shown, with trimethylamine, trimethyl phosphite, and dimethyl and diethyl ethers. The stability of these complexes diminishes in the sequence N > P > O. The affinity of trimethylamine for dimethylberyllium is sufficient to break down the polymeric structure of the latter, and it therefore yields a volatile substance to which can be assigned the structure $(CH_3)_2Be^- - N^+(CH_3)_3$, whereas the weak donor properties of trimethyl phosphite result in its forming a series of coordination compounds with different Be : P ratios. The formation of an unstable compound $[(CH_3)_2Be]_2[N(CH_3)_3]_3$ [24] has also been demonstrated. Dimethylberyllium does not form coordination complexes with trimethylphosphine or with dimethyl sulphide[24].

Dimethylberyllium reacts with methylamine, dimethylamine, dimethylphosphine, methanol, methanethiol, and

also HCl to give methane and dimeric, trimeric, or polymeric products. Dimethylamine yields a trimeric compound $[CH_3BeN(CH_3)_2]_3$, to which may be assigned the cyclic structure:



Methyl alcohol gives the dimer $(CH_3Be.OCH_3)_2$



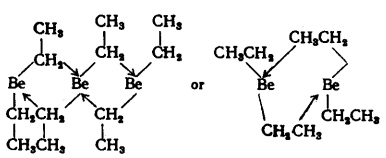
which readily disproportionates into dimethylberyllium and beryllium dimethoxide. The other substances mentioned yield non-volatile or relatively non-volatile products which undoubtedly have a polymeric structure[44].

The reaction of dimethylberyllium with an ethereal solution of hydrogen peroxide yields a gelatinous precipitate of beryllium peroxide[21].

Diethylberyllium $(C_2H_5)_2Be$

In 1873 Cahours[10] published a synthesis of diethylberyllium by means of an organomercury compound, the product being distilled in an atmosphere of carbon dioxide. Later, however, Gilman and Schulze[13] were unable to repeat this synthesis, and they prepared diethylberyllium by a Grignard reaction. Their product was a colourless liquid boiling at 93°–94°/4 mm, and at 110°/15 mm; under atmospheric pressure it distils between 180° and 240° with considerable decomposition. Some of the purest material solidifies in a solid CO_2/ether mixture to form white crystals melting between -13° and -12°.[13] Goubeau[45] obtained diethylberyllium by carrying out the reaction with excess of ethylmagnesium bromide in nitrogen. The purest product, containing only 2% of ether, was obtained by leaving diethylberyllium for 6 days after separating most of the ether, and then distilling at 0.3–0.5 mm; the yield was 80–90%.

Diethylberyllium containing ~2% of ether boils at 63°/0.3 mm and sets to a glass at -80°.[45] Its high boiling point compared with those of diethylzinc and diethylmercury, and also the fact that the pure substance boils at a higher temperature than its ether complex, indicate strong association This explains the formation of a glass on setting and the stable link with ether. Goubeau suggests the following structures for the associated molecules



and points out that, since such molecules terminate in a beryllium atom with coordination number 3, which means that it is coordinatively unsaturated, it is able to add ether, the ratio of ether to diethylberyllium depending on the different lengths of the polymer chain and varying between 1 : 2 and 1 : 50.

Diethylberyllium is monomeric in dioxan, but is associated in cyclohexane and in benzene[20], its molecular weight in these two solvents being 160 and 140 respectively two days after preparation of the solution, and 212 and 224 after 240 days (the molecular weight of the monomer is 67.1).

The dipole moment of diethylberyllium in various solvents is intermediate between that of the corresponding derivatives of magnesium and of zinc. Its moment is 1.0 D in heptane (the monomer is not present), 1.69 D in benzene, and 4.3 D in dioxan[46,47].

Diethylberyllium is a very reactive compound[45]. It reacts with water extremely violently, sometimes even explosively. Methyl and isopropyl alcohols react with it at -80° extremely vigorously with formation of fumes; with ethyl alcohol the reaction takes place more smoothly. At the temperature of liquid air HCl reacts forming beryllium chloride, but the reaction does not proceed to completion, since the resulting $BeCl_2$ envelops the particles of diethylberyllium and prevents further reaction. With diethylamine the reaction goes smoothly with the evolution of ethane; this substitution occurs to the extent of 75%, and it is only on heating that it can with difficulty be made complete. With triethylamine neither heat nor gas is evolved, but some of the amine probably reacts, since it cannot all be recovered. Reaction of diethylberyllium in ethereal solution with CO_2 yields triethylmethanol, the anilide being obtained with phenyl isocyanate, and diphenylmethanol with benzophenone[13]. This last reaction is supposed to involve the intermediate formation of free radicals. Diethylberyllium reacts vigorously with iodine, and also with excess of an ethereal solution of beryllium chloride, probably yielding the corresponding ethylberyllium halides[13].

Pyrolysis of diethylberyllium[45] at 190°–200° evolves ethylene, ethane, and but-2-ene in the proportions 1 : 2 : 1.5 and ether†; the Raman spectrum indicates that hex-3-ene, cyclohexa-1,3-diene, and benzene are also present. From one molecule of diethylberyllium about 0.9 ethyl group is involved in the formation of gaseous products, the residue being a mixture of a viscous oil boiling at 95°–100°/0.1–0.2 mm having the composition $(HBeCH_2CH_2BeH)_x$ and a crystalline deposit of $[HBe_2(CH_2)_3]_x$ or $[Be_2(CH_2)_3]_x$.

Diethylberyllium reacts readily with diphenylamine in benzene with the evolution of ethane and the formation of bisdiphenylamideberyllium $Be[N(C_6H_5)_2]_2$.[48]

Addition of hydrogen peroxide to an ethereal solution of diethylberyllium first causes the appearance of a brown coloration, and then the precipitation of a solid deposit of beryllium peroxide[21].

Dipropylberyllium $(n\text{-}C_3H_7)_2Be$

The only reference to the synthesis of this compound occurs in the paper by Cahours[10], who, on heating metallic beryllium with dipropylmercury in a sealed tube at 130°–150°, observed the rapid disappearance of the metal and the appearance of metallic mercury. After distilling twice in an atmosphere of carbon dioxide (?), a colourless liquid was obtained boiling at 244°–246°. It fumed strongly in air, but did not ignite. On being cooled to -17° it became a thick oily liquid, but did not solidify. It was violently

† Present in the original compound as an impurity (Ed. of Translation).

decomposed by water with evolution of gas and formation of a deposit of beryllium hydroxide on the walls of the vessel.

