Diïsopropylberyllium and Some Beryllium Hydrides.

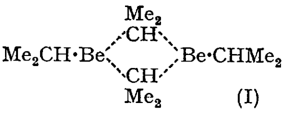
By G. E. Coates and F. Glockling.

[Reprint Order No. 4526.]

Di*iso*propylberyllium, m. p. −9·5°, is dimeric in benzene solution at 25°. Pyrolysis at 200° gives polymeric *iso*propylberyllium hydride. With trimethylamine, the monomeric adduct $Pr^i_2\overset{-}{Be}-\overset{+}{N}Me_3$ is formed which loses a mol. of propene and some trimethylamine when heated at 200°. With 1 mol. of dimethylamine, propane and dimethylamino*iso*propylberyllium are formed; the latter decomposes when heated, with formation of propene and dimethylaminoberyllium hydride. Excess of dimethylamine gives bisdimethylaminoberyllium which is trimeric in benzene solution. Some factors which affect the association of organo-metallic compounds are discussed.

Dimethylberyllium, like trimethylaluminium, is a typical electron-deficient compound in that its polymeric structure (Rundle and Snow, *Acta Cryst.*, 1951, **4**, 348; Coates, Glockling, and Huck, *J.*, 1952, 4496) requires the presence of " half bonds." Since tri*iso*propylaluminium (Pitzer and Gutowsky, *J. Amer. Chem. Soc.*, 1946, **68**, 2204) is monomeric and hence not electron deficient, the preparation and examination of di*iso*propylberyllium appeared of interest and likely to provide more information about the factors which influence the formation of half bonds.

Di*iso*propylberyllium (I) may be prepared from beryllium chloride–diethyl ether and *iso*propylmagnesium bromide; like the few other known organoberyllium compounds, it retains ether with great tenacity. One preparation which had twice been distilled and pumped *in vacuo* for two days was found, on hydrolysis, to have retained 16% by weight of ether. An ether-free product could only be obtained by reflux distillation with continuous pumping for about two days; it then melted at −9·5°, and the (extrapolated) boiling point was 280°. Vapour-pressure data for this and some other compounds are given in the Table. Di*iso*propylberyllium can be distilled only very slowly in a good vacuum at room temperature (v. p. = 0·17 mm. at 20°), but at a convenient rate at 40° (v. p. = 0·53 mm.); manipulation is complicated by the slow decomposition which occurs above 40—50°, giving propene. It fumes strongly on exposure to air, but does not take fire; reaction with water is of explosive violence unless controlled by cooling.



(I)

The boiling points of both di*iso*propyl- and diethyl-beryllium (Goubeau and Rodewald, *Z. anorg. Chem.*, 1949, **258**, 162), 280° and 194°, are compatible with both compounds having dimeric structures, by analogy with the boiling points of the hydrocarbons tetradecane (253°) and *n*-decane (174°) whose molecular weights are similar to those of the dimeric di*iso*propyl- and diethyl-beryllium. In contrast to dimethylberyllium, which is highly polymerised in the solid state, di*iso*propylberyllium is very soluble in benzene, and its molecular weight in that solvent has been measured (at 25°) by a vapour-pressure method described in the experimental section. The compound is dimeric and no change in the degree of association was observed over the concentration range studied. A bridged structure (I) is suggested for di*iso*propylberyllium, analogous to that assigned to the dimeric component of dimethylberyllium vapour (Coates, Glockling, and Huck, *loc. cit.*) and to the trimethylaluminium dimer (Pitzer and Sheline, *J. Chem. Phys.*, 1948, **16**, 552; Lewis and Rundle, *ibid.*, 1953, **21**, 986).

The Be–C(bridge)–Be bond is regarded as being formed by one doubly occupied, bent, three-centre molecular orbital, derived from the beryllium *sp*^{2} and carbon *sp*^{3} atomic orbitals, thus each Be–C (bridge) bond is regarded as a half bond (represented by a dotted line). Pitzer and Gutowsky (*loc. cit.*), who observed a decreasing tendency to association in the series Me_3Al, Et_3Al, $Pr^i{}_3Al$, consider that increasing substitution by methyl at the carbon atom directly bonded to aluminium diminishes association by steric effects. This does not appear to be an adequate explanation since the metal–carbon bonds in these electron-deficient compounds are rather long and the metal–carbon–metal angle unusually small, *e.g.*, 1·92 Å and 66° in the solid dimethylberyllium polymer (Rundle and Snow, *loc. cit.*). We consider that the decreasing association in the series methyl to *iso*propyl, now observed both with aluminium and beryllium, is due, not mainly to steric effects, but more to the decreasing electronegative character of the alkyl group.

