863. *Dimethylberyllium. Part III.* Reactions with some Compounds containing Reactive Hydrogen.*

By G. E. Coates, F. Glockling, and N. D. Huck.

Dimethylberyllium reacts with methylamine, dimethylamine, dimethylphosphine, methyl alcohol, methanethiol, or hydrogen chloride, forming methane and di-, tri-, or poly-meric products. Dimethylamine affords a trimeric compound $(MeBe{\cdot}NMe_2)_3$, to which a cyclic structure (I) has been assigned. Methyl alcohol gives a dimeric methoxide $(MeBe{\cdot}OMe)_2$ (VII), which readily disproportionates to dimethylberyllium and beryllium dimethoxide. The other substances studied lead to involatile or but slightly volatile products of doubtless polymeric constitution.

Like Grignard reagents and other active organometallic compounds, dimethylberyllium reacts with substances containing even very weakly acidic hydrogen, *e.g.*, primary and secondary amines, and alcohols. In very few instances, however, have the primary products been isolated or characterised. We have investigated several such reactions and find the products to be polymeric.

EXPERIMENTAL

Preparations and most of the manipulations of the compounds described below were carried out in a high-vacuum apparatus. The reagents were prepared and purified as described in Part I of this series (*J.*, 1952, 4496) and in Part I of the Trimethylgallium series (Coates, *J.*, 1951, 2003), with the exception of methanethiol, which was obtained by alkaline hydrolysis of methyl*iso*thiourea sulphate, the product being washed with dilute sulphuric acid, dried ($CaCl_2$), and fractionally condensed from a solution in dry propanol containing a little sodium propoxide. The v. p. of the product was 600 mm. at 0° (Davidson and Brown, *J. Amer. Chem. Soc.*, 1942, **64**, 316, give 601 mm.).

Compounds were not analysed but their compositions were established by quantitative synthesis, a procedure usual with this class of substance, since in working with a vacuum-apparatus nothing can be lost. Quantities are expressed as N-c.c. (c.c. reduced to N.T.P.).

cyclo-μμ′μ″-Trisdimethylaminotrimethyltriberyllium (I).—Dimethylamine (125·7 N-c.c.) was condensed on dimethylberyllium (56·5 N-c.c.); on warming to room temperature there was no visible reaction but only 68·7 N-c.c. of dimethylamine (v. p. 564 mm. at 0°) were recovered; hence 57·0 N-c.c. had reacted, to form a 1 : 1 addition compound. At room temperature the pressure in the reaction vessel increased very slowly, reaching 5 mm. (in a volume of 139·2 c.c.) after 4 hours. The reaction vessel was then slowly warmed, with a noticeable increase in the rate of gas evolution, until the compound melted at 44° with a vigorous evolution of gas. The mixture was then heated at 50° until gas evolution ceased, and the gas [identified as methane by its v. p. (83 mm. at −183°)] was transferred to a gas burette; 55·9 N-c.c. of methane were formed. Since 56·5 N-c.c. of dimethylberyllium reacted with 57·0 N-c.c. of dimethylamine and formed 55·9 N-c.c. of methane, the composition of the residue was $[BeNMe_3]_x$.

A larger quantity, prepared by the same method, was distributed among several sample tubes (for subsequent opening with a magnetic breaker) by distillation in a high vacuum. It was important to avoid overheating in this operation since thermal decomposition takes place rather easily with the formation of permanent gas and a non-volatile white residue.

The compound forms white crystals, m. p. 55—56°, which fume slowly in the air; it is rapidly hydrolysed by water. The v. p., from 60° to 100°, is given by the equation $\log_{10} p_{\text{mm.}} = 8{\cdot}605 - 2889/T$; hence the latent heat of vaporisation is 13·2 kcal./mole. Vapour-density measurements showed that a 63·2 mg. sample, equivalent to 20·8 N-c.c. of monomeric $MeBe{\cdot}NMe_2$ occupied a volume of 6·65 N-c.c. at 180° and 6·85 N-c.c. at 190°, corresponding to degrees of association of 3·13 and 3·04 respectively. Since some thermal decomposition takes place at these temperatures, the molecular weight was also measured with a Swiętoslawski differential ebulliometer (14-junction thermocouple) in carefully dried benzene [Found : *M*, 207·7 in 0·202% solution; 205·0 in 0·362% solution. $C_9H_{27}Be_3N_3$ requires *M*, 204·4]. The material is therefore cyclo-μμ′μ″-*trisdimethylaminotrimethyltriberyllium* (I).