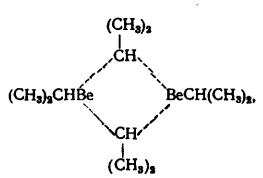
Diisopropylberyllium (iso-$C_3H_7)_2Be$

This compound has been obtained by the Grignard method[49]. It retains ether very strongly, for distilling twice and treatment in a vacuum for two days yields a product containing 16% of ether; complete elimination requires refluxing for two days with continuous removal of ether in a vacuum. The product melts at -9.5° and has a b.p. of 280° (extrapolated value). The vapour pressure is 0.17 mm at 20°, and 0.53 mm at 40°; it can be represented by the equation $\log p = 7.01 - 2280/T$. The heat of vaporisation, ΔH, is 10.45 kcal mole^{-1}. When diisopropylberyllium is distilled *in vacuo*, slow decomposition with the evolution of propene is observed even at 40°; at 200° pyrolysis takes place rapidly according to the equation:

$$n\ (\text{iso-}C_3H_7)_2Be \rightarrow 2/n\ (\text{iso-}C_3H_7BeH)_n + 2C_3H_6.$$

Isopropylberyllium hydride is a colourless, non-volatile, viscous oil, which hydrolyses [pyrolyses? (Ed.of Translation)] to beryllium, propane, and hydrogen, and is obviously polymeric. Pyrolysis of this hydride at 220°–250° does not yield beryllium hydride: the substance decomposes into metallic beryllium, hydrogen, propane, propene, and an organic residue.

Diisopropylberyllium dissolves readily in benzene, in which it is dimeric, the degree of association being independent of the concentration. The structure of the dimer is represented[49] as



i.e. as being analogous to the structure of dimethylberyllium in the vapour state. The Be–C–Be bond is formed by the sp^2 orbitals of the beryllium and the sp^3 orbitals of the carbon, so that each Be–C bridge may be regarded as a half-bond. The decrease in the degree of association on passing from a methyl to an isopropyl derivative of beryllium is probably associated not only with a steric effect but mainly with a decrease in the electronegative character of the alkyl group.

Like dimethylberyllium, diisopropylberyllium forms a 1 : 1 addition compound with trimethylamine, which is somewhat more volatile and thermally stable than the dialkyl itself; the addition compound is monomeric in benzene, and decomposes on being heated to 100°.

Although uncontrolled hydrolysis of diisopropylberyllium occurs explosively, the reaction with methanol involves the smooth evolution of one mole of propene and the formation of isopropylberyllium methoxide, which consists of crystals melting at 133°. Reaction with dimethylamine is accompanied by the evolution of propane and the formation of dimethylaminoisopropylberyllium, a colourless liquid which at 100° loses propene with the formation of the vitreous polymeric dimethylaminoberyllium hydride‡. Diisopropylberyllium reacts with excess of dimethylamine to form the crystalline beryllium bisdimethylamide together with two molecules of propane.

Di-n-butylberyllium (n-$C_4H_9)_2Be$

Gilman and Schulze[13] were unable to obtain this compound *via* dibutylmercury, but synthesised it by a Grignard reaction in an atmosphere of dry nitrogen. Dibutylberyllium is a colourless liquid with a mercaptan-like odour; it can be distilled in a vacuum, boiling point 170°/25 mm. It does not ignite in air, but is rapidly oxidised with the evolution of heat. It reacts vigorously in ethereal solution with phenyl isocyanate, yielding the corresponding anilide.

Di-t-butylberyllium (t-$C_4H_9)_2Be$

This compound was first obtained by Coates and Glockling[50] by the Grignard reaction. However, their product contained a large quantity of ether (up to 30%), and a special method was subsequently worked out for preparing pure di-t-butylberyllium from its ether addition compound by treating the latter with anhydrous beryllium chloride[51]; the ether addition compound of t-butylberyllium chloride is apparently formed as a by-product.

The ether complex of di-t-butylberyllium, containing 51–52 mole % of the beryllium dialkyl, is a colourless transparent liquid of density 0.78 g cm^{-3}. It is stable on storage[51].

The ether-free di-t-butylberyllium is a colourless, transparent, mobile liquid, of density 0.65 g cm^{-3}, freezing at -16°. The vapour pressure of the freshly prepared material is ~35 mm at 25°. At room temperature it slowly decomposes with the evolution of isobutane and apparently polymerisation of the remaining liquid[51].

Hydrolysis of di-t-butylberyllium gives complete decomposition into isobutane and isobutene in the molar ratio 60 : 1, whereas hydrolysis of the ether adduct yields 36.1% of ether and isobutane and isobutene in the molar ratio 4 : 1.[51]

In contrast to diisopropylberyllium, the di-t-butyl derivative does not yield the half-hydride $(CH_3)_3CBeH$ on thermal decomposition, but smoothly forms isobutene and beryllium hydride, in which, however, some butyl groups remain, since hydrolysis of this hydride yields a little isobutene[50]

$$[(CH_3)_3C]_2Be \rightarrow BeH_2 + 2(CH_3)_2C{=}CH_2.$$

The ratio of t-butyl groups to hydrogen atoms in the product decreases with increase in the temperature of pyrolysis: at 150° the product contains 89 mole % of beryllium hydride, whereas on pyrolysis at 210° the proportion is 96 mole %.

Vacuum pyrolysis of di-t-butylberyllium containing no ether gave beryllium hydride in yields up to 80%.[51]

Trimethylamine displaces ether from its addition compound with di-t-butylberyllium[50] with the formation of a readily volatile crystalline compound, which is probably a highly symmetrical di-t-butylberyllium–trimethylamine.

‡ Presumably dimethylamidoberyllium hydride, $(Me_2N.BeH)_n$ (Ed. of Translation).

Diphenylberyllium $(C_6H_5)_2Be$

Diphenylberyllium has been synthesised by heating metallic beryllium with an equivalent quantity of diphenylmercury in the presence of traces of mercuric chloride as catalyst[13] in a sealed tube at 225°. Wood and Brenner suggested a method for obtaining this compound by the reaction of beryllium chloride with phenyllithium in ethereal solution[16].