There is increasing evidence (Gillespie, *J.*, 1952, 1002) that an increase in the number of orbitals used for bonding by an atom is facilitated when the atom is bonded to the more electronegative atoms or groups. Gillespie gives such examples as phosphorus pentachloride and sulphur hexafluoride, but the effect would seem to be apparent in many different elements. For example, the alkali metals form covalent co-ordination compounds, not normally with nitrogen (usually regarded as the strongest donor atom) but more particularly with oxygen which is *more electronegative*. In the aluminium alkyls dimerisation requires an increase in the number of orbitals used by the aluminium atom from three *sp*^{2} to four *sp*^{3}; since this process would be facilitated by bonding to the more electronegative groups it is reasonable that while bonding to methyl results in dimerisation, bonding to the more electropositive *iso*propyl does not. Also nearly all the known compounds of beryllium contain that element in a four-covalent state, and bonded to highly electronegative atoms, usually oxygen, nitrogen, or halogens. With dimethylberyllium, reversible equilibria may be realised between the solid polymer in which the beryllium atom uses four orbitals, and low polymers including the dimer, in which it uses only three orbitals. When beryllium is bonded to the more electropositive *iso*propyl group it apparently cannot make use of four orbitals, but only three, hence it remains dimeric.

Pyrolysis of di*iso*propylberyllium at 200° proceeds according to the equation

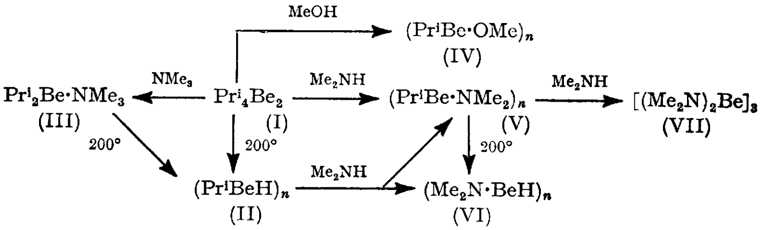
$$(i\text{-}C_3H_7)_4Be_2 \longrightarrow \frac{2}{n}(i\text{-}C_3H_7\cdot BeH)_n + 2C_3H_6$$

*iso*Propylberyllium hydride (II) is a colourless, non-volatile, viscous oil, hydrolysed to beryllia, propane, and hydrogen, and evidently polymerised. The more extensive polymerisation of the half hydride is consistent with the behaviour of the alkyls and hydrides of other elements which form electron-deficient compounds; hydrides and mixed alkyl hydrides are always more associated than the alkyls, compare, for example, B_2H_6, $B_2H_2Me_4$, and Me_3B; $(AlH_3)_n$, $(Me_2AlH)_n$ (a viscous oil), and Me_6Al_2; Ga_2H_6 and Me_3Ga. It is probably due partly to the greater electronegativity of hydrogen, which certainly forms an anion more readily than a methyl group, and partly to the more satisfactory overlap in the formation of three-centre molecular orbitals with the directionless H(1 *s*) atomic orbitals as central component.

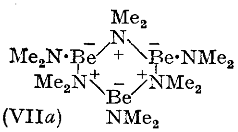
A further pyrolysis of *iso*propylberyllium hydride does not afford beryllium hydride, but, between 220 and 250°, complex decomposition results in the formation of metallic beryllium, hydrogen, propene, propane, and an orange-coloured residue. In contrast to the simple decomposition of di*iso*propylberyllium up to 200°, diethylberyllium (Goubeau and Rodewald, *loc. cit.*) appears to decompose in a complex manner at 190—200° giving ethane, ethylene, and butene, together with traces of hexene, *cyclo*hexadiene, and benzene. Although *iso*propylberyllium hydride is rapidly hydrolysed by water, reaction with dimethylamine, in which the hydrogen is much less reactive, was investigated to see whether the *iso*propyl group or the hydrogen was preferentially eliminated. The reaction was not quantitative but propane and hydrogen were formed in the ratio of 2·5 : 1.