The dipole moment of diphenylberyllium is 1.64 D in benzene and 4.33 D in dioxan[46]. This compound, just like diethylberyllium, is acting here as an electron-acceptor in the intermolecular exchange interaction with solvents which act as electron-donors. In heptane, which possesses no electron-donor properties, the dipole moment of diphenylberyllium is zero[47].

Data have been published on the infra-red spectrum of diphenylberyllium[52].

In its addition reactions with benzylideneacetone and with *p*-(dimethylamino)benzylideneacetone, diphenylberyllium, like the magnesium, aluminium, zinc, and manganese compounds, shows almost exclusively 1,4-addition, giving respectively a 90% yield of ββ-diphenylpropiophenone§ and a 71% yield of β-dimethylaminophenyl-β-phenylpropiophenone¶[53]. Diphenylberyllium reacts symmetrically with azobenzene, the metal adding at the azo-bond, and ultimately forming hydrazobenzene in 55.4% yield[54]. The presence of diphenylberyllium changes the course of the reaction between triphenylmethylsodium and isoprene, with the predomination of 1,4-addition (not 1,2) and the formation of 3-methyl-5,5,5-triphenylpent-2-ene[55].

Wittig has shown[56,57] that diphenylberyllium reacts in ethereal solution with phenyllithium to give lithium triphenylberyllate $Li[Be(C_6H_5)_3]$. This is a solid which crystallises from dioxan with four molecules of the solvent, and from xylene without solvent molecules; in the latter case it is quite stable to heat and remains unchanged up to 200°, whereas diphenylberyllium starts to decompose at 160°.[57] In the light of these results, the possibility of obtaining pure diphenylberyllium by Wood and Brenner's method is open to doubt. Lithium triphenylberyllate is not in equilibrium with its ligands, since it does not form a fluorenyllithium complex with fluorene, and does not yield phenylacetic acid after carboxylation[56,57]. It is less stable than its aluminium analogue, and reacts slowly with benzophenone, giving a 31% yield of triphenylmethanol[57]. In the reaction of the addition compound with benzylideneacetophenone the yield of the diphenylpropiophenone† was 41%, whereas diphenylberyllium itself gave a yield of 58%.[57] The stability of the complexes decreases in the sequence $Li[Al(C_6H_5)_4]$, $Li[B(C_6H_5)_4]$, $Li[Zn(C_6H_5)_3]$, and $Li[Be(C_6H_5)_3]$.[58]

Cyclic ethers have been cleaved by the action of pairs of antagonistic Lewis bases and acids — triphenylmethylsodium with triphenylboron, diphenylberyllium, or triphenylaluminium[59]. The action of the pair triphenylmethylsodium–diphenylberyllium on benzofuran gave an 83% yield of 1-[*o*-hydroxyphenyl]-3,3,3-triphenylpropane. The reactivity of the complexes falls in the sequence $Na[(C_6H_5)_3.AlC(C_6H_5)_3]$, $Na[(C_6H_5)_3BC(C_6H_5)_3]$, and $Na[(C_6H_5)_3BeC.(C_6H_5)_2]$. This sequence agrees neither with that of the electrophilic character of the complexes nor with that for their activity as polymerisation initiators.

Fusion of diphenylberyllium with lithium hydride yields lithium diphenylhydroberyllate $Li[BeH(C_6H_5)_2]$,[60] which can be recrystallised from ether. This hydride reacts vigorously with water with the evolution of hydrogen, and has therefore been used as a reducing agent for phenylnonatetraenoylcarbazole, giving a 37% yield of 9-phenylnonatetraenal.

Di-*p*-tolylberyllium $(p\text{-}CH_3C_6H_4)_2Be$

This compound is readily obtained by reaction between metallic beryllium and di-*p*-tolylmercury[13].

Dicyclopentadienylberyllium $(C_5H_5)_2Be$

This compound was prepared in 1959 in 74% yield by reaction between beryllium chloride and cyclopentadienylsodium in ether[61]. Initially an attempt had been made to obtain the dicyclopentadienyl derivative by passing cyclopentadiene over metallic beryllium under various conditions (150°–550°, at atmospheric pressure and *in vacuo*), but without success. A very low yield of dicyclopentadienylberyllium is formed by reaction between beryllium chloride and cyclopentadienylpotassium under almost completely heterogeneous conditions.

Dicyclopentadienylberyllium consists of colourless crystals, which sublime in a high vacuum at 25°–60°.[61] It dissolves in benzene, ether, and in petroleum ether, from which it can be recrystallised on cooling to -60°. In such solvents as carbon disulphide, carbon tetrachloride, methylene chloride, and tetrahydrofuran, slow decomposition ensues with the formation of yellow solutions. If a solution of $(C_5H_5)_2Be$ in tetrahydrofuran was left for not more than 15 min, a good yield of unchanged dicyclopentadienylberyllium could be recovered unchanged after removal of the solvent and sublimation of the residue, but if the solution was left for a long period, a yellowish gel was formed, from which the substance could not be isolated. This explains the previous unsuccessful attempts to prepare dicyclopentadienylberyllium in tetrahydrofuran. $(C_5H_5)_2Be$ is extraordinarily sensitive to the presence of oxygen; water decomposes it rapidly with the formation of beryllium hydroxide.

The physical properties of dicylopentadienylberyllium have been studied in detail[61]. In an atmosphere of nitrogen or in a high vacuum it melts at 59°–60°; the boiling point is 233° (by extrapolation). The vapour pressure obeys the equation $\log p = 8.2242 - 2671/T$ over the range 110°–190°. Cryoscopic measurements in benzene indicate the absence of association between $(C_5H_5)_2Be$ molecules.

The following values have been obtained for the magnetic susceptibility of dicyclopentadienylberyllium[61]

$$\chi_M^{291°K} = (-107 \pm 4) \times 10^{-6} \text{ cm}^3 \text{ mole}^{-1},$$

$$\chi_M^{190°K} = (-99 \pm 4) \times 10^{-6} \text{ cm}^3 \text{ mole}^{-1},$$

$$\chi_M^{77°} = (-86 \pm 4) \times 10^{-6} \text{ cm}^3 \text{ mole}^{-1}.$$

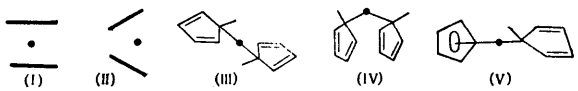
§ Presumably benzyl 2,2-diphenylethyl ketone is intended (Ed. of Translation).