	V. p. equation : $\log_{10} p = B - A/T$ B	A	Temp. range	ΔH	Trouton const.	B. p. (extrap.)
Di*iso*propylberyllium	7·01	2280	35—60°	10·45	19·1	280
Di*iso*propylberyllium–trimethylamine	7·95	2535	20—100	11·6	23·2	227
Bisdimethylaminoberyllium	8·8	3135	90—150	14·3	27·0	257

Like dimethylberyllium (Coates and Huck, *J.*, 1952, 4501), di*iso*propylberyllium forms a 1 : 1 co-ordination compound (III) with trimethylamine, but there was no evidence for a 2 : 3-compound stable at room temperature analogous to $(Me_2Be)_2(NMe_3)_3$. The 1 : 1-adduct is somewhat more volatile and thermally stable than the dialkyl. Its molecular weight in benzene corresponds to a monomeric structure $Pr^i_2\overset{-}{Be}-\overset{+}{N}Me_3$, in contrast to $Me_2\overset{-}{Be}-\overset{+}{N}Me_3$ for which there is evidence of association. Above 100° thermal decomposition (rapid at 200°) gave one mol. of propene and some of the trimethylamine; the crystalline residue was *iso*propylberyllium hydride (in combination with trimethylamine) since equimolar quantities of propane and hydrogen were formed on hydrolysis.



Although the uncontrolled hydrolysis of di*iso*propylberyllium is of explosive violence, one mol. of propane is readily and smoothly evolved on reaction with methanol, giving *iso*propylberyllium methoxide (IV) as a crystalline solid, m. p. 133°. With the less reactive hydrogen atom in dimethylamine a mol. of propane is slowly evolved at room temperature, forming dimethylamino*iso*propylberyllium (V) as a colourless liquid which loses propene above 100° (rapidly at 200°) with the formation of polymeric (glassy) dimethylaminoberyllium hydride (VI); the latter is rapidly hydrolysed with the formation of a mol. of hydrogen, but does not react with trimethylamine. With excess of dimethylamine two mols. of propane are formed, leading to the crystalline bisdimethylaminoberyllium (VII) (m. p. 88—90°), which Goubeau and Rodewald (*loc. cit.*) did not isolate from the apparently more complex reaction between dimethylamine and diethylberyllium. Bisdimethylaminoberyllium is sufficiently stable to be vaporised, and its vapour density indicates a degree of association varying steadily from 2·9 at 160° to 2·5 at 200°. In boiling benzene it is trimeric and probably has a cyclic structure analogous to that assigned (Coates, Glockling, and Huck, *J.*, 1952, 4512) to the trimeric compound $(MeBe{\cdot}NMe_2)_3$, *viz.* (VII*a*).



(VII*a*)

EXPERIMENTAL

Quantities of material are usually expressed as N-c.c., which refers to the N.T.P. volume of monomeric vapour.

*Di*iso*propylberyllium.*—Anhydrous beryllium chloride (14 g.), prepared by heating lumps of the metal in a stream of hydrogen chloride (Goubeau and Rodewald, *loc. cit.*), in ether (200 c.c.) was added slowly to a solution in ether (150 c.c.) of *iso*propylmagnesium bromide [from magnesium (17 g.) and *iso*propyl bromide (88 g.)] with mechanical stirring in a nitrogen atmosphere. The reaction flask was then slowly evacuated through a sealed-on ampoule cooled to −10°. In this way a large part of the ether was collected elsewhere in the apparatus. The reaction flask was then heated to 50—70° for 4 hr. with continuous pumping, and the clear distillate, which is an etherate of di*iso*propylberyllium, collected in an ampoule cooled to −78°. This initial heating and distillation, in addition to separating ether, gave 1·4 litres of propene (b. p. −48°). The etherate was then distilled in high vacuum into the flask *A* (Fig. 1) by heating at 50°. The reaction flask and first ampoule were then separated by sealing at the constriction *a*. The etherate thus obtained in *A* was gently boiled under reflux for 16 hr. (bath temp. 40—50°; condenser temp. −10° to −20°) with continuous pumping through T_1, by which time evolution of ether had ceased. No appreciable quantity of propene was formed. By tilting the apparatus the condensate was then made to run into *B*, and the constriction at *b* sealed. Small amounts of di*iso*propylberyllium were introduced into the sample tubes by inverting the apparatus. The tubes were cooled and sealed with continuous pumping through T_2. Finally, the main stock of di*iso*propylberyllium was isolated by sealing at *c*. It was obtained as a clear liquid, which, on cooling, formed needles, m. p. −9·5°. In each experiment involving di*iso*propylberyllium, a weighed sample tube was broken *in vacuo* and the weight of the sample obtained by collecting and weighing the broken glass.