¶ Presumably benzyl 2-*p*-(dimethylamino)phenyl-2-phenylethyl ketone is intended (Ed. of Translation).

† Phenyl 1,2,2-triphenylethyl ketone? (Ed. of Translation).

In contrast to the analogous compounds of magnesium and iron, which possess no dipole moment, the $(C_5H_5)_2Be$ molecule is unsymmetrical, having a dipole moment at 25° of 2.46 ± 0.06 D in benzene, and 2.24 ± 0.09 D in cyclohexane[62]. The infra-red spectrum of solid $(C_5H_5)_2Be$ contains many intense bands in the region of the C–C bond, at 1524, 1610, 1669, 1715, and 1773 cm^{-1}, the spectrum differing substantially from those of ferrocene and dicyclopentadienylmagnesium[61]. Thus a purely organometallic structure for dicyclopentadienylberyllium is evidently excluded. The suggestion has been made[61] that the bond between beryllium and the cyclopentadienyl rings involves π electrons, but it is stressed that a structure with non-parallel rings, analogous to that accepted for $(C_5H_5)_2Pb$ and $(C_5H_5)_2Sn$, cannot be excluded. The latter hypothesis has been confirmed by the nuclear magnetic resonance spectrum of dicyclopentadienylberyllium, which contains only one proton line[63].

Fritz and Schneider have investigated the far infra-red spectra of dicyclopentadienyl compounds, and found[64] with $(C_5H_5)_2Be$ a weak band at 662 cm^{-1}, a very weak band at 587 cm^{-1}, and a band of medium intensity at 414 cm^{-1}. They have considered the spectra and the values found for the force constants in relation to the various possible positions of the cyclopentadienyl rings with respect to the metal atom, and also conclude that, of the possible structures (I)–(V) for dicyclopentadienylberyllium, the structure (II) is the most probable, the angle between the rings being ~90°.

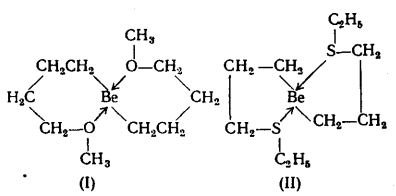


Reaction between $(C_5H_5)_2Be$ and ferrous chloride in tetrahydrofuran gives a 19% yield of ferrocene; if ferric chloride is used in the presence of iron powder, the yield of ferrocene is 76%.[61]

There is mention of the existence of a bismethylcyclopentadienylberyllium $(CH_3.C_5H_4)_2Be$, which is liquid at room temperature[61].

Spiro-Compounds of Beryllium

Bähr and Thiele[26] have synthesised di-(4-methoxybutyl)-beryllium (I) and di-(3-ethylthiopropyl)beryllium (II):



The first compound can be obtained in 45% yield by the reaction of beryllium chloride with $CH_3O[CH_2]_4MgCl$ in ether; alternatively, beryllium chloride can be treated with $CH_3O[CH_2]_4Cl$ (the process is strongly exothermic), and then magnesium added to the intermediate complex, but the yield is then considerably lower (22%). The second substance is obtained by the Grignard method according to the equation

$$2C_2H_5S(CH_2)_3MgCl+BeCl_2 \rightarrow II+2MgCl_2.$$

The reaction can be carried out in dimethyl sulphide or in ether, the yields being 35% and 60% respectively.

Di-(4-methoxybutyl)beryllium and di-(3-ethylthiopropyl)-beryllium are liquids which are completely miscible with isooctane (2-methylheptane), ether, and benzene, and possess comparatively low boiling points, in the first case 108°/4 mm and 222°–224°/765 mm, and in the second 122°–123°/2 mm and 220°–225° at 760 mm, the latter compound being so stable to heat that in an atmosphere of nitrogen it boils without appreciable decomposition (*cf.* diethylberyllium, which boils at 93°–95°/4 mm)[26]. On being cooled to -60° and -80° respectively, the two substances first set to a glassy mass, but when the temperature is raised to -40° and -30° they pass into a crystalline state. The first substance melts at 7.5°–7.8°, and the second at 7°–8°. The compounds fume in air and even ignite. On contact with water they strongly deflagrate. However, they are less reactive than the lower beryllium dialkyls. They are monomeric in benzene[26].

Alkylberyllium and Arylberyllium Halides RBeHal

As stated above, these compounds are known only in the reaction mixture, their formation being demonstrated by analysis of the decomposition products and by their participation in various reactions, in particular the test with Michler's ketone.

In 1923 Gilman reported an unsuccessful attempt to prepare alkylberyllium halides by the interaction of metallic beryllium with methyl and ethyl iodides, phenyl bromide and chloride, tolyl bromide, and finally 1-bromonaphthalene[65]. Reaction was carried out in various solvents at temperatures up to 245°–250°, the duration of heating being varied from 12 h to 2 weeks. Formation of RBeHal was checked by the colour test with Michler's ketone, but in no experiment was any evidence obtained of reaction between the beryllium and the alkyl or aryl halide. In the same paper Gilman, referring to private communications, enumerated a series of equally unsuccessful attempts by other workers (Grignard and others) to obtain compounds of the type RBeHal. The use as catalyst of free bromine, iodine, dimethylaniline, or even a freshly prepared Grignard reagent was also unsuccessful[65].

In 1926 Durand[66] reported the synthesis of methylberyllium iodide by heating metallic beryllium with methyl iodide in the presence of mercuric chloride; a grey mass was formed, which was insoluble in ether, and which on treatment with HCl evolved a gas which burned in oxygen to carbon dioxide. However, Durand's results were soon disputed by Gilman and Schulze[9], who obtained a series of alkylberyllium and arylberyllium halides (CH_3BeI, C_2H_5BeI, $n\text{-}C_4H_9BeBr$, and C_6H_5BeI) by heating metallic beryllium with the corresponding alkyl or aryl halide in the presence of a catalyst and ether in a sealed tube. Phenylberyllium iodide is formed particularly readily on heating to 150°–170° in the presence of mercuric chloride or beryllium chloride as catalyst. t-Butyl chloride and bromide probably react with metallic beryllium when heated (at 80°–90°) for 15 h, but the reaction mixture does not give the colour test with Michler's ketone[67]. Under similar conditions benzyl bromide and n-butyl chloride showed no signs of

reaction[9]. The use of ether as solvent is probably not essential, since methylberyllium iodide was successfully prepared by heating a mixture of beryllium, mercuric chloride, and a large excess of methyl iodide in a sealed tube‡[35].