FIG. 1.

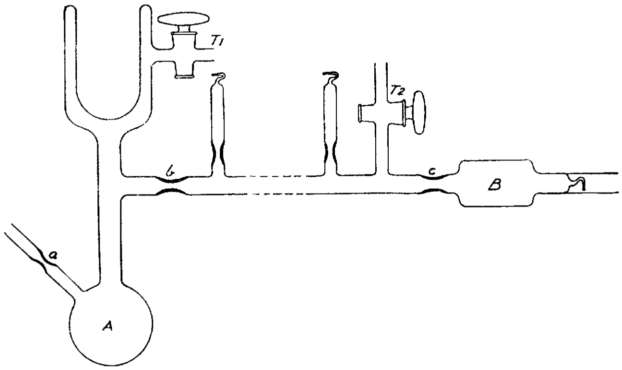
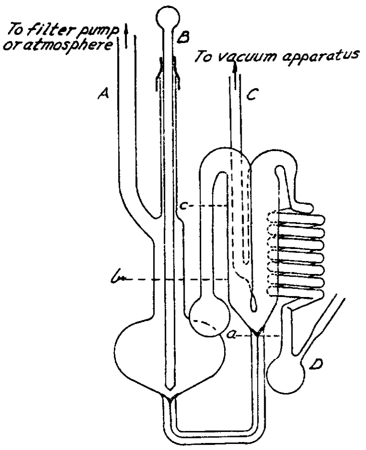


FIG. 2.



Analysis of Di*iso*propylberyllium.—Anhydrous methanol in large excess was condensed on di*iso*propylberyllium (28·15 N-c.c.), and the reaction allowed to proceed slowly with occasional cooling. The mixture was boiled gently, then treated with 0·1N-hydrochloric acid, and again boiled. No hydrogen or methane was formed. Propane (Found: 55·0 N-c.c.; v. p. at −78·5°, 106 mm. Calc.: 56·3 N-c.c.) was separated by fractional condensation through two methylene chloride slush baths (−96°). No ether was detected in the fractional-condensation process.

Hydrolysis of di*iso*propylberyllium with water, even when carefully controlled, gave a small amount of hydrogen. In one experiment where the hydrolysis proceeded vigorously, 32·6 N-c.c. of hydrogen were formed from 305·7 mg. of di*iso*propylberyllium and much of the vacuum apparatus was coated with beryllium hydroxide.

Molecular Weights of Di*iso*propylberyllium *and* Di*iso*propylberyllium–Trimethylamine.—The apparatus shown diagrammatically in Fig. 2 was used. With the mercury drawn down to position *a* (by evacuating at *A* and raising the plunger *B*, which has a ground seating), the apparatus was evacuated and thoroughly dried. Dry benzene, stored elsewhere in the apparatus, was condensed *via* tube *C* into the left-hand bulb, cooled in liquid air, and the mercury level raised to *b*, by lifting the plunger *B* with atmospheric pressure at *A*, thus isolating the left-hand side of the apparatus. A weighed sample tube of di*iso*propylberyllium was broken magnetically and the specimen distilled into the right-hand bulb cooled in liquid air, through the constriction

D (subsequently sealed). At room temperature the rate of transfer was slow, but at 40° a suitable sample (0·2—0·3 g.) could be introduced in the course of a day. A known weight of dry benzene was then condensed on the sample and the mercury level raised to *c*. Both solvent and solution were then allowed to warm to room temperature simultaneously. Seven turns of spiral in the tube connected to the right-hand bulb enabled it to be stirred effectively by tapping it with the finger. After several hours at room temperature both bulbs were cooled to −20° and a small amount of benzene (together with any traces of propane) removed from the right-hand bulb, by lowering the mercury to *b* and weighed. The mercury level having been returned to *c* and the solution again mixed, the whole apparatus was immersed in thermostat maintained at 25° or 30° and the pressure difference between the pure solvent and solution measured when constant. A portion of benzene was then removed from the solution, in the manner described above, and weighed, thus allowing measurements to be taken over a series of concentrations. The sample weights were checked by reaction with excess of dimethylamine, and measurement of the propane formed. The molecular weight of the solute, Raoult's law being assumed, is given by $M = 78\,m_s[(p_0/\Delta p) - 1]/m_0$, where m_s = wt. of solute (g.), m_0 = wt. of solvent (g.), p_0 = vapour pressure of pure benzene at the bath temp., and Δp = pressure difference (mm.).

The method was checked with diphenyl (Found: *M*, 153, 160. Calc.: *M*, 154).

Di*iso*propylberyllium–trimethylamine (III) was prepared in the right-hand bulb with the mercury level at *b*, care being taken to avoid sudden increases of pressure which would blow mercury and gases into the left-hand bulb.

Results.—These are given in the Table.

	Mol. fraction of solute	*M* of solute	Degree of assocn.	Mol. fraction of solute	*M* of solute	Degree of assocn.
Di*iso*propylberyllium	0·06176	188	1·98	0·06281	185	1·95
	0·06368	187	1·97	0·08489	189	1·99
	0·08024	183	1·93	0·09614	189	1·99
Di*iso*propylberyllium–trimethylamine	0·0487	156	1·01	0·1229	158	1·03
	0·08175	159	1·03			

iso*Propylberyllium Hydride* (II).—Di*iso*propylberyllium (21·2 N-c.c.) was condensed in a tube equipped with a breaker and heated in an air-furnace at 200° for 8 hr. giving *iso*propylberyllium hydride, as a viscous liquid, and propene (21·5 N-c.c.; v. p. at −78·5°, 144 mm.). The *iso*propylberyllium hydride, on hydrolysis with water, gave hydrogen (22·6 N-c.c.) and propane (20·6 N-c.c.; v. p. at −78·5°, 104 mm.).

Reaction of iso*Propylberyllium Hydride with Dimethylamine.*—*iso*Propylberyllium hydride was prepared by heating di*iso*propylberyllium (10·65 N-c.c.) to 200° for 5 hr. in a sealed bulb and removing the propene formed (10·2 N-c.c.). Dimethylamine (10·0 N-c.c.) was condensed on the sample by cooling in liquid air. At room temperature a lively reaction occurred with much frothing. The viscous, semi-solid residue was heated at 100° for 6 hr. and the gaseous products, hydrogen (2·4 N-c.c.) and propane (6·0 N-c.c.), were separated.

*Di*iso*propylberyllium–Trimethylamine* (III).—Di*iso*propylberyllium (14·2 N-c.c.) was introduced into a high-temperature bulb (Burg and Schlesinger, *J. Amer. Chem. Soc.*, 1937, **59**, 780) and trimethylamine (14·2 N-c.c.) condensed on it. The residual pressure at room temperature corresponded to 0·5 N-c.c. excess of trimethylamine which was removed by pumping for a few seconds. The clear liquid residue thus corresponds to the 1 : 1 addition compound, $(Me_2CH)_2\overset{-}{Be}\cdot\overset{+}{N}Me_3$. A linear log p–T^{-1} relationship was found up to 100° whereafter a rapid increase in pressure occurred. Having been heated to 200° and cooled to room temperature, the gaseous products (16·2 N-c.c.) were removed. Trimethylamine was separated by shaking the products with dilute sulphuric acid, and the residual volume shown to be propene (13·4 N-c.c.). Thus pyrolysis at 200° results in the elimination of 2·8 c.c. of trimethylamine as well as formation of almost one equivalent of propene. The residue, long feathery needles at room temperature, was hydrolysed with water vapour followed by a large excess of water, giving hydrogen (13·3 N-c.c.) and propane (14·0 N-c.c.).