In contrast to magnesium, metallic beryllium does not react with alkyl halides under the influence of ultrasonic vibrations[68].

The ether addition compound of t-butylberyllium chloride was probably obtained by Head *et al.*[51] on treating the di-t-butylberyllium–ether with beryllium chloride; it is a volatile white solid melting at 50° and subliming in a vacuum at a considerably lower temperature.

There are indications of the formation from beryllium chloride and chloroform of CCl_3BeCl at 25° and of $(CCl_3)_2Be$ at a higher temperature, but neither of these compounds has been isolated. With bromoform beryllium chloride yields Br_3CBeCl.[69]

From the facts of the formation of beryllium dialkyls by the cautious heating of alkylberyllium halides, and of the formation of the latter when beryllium dialkyls are treated with beryllium halides, it was suggested that the following equilibrium can exist[9,34]

$$2AlkBeHal \rightleftarrows Alk_2Be + BeHal_2.$$

Until quite recently alkylberyllium halides were assigned the structure RBeHal, but in 1960 Dessy[70] showed, by using $^7BeBr_2$, that no isotopic exchange occurs in the $(C_6H_5)_2Be$–$BeBr_2$ system, and hence that an equilibrium of the Schlenk type

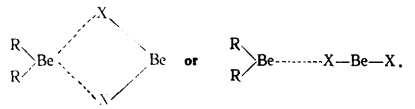
$$R_2M + MX_2 \rightleftarrows 2RMX,$$

where M = metal and X = halogen, is absent.

Thus true organoberyllium compounds of mixed type do not exist; such compounds must be assigned a complex structure $R_2Be.BeX_2$, and the existence of the following equilibrium assumed

$$R_2Be + BeX_2 \rightleftarrows R_2Be \cdot BeX_2.$$

In Dessy's work the presence of the complex $(C_6H_5)_2Be.BeBr_2$ follows also from the fact that beryllium bromide gives a two-phase system in ether, which is converted into a single phase on the addition of diphenylberyllium. The structure of this complex has not yet been determined, but it can be presumably represented[70] as



The alkylberyllium halides are decomposed by water with the formation of the corresponding hydrocarbons[35]; their reaction with Michler's ketone is slow at room temperature, but becomes rapid on heating; they do not react with carbon dioxide, but with phenyl isocyanate they give the corresponding anilides[35]. It is concluded[35] that, on the whole, the alkylberyllium halides are less reactive than the beryllium dialkyls or the corresponding organomagnesium compounds.

‡ It has been shown recently that alkylberyllium halides can actually be obtained by boiling alkyl halides with metallic beryllium in the complete absence of catalysts; L.I. Zakharkin, O.Yu. Okhlobystin, and B.N. Strunin, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 2254 (1961).

ORGANIC COMPOUNDS OF CALCIUM

Organic compounds of calcium are still less readily available and less well known than those of beryllium, most of the work in this field being concerned with the preparation of calcium analogues of Grignard reagents: only a few representatives of symmetrical compounds, R_2Ca, are known. The methods employed for preparing dialkyl and diaryl derivatives of beryllium are probably of little use for the preparation of the corresponding calcium compounds. Thus, for example, Schulze[35] obtained no evidence of the formation of calcium compounds when the metal was heated with the diethyl, di-n-butyl, diphenyl, and di-*p*-tolyl derivatives of mercury in a sealed tube. However, the search for methods of preparing organocalcium compounds may be expected to continue, since such compounds are of interest for synthetic purposes since an unusual orientation of the substituent occurs in addition reactions[53,71].

Dimethylcalcium $(CH_3)_2Ca$

Jones and Gilman[2], referring to the Rices' book[72], report that free methyl radicals react readily with metals, including calcium to form the corresponding methyl derivatives. In 1958 dimethylcalcium was prepared by the reaction of metallic calcium with methyl iodide in pyridine in an atmosphere of helium[73]. An insoluble dark precipitate first separates, from which iodine is removed by continuous extraction with fresh pyridine, and then the pyridine in a vacuum at 20°. A pale yellow residue is obtained containing up to 95% of dimethylcalcium. This deposit remains unchanged when heated in a vacuum to 400°; it is rapidly decomposed by water.

Diethylcalcium $(C_2H_5)_2Ca$

A 52.8% yield of this compound has been obtained by the action of calcium on diethylzinc in benzene[74]. Early work had indicated that a solution of diethylcalcium obtained by heating calcium with diethylzinc did not conduct electricity[75].

Diethylcalcium gives no colour reaction with benzylamine or dibenzylamine in petroleum ether, whereas diethylstrontium, diethylbarium, and diphenylbarium give such a reaction[76].

Calcium Acetylide $[Ca(C_2H)_2$ (Ed. of Translation)]

This compound can be obtained either by passing acetylene into a solution of calcium in ammonia, or else by adding the calcium solution to an ammoniacal solution of acetylene[77], the second method giving the more satisfactory results.

Diethyl sulphate reacts vigorously with calcium acetylide in liquid ammonia, giving the theoretical yield of pure but-1-yne; pentyl chloride and bromide also react well, as does butyl bromide, the yields of the corresponding acetylenes being 56%, 31%, and 45% respectively[77].

Dicyclopentadienylcalcium $(C_5H_5)_2Ca$

Ziegler and coworkers[78,79] reported that a suspension of calcium chloride in decalin reacts with a solution of cyclopentadiene in liquid ammonia to form $(C_5H_5)_2Ca.2NH_3$. The

very strongly held ammonia can be removed by heating in a high vacuum to 170°, or by prolonged refluxing in decalin. The ammonia-free dicyclopentadienylcalcium reacts with carbon dioxide yielding a dicyclopentadienedicarboxylic acid. In the presence of ammonia the carbamic acid which is first formed decomposes the $(C_5H_5)_2Ca$, so that cyclopentadiene and calcium carbamate result. The ammonia used in the preparation of $(C_5H_5)_2Ca$ can be replaced by diethylamine or ethylenediamine; in the latter case reaction can also be effected between dicyclopentadiene at 160° and calcium carbide[78]. The dicyclopentadienylcalcium obtained in this way is a yellowish-black powder contaminated with CaC_2, CaO, and other impurities; it smoulders in air. Its solubility is negligible.

Ziegler has also patented[79] the preparation under the above conditions of dicyclopentadienylcalcium in the form of a pale yellow powder which smoulders in air. Quite recently its preparation has been reported, in ~17% yield, by the action of metallic calcium on cyclopentadiene in tetrahydrofuran heated in an atmosphere of nitrogen[80]. A reddish 1 : 2 complex $(C_5H_5)_2Ca.2C_4H_8O$ is formed at first, but is unstable and loses tetrahydrofuran in a high vacuum at 110°. The product sublimes at 265° with partial decomposition and the formation of colourless crystals of pure $(C_5H_5)_2Ca$. The method[80] of obtaining dicyclopentadienylcalcium from calcium hydride and cyclopentadiene at 400° is less valuable for preparative purposes, since the yield is only 9.3%.

The spectrum in the far infra-red[64] confirms the ferrocene-like structure (I, see above) of dicyclopentadienylcalcium, and reveals the electrostatic nature of the bonds between the rings and the central metal atom. In contrast to the beryllium and magnesium derivatives, homopolarity of the bonds is not observed in the calcium derivative, and the salt-like character of the compounds is intensified[80].

Alkylcalcium and Arylcalcium Halides RCaHal

Beckmann[81] observed the formation of an amorphous white deposit when metallic calcium was heated with ethyl iodide in ether, and on the basis of an analysis assumed that it was an ether addition compound of ethylcalcium iodide $(C_2H_5)_2O.C_2H_5CaI$. However, Gilman and Schulze[27] showed later, using the colour test with Michler's ketone, that only traces of ethylcalcium iodide are formed in the solution in Beckmann's reaction, the precipitate being an ether complex of calcium iodide.

Gilman and Schulze[27] obtained butylcalcium iodide by the interaction of metallic calcium with butyl iodide in ether; the reaction started after 10 h, a considerable amount of an insoluble deposit being formed. After two days the reaction mixture was hydrolysed with dilute HCl, and n-octane was isolated from the ether layer, its amount indicating a 59% yield of the organocalcium compound.

The same workers observed a reaction between equimolecular quantities of calcium and octyl iodide in ether. After 24 h a heavy white deposit was formed, while the supernatant liquid gave a positive colour reaction for the presence of octylcalcium iodide; hydrolysis of the ether layer gave a 17.8% yield of hexadecane[27].

The course of the reaction between alkyl iodides and metallic calcium is very dependent on the grade of the calcium and on its state of division, as well as on whether the metal had been in contact with air and with traces of moisture. Greater amounts of iodine are required to catalyse the reaction than in the preparation of the corresponding Grignard reagents[27].

The technique for preparing the iodides was then improved[82] by introducing a seed, either RMgHal or previously prepared RCaHal. In addition, the condenser was closed by a tube immersed in mercury, which enabled the boiling point to be raised and the reaction to be accelerated somewhat. Under these conditions the following compounds react readily with metallic calcium (the use of shavings of size 0.2–0.5 mm is recommended): CH_3I, C_2H_5I, C_3H_7I, C_4H_9I, C_6H_5I, $CH_2:CHCH_2I$, iso-$C_5H_{11}I$, n-$C_8H_{17}I$, and m-$CH_3C_6H_4I$. The iodides $CH_3CHIC_2H_5$ and CH_3CHICH_3 do not react very well, while $C_2H_5CI(CH_3)_2$ and $(CH_3)_3CI$ do not react at all.

Bryce-Smith and Skinner[83] showed, from an investigation of the reaction between metallic calcium and alkyl halides, that the following factors facilitate the formation of alkylcalcium halides: activation of the calcium by heating (preferably in argon) at 150° with a few atomic per cent of mercury, the presence of a few atomic per cent of magnesium in the calcium, use of an ether as medium (in particular tetrahydrofuran), and finally the choice of a suitable temperature, which is different for different preparations, and in particular may be considerably below 0°. The catalytic effect of magnesium is explained[83] by the formation of traces of a Grignard reagent. Thus if the reaction is carried out between n-butyl iodide and calcium not containing magnesium as impurity (this is usually present in commercial calcium), traces of n-butylmagnesium iodide catalyse this reaction. The presence of traces of sodium in the calcium is undesirable, since this diminishes the yield of organocalcium compounds.

An attempt to prepare alkylcalcium halides by the action of ultrasonic vibrations on a mixture of metallic calcium and an alkyl halide was unsuccessful[68].

To prepare phenylcalcium iodide, iodobenzene is heated with metallic calcium in anhydrous ether, with addition of traces of iodine as catalyst[61]. Phenylcalcium iodide and also calcium dialkyls give a positive reaction with Michler's ketone[27,67].

In an assessment of the prospects for the use of organocalcium compounds for preparative purposes, Gilman and Schulze[27] considered that attempts to use these compounds like Grignard reagents were doomed to failure. The main defects of substances of the RCaHal type were regarded as the following: (*a*) the formation of RCaHal is probably confined to the iodides; (*b*) only primary alkyl iodides react with calcium, and by no means all of these do so, benzyl iodide, for example, not reacting; (*c*) reaction between alkyl iodides and calcium is extremely slow and is accompanied by numerous side reactions, resulting in a low yield of the organocalcium derivative; and (*d*) alkylcalcium halides are in general less reactive than the corresponding magnesium compounds.

Further work, however, compelled a change in this opinion, and the recognition that phenylcalcium iodide is more reactive than the phenylmagnesium halide. This assertion is based on the following three reactions[84]: phenylcalcium iodide reacts more rapidly than phenylmagnesium bromide with benzonitrile; it metallates dibenzofuran in a similar manner to the organic compounds of lithium, sodium, and potassium, whereas the Grignard reagent does not react; and finally phenylcalcium iodide, like phenyllithium but in contrast to phenylmagnesium

bromide, adds to several double bonds, yielding, for example, triphenylmethylaniline with benzophenone-anil.