In a further experiment, with 14·4 N-c.c. of $Pr^i_2\overset{-}{Be}\cdot\overset{+}{N}Me_3$, pyrolysis at 200° gave propene (15·1 N-c.c.) and trimethylamine (3·3 N-c.c.). Reheating of the residue to 170° gave a further quantity (5·3 N-c.c.) of propene. Hydrolysis of the residue gave hydrogen (19·0 N-c.c.) and propane (8·3 N-c.c.).

iso*Propylberyllium Methoxide* (IV).—Methanol (28·6 N-c.c.) was condensed on di*iso*propylberyllium (28·6 N-c.c.) by cooling with liquid air. The reaction started as the methanol melted and was controlled by occasional cooling. After ½ hr. at room temperature the propane formed was separated (28·6 N-c.c.; v. p. at −78·5°, 100 mm.). The *iso*propylberyllium methoxide formed transparent plates, m. p. 133°. It appeared to be unaffected by short exposure to air, but was vigorously hydrolysed by water.

*Dimethylamino*iso*propylberyllium* (V) *and Dimethylaminoberyllium Hydride* (VI).—Di*iso*propylberyllium (26·7 N-c.c.) and dimethylamine (26·7 N-c.c.) were allowed to warm from liquid-air temperature. Reaction occurred slowly at room temperature giving propane (26·7 N-c.c.; v. p. at −78·5°, 102 mm.) and the liquid dimethylamino*iso*propylberyllium. The latter was then slowly heated: evolution of propene became quite rapid at 100° and was practically complete after 15 min. at 220° giving dimethylaminoberyllium hydride, which formed a glass at room temperature, and propene (22·4 N-c.c.; v. p. at −78·5°, 144 mm.). Trimethylamine (43·4 N-c.c.) was then added to the dimethylaminoberyllium hydride and next morning the excess of trimethylamine (43·0 N-c.c.) removed by pumping at room temperature; hence no stable adduct was formed. The residue was then hydrolysed in the usual manner giving hydrogen (22·5 N-c.c.) and propane (0·5 N-c.c.). It is difficult to prevent the formation of a little bisdimethylaminoberyllium in the preparation of dimethylamino*iso*propylberyllium, and the above figures are most satisfactorily explained if the true volume of di*iso*propylberyllium was 24·55 N-c.c. The products of the reaction with 26·7 N-c.c. of dimethylamine then become: propane (26·7 N-c.c.), dimethylamino*iso*propylberyllium (22·4 N-c.c.), and bisdimethylaminoberyllium (2·15 N-c.c.). The volumes of propene formed in the pyrolysis at 220° and hydrogen formed in the hydrolysis of the dimethylaminoberyllium hydride then follow almost quantitatively.

Bisdimethylaminoberyllium (VII).—Di*iso*propylberyllium (10·8 N-c.c.) was treated with excess of dimethylamine (40·0 N-c.c.). The reaction occurred in two stages; the first slowly at room temperature, giving the liquid dimethylamino*iso*propylberyllium, and the second on slight warming, giving *bisdimethylaminoberyllium* as prisms, m. p. 88—90°. The excess of dimethylamine and propane (40·3 N-c.c.) were collected and condensed on excess of standard acid. Back titration with sodium hydroxide gave the volume of dimethylamine combined as 19·5 N-c.c. (Calc., from sample weight: 21·6). The volume of propane obtained was 22·0 N-c.c. (Calc.: 21·6). The sample weight was checked by hydrolysis of the bisdimethylaminoberyllium which had been heated to 200° for vapour-pressure and molecular-weight measurements, and estimation of the dimethylamine produced (Found: 21·4 N-c.c. Calc.: 21·6 c.c.).

The above preparation of bisdimethylaminoberyllium was carried out in a standard type of high-temperature bulb of volume 182·2 c.c. Between 160° and 200° the compound was present entirely as vapour. Its molecular weight within this temperature range was in the range 280—244 and decreased steadily with increasing temperature. The degree of association of bisdimethylaminoberyllium vapour under the conditions employed was therefore between 2·89 and 2·52. The molecular weight was also measured ebullioscopically in benzene by the Swietoslawski method [Found: *M*, 296, 291, 295 (in 0·83, 1·51, and 2·48% solution). $C_6H_{18}N_3Be_3$ requires *M*, 291].

THE UNIVERSITY, BRISTOL.

[*Received, July* 27*th*, 1953.]