Compounds of the type RCaI are more convenient than the corresponding bromides or chlorides for synthetic purposes, since the latter react considerably more slowly[83]. Although preparations proceed more rapidly in tetrahydrofuran than in diethyl ether, the solution obtained in the former solvent is less stable owing to the greater rate of cleavage. Organocalcium compounds are closer to organolithium than to organomagnesium compounds in reactivity. This closeness appears, for example, in the cleavage of ethers and in the reactions with pyridine and with CO_2.[83] Phenylcalcium iodide reacts readily with pyridine at 5° and above, forming 2-phenylpyridine. With carbon dioxide the n-butylcalcium halide gives mainly di-n-butyl ketone and tri-n-butylmethanol: very little n-valeric acid is formed, even with a high rate of carboxylation. Phenylcalcium iodide and bromide, on the other hand, yield principally benzoic acid, in a similar manner to the organomagnesium compounds[81,83]. Like the corresponding magnesium compounds, n-butylcalcium and phenylcalcium iodides do not give a colour reaction with benzylamine or dibenzylamine in petroleum ether[76].

The reaction of benzaldehyde with methyl-, ethyl-, n-propyl-, and isopentyl-calcium iodides gave the corresponding α-alkylbenzyl alcohols in 30–40% yield[82].

Ethylcalcium iodide reacts with nitriles, giving ethyl phenyl ketone (yield 30%) with benzonitrile, and ethyl methyl ketone with acetonitrile[82]. With ethyl formate and ethyl acetate, ethylcalcium iodide forms the corresponding alcohols, pentan-3-ol and 3-methylpentan-3-ol, in 20% yield[82].

Reaction of butylcalcium iodide with ethyl methyl ketone gives a 40% yield of 3-methylheptan-3-ol.[82] It reacts with naphth-1-yl isocyanate forming *N*-naphth-1-ylvaleramide[27]. Phenylcalcium iodide reacts analogously with phenyl isocyanate to yield benzanilide[27]. An attempt to synthesise the imidic ester $C_6H_5.C(:N.C_6H_5).OC_2H_5$ by treating phenylcalcium iodide with phenyl isocyanate and then adding excess of diethyl sulphate was unsuccessful[27]. Phenylcalcium iodide reacts vigorously with benzoyl chloride, but greatly varying yields of triphenylmethanol are reported, from 1%[27] to 94%.[83] Triphenylmethanol is formed also by the reaction of phenylcalcium iodide with benzophenone (yield 16%) and with ethyl benzoate (yield 26%)[82]. Addition of benzaldehyde to an ethereal solution of phenylcalcium iodide results in the formation of diphenylmethanol by the reaction[81]

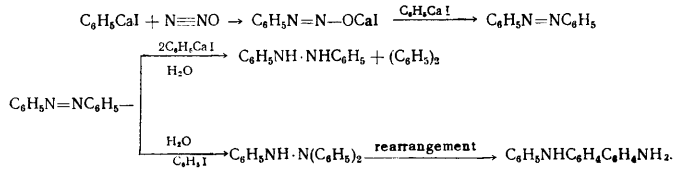
$$C_6H_5CaI + C_6H_5CHO \rightarrow C_6H_5CH(C_6H_5)OCaI,$$
$$C_6H_5CH(C_6H_5)OCaI + H_2O \rightarrow C_6H_5CH(C_6H_5)OH + ICaOH.$$

Dibenzofuran-4-carboxylic acid has been obtained by the action of phenylcalcium iodide on dibenzofuran, the resulting calcium derivative being treated with carbon dioxide[84].

Used of an organocalcium compound as metallating agent leads in some cases to an unusual orientation of the substituent. Whereas dibenzothiophen is metallated by diethylcalcium[85], as by butyllithium and potassium[86], in position 4, with phenylcalcium iodide metallation takes place in the 3-position, resulting in the formation on subsequent carboxylation of dibenzothiophen-3-carboxylic acid[71,85]. Phenylcalcium iodide adds to phenyl styryl ketone in the 1,2-position, with the formation of αα-diphenylcinnamyl alcohol[57]. The yield of this carbinol reaches 45%,[53] and with *p*-dimethylaminostyryl phenyl ketone 64% of *p*-dimethylamino-αα-diphenylcinnamyl alcohol is formed, *i.e.* 1,2-addition takes place in both cases[53].

In contrast to phenylmagnesium bromide, phenylcalcium iodide does not reduce azobenzene[87]; as in the case of phenylpotassium, unsymmetrical addition takes place, resulting in the formation of an 18.5% yield of triphenylhydrazine, 64.4% of the azobenzene being recovered unchanged[54].

Phenylcalcium iodide reacts with nitrous oxide[88]: biphenyl, azobenzene, *N*-phenylbenzidine, and benzidine have been isolated from the reaction mixture by means of chromatography, which enables the following scheme of reactions to be suggested



Dufford *et al.*[89] observed a feeble chemiluminescence during the oxidation of phenylcalcium iodide with oxygen, and the product of this oxidation also showed a weak fluorescence.

In conclusion we may mention the formation of organocalcium compounds by the action of metallic calcium on some phenylated alkenes in liquid ammonia[90]. Thus calcium adds to the ethylenic bond of 1,1-diphenylethylene, the solution turning red; after ammonolysis, 1,1-diphenylethane (70%) and 1,1,4,4-tetraphenylbutane (14%) were isolated from the reaction mixture. Addition of calcium to 1,1,2-triphenylethylene yields after ammonolysis 1,1,2-triphenylethane (40%).

ORGANIC COMPOUNDS OF BARIUM AND STRONTIUM

The first attempts to obtain dialkyl and diaryl compounds of barium and strontium were made as early as 1933. However, these compounds could not be obtained by reaction of the metal with the corresponding organomercury compounds[35]. The formation of organometallic compounds by the action of strontium and barium on 1,1-diphenylethylene in liquid ammonia was noted by Gilman and Bailie[90], since 1,1-diphenylethane and 1,1,4,4-tetraphenylbutane were isolated from the reaction mixture after ammonolysis. The analogous addition of strontium and barium to 1,1,2-triphenylethylene yields 1,1,2-triphenylethane; barium reacts also with triphenylmethane with the formation of traces of triphenylmethylbarium[90].

Dimethylbarium and dimethylstrontium were obtained only in 1958, in a similar manner to dimethylcalcium, by reaction of the metal with methyl iodide in anhydrous pyridine in an atmosphere of helium[73]. After extraction of iodine with fresh pyridine and removal of the latter in a vacuum, preparations of 95% purity were obtained, stable on heating in a vacuum to 400°, but unstable in the presence of moisture, oxygen, and carbon dioxide.

Diethylstrontium was obtained in the form of a complex with diethylzinc by heating metallic strontium filings with diethylzinc in benzene in an atmosphere of nitrogen in a

sealed tube[91]. A 51% yield of the complex $(C_2H_5)_2Sr.(C_2H_5)_2Zn$ was obtained as brown crystals which decomposed at 170° with the formation of a metallic mirror, the liberation of diethylzinc, and the evolution of a considerable quantity of gas. The complex is readily soluble in benzene.

In a similar manner diethylbarium and dibutylbarium were obtained by the reaction of barium with diethylzinc and dibutylzinc respectively[85]. Diphenylbarium could not be obtained by this method, but it was prepared from diphenylcadmium and barium[85].

Barium and strontium dialkyls and diaryls, and also phenylbarium iodide, give a positive reaction with Michler's ketone[27,67]. When a solution of diethylstrontium, diethylbarium, or diphenylbarium is shaken up with benzylamine or dibenzylamine in petroleum ether, a cherry-red coloration appears[76]. A similar reaction is given by alkyl and aryl derivatives of the alkali metals, but not by organocalcium or organomagnesium compounds.

Diethylstrontium and diethylbarium add to the olefinic bond in 1,1-diphenylethylene with the formation of organostrontium and organobarium compounds, which have been identified by carboxylation to the corresponding acid $(C_6H_5)_2C(C_3H_7)COOH$.[85,91] Diethylstrontium metallates anisole in the *ortho*-position with the formation of di-(*o*-methoxyphenyl)strontium; dibenzofuran and dibenzothiophen are metallated in position 4.[91] Diethylbarium also metallates anisole in the *ortho*-position[85]. The action of diethylbarium or diethylstrontium on methyl phenyl sulphide results in *ortho*-metallation in the ring with the formation of o-$CH_3SC_6H_4COOH$ after carboxylation[85].

Diethylbarium does not add to stilbene (in contrast to butyllithium and $\alpha\alpha$-dimethylbenzylpotassium)[85]. Diethylbarium and ethyllithium (but not diethylstrontium) to a limited extent add to styrene, yielding after carboxylation 2-phenyl-n-valeric acid[85]. Diethylstrontium and diethylbarium add to diphenylmethyleneaniline with the formation of the secondary amine $(C_6H_5)_2C(C_2H_5)NHC_6H_5$.[85] Addition to azobenzene results in 1-ethyl-1,2-diphenylhydrazine, which rearranges to *N*-ethylbenzidine[85].

With 1-bromonaphthalene an exchange reaction takes place with both metal diethyls and naphthoic acid can be isolated after carboxylation[85]. The following reaction also takes place in low yield[85]:

$$(C_6H_5)_3PbC_6H_4Br\text{-}p + (C_2H_5)_2Ba \xrightarrow[H_2O]{CO_2} (C_6H_5)_3PbC_6H_4COOH\text{-}p.$$

Exchange of the metals occurs in the reaction between tetraphenyltin and diethylbarium and diethylstrontium with the formation after carboxylation of benzoic acid in yields of 32% and 11% respectively[85]. Exchange reactions do not take place with tetraphenylsilane, tetraphenylgermanium, or tetraphenyllead. Triphenyltin chloride and diethylbarium give a good yield of ethyltriphenyltin[85]. Triphenyllead chloride yields not only ethyltriphenyllead but also an appreciable quantity of tetraphenyllead[85].

The preparation of barium acetylide has been mentioned, its formula in liquid ammonia being $Ba(C_2H)_2.4NH_3$.[92]

Just recently dicyclopentadienylstrontium has been prepared by the reaction of metallic strontium with cyclopentadiene in dimethylformamide at 50°. The resulting addition compound, a reddish substance, is heated at ~250° for 1 h, and a 4.1% yield of colourless crystals of $(C_5H_5)_2Sr$ is obtained by sublimation at 360°–440°. The yield of dicyclopentadienylstrontium obtained from strontium hydride and cyclopentadiene was ~1.4%.[80]

Dicyclopentadienylbarium has been obtained with great difficulty only by the action of barium hydride on cyclopentadiene at 400°.[80] Extraction with dimethylformamide and sublimation at 420°–460° gave a 0.2% yield of colourless crystals of $(C_5H_5)_2Ba$.

From the far infra-red spectra of these dicyclopentadienyls it has been concluded that their structure is analogous to that of dicyclopentadienylcalcium[64].

Attempts to prepare organostrontium and organobarium compounds by reaction of the metal with alkyl iodides were unsuccessful[35]. However, the reaction mixture obtained with ethyl iodide and barium gave a positive colour reaction, indicating formation of ethylbarium iodide[93].

Phenylbarium iodide is prepared from iodobenzene and barium[93], only the electrolytic metal being suitable. Several reactions of phenylbarium iodide have been studied[93]: carboxylation gives benzoic acid, naphthyl isocyanate yields *N*-1-naphthylbenzamide, and with ethyl benzoate triphenylmethanol is obtained. It is stressed[93] that it is more difficult to obtain phenylbarium iodide than phenylcalcium iodide, and that the former compound cannot compete with a Grignard reagent.

In 1936 Gilman *et al.*[84] suggested that organostrontium compounds should be more reactive than organocalcium compounds, but less reactive than the organobarium compounds. This postulate was later tested[74] in the case of the reaction between the phenylethynyl derivatives and benzonitrile:

$$(C_6H_5C{\equiv}C)_2M + C_6H_5CN \xrightarrow{H_2O} C_6H_5C{\equiv}CCOC_6H_5,$$

where M = Ba, Sr, Ca, Mg, and Be. The following reactivity sequence was established: $R_2BA > R_2Sr > R_2Ca > R_2Mg > R_2Be$. This sequence correlates with the ionisation potentials of the corresponding metals: Ba 5.19, Sr 5.67, Ca 6.09, Mg 7.61, and Be 9.28 eV. A decrease in the ionisation potential of a metal in this group results in greater reactivity of its simple organic compounds.

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Thus the general progress in the chemistry of organometallic compounds during recent years has made the organic compounds of the alkaline-earth metals more readily available. At the present time they are still unable to compete with the organomagnesium compounds; nevertheless, the possibility of using them in some syntheses is not excluded.

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Institute of Organoelemental Compounds,
Academy of Sciences of the USSR