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* Part II, preceding paper.

Heating equimolar quantities of (I) with trimethylamine caused no change in volume (reduced to N-c.c.) between $-20°$ and 50°, indicating absence of combination.

The thermal decomposition of (I) was examined by the prolonged heating of 7·8 N-c.c. at 180° until there was no further pressure change; a white solid of amorphous appearance was deposited and, on cooling, 3·5 N-c.c. of gas were removed and analysed by combustion (Found : CH_4, 98%; H_2, 2%).

Dry hydrogen chloride (120·7 N-c.c.) was condensed on (I) (9·8 N-c.c.), and the mixture allowed to warm to room temperature; no reaction appeared to take place. On slow heating, reaction began at 80° (decrease of pressure), and became quite rapid at higher temperatures. The reaction vessel was kept at 140° until the pressure was constant. The mixture was liquid at 140°, but gradually crystallised at room temperature. The residual gas consisted of hydrogen chloride (48·5 N-c.c.) and methane (9·8 N-c.c.); hence one mole of (I) had reacted with 7·4 moles of hydrogen chloride with the formation of one mole of methane.

Reaction of Dimethylberyllium with Methylamine.—Methylamine (36·7 N-c.c.) was condensed on dimethylberyllium (37·0 N-c.c.) at $-183°$. On gradual warming, a crystalline solid (III) appeared very soon after the methylamine melted ($-90°$), but almost immediately began to decompose with the evolution of gas and formation of a white amorphous solid (IV). When the temperature had reached 0° the gas evolution had practically ceased, and the pressure in the reaction vessel indicated that 16 N-c.c. of gas (identified as methane) had been formed; hence one mole of each reactant had produced slightly less than 0·5 mole of methane. On continued warming, the white solid melted at 10° with subsequent decomposition to form another white solid (V) and more methane. The reaction vessel was kept at 40° until the pressure was constant. The volatile contents were then pumped off (37·2 N-c.c.) and identified as methane (v. p. at $-183°$); hence one mole of methane had been formed from each mole of reactant. The non-volatile residue (V), when gradually heated, evolved gas very slowly at 80°. The decomposition became rapid at 110°, and was completed at 200°, 17·6 N-c.c. of methane being collected; hence a total of 54·8 N-c.c. of methane had been formed at this stage, *i.e.*, 1·47 moles per mole of dimethylberyllium. The residue (VI) evolved 14·1 N-c.c. of methane on hydrolysis; the total amount of methane produced was thus 68·7 N-c.c. (93% of the theoretical quantity for decomposition of all the dimethylberyllium).

cyclo-$\mu\mu'$-*Dimethoxydimethyldiberyllium* (VII).—Methyl alcohol (56·1 N-c.c.) was condensed on dimethylberyllium (57·1 N-c.c.) at $-183°$; on slow warming a violent reaction was observed just after the methyl alcohol had melted. On reaching room temperature the gas formed in this reaction was pumped off (56·7 N-c.c.) and identified as methane by its v. p. at $-183°$. The residue in the reaction vessel consisted of a white solid and a colourless liquid; it became entirely liquid at 90°, and, on cooling, completely solidified to clear crystals (VII), m. p. 23—25°. The v. p. of this substance could not be measured since at $>120°$ white solid appeared again and increased in quantity with increasing temperature. This effect was reversible but above 150° methane was irreversibly formed, so neither vapour pressures nor vapour densities were measured. The molecular weight was measured ebullioscopically in benzene (Found : M 103·6 in 0·159% solution; 112·0 in 0·265% solution. $C_4H_{12}O_2Be_2$ requires M, 110·2). cyclo-$\mu\mu'$-*Dimethoxydimethyldiberyllium* reacts slowly with moist air and vigorously with water, forming methane and white clouds of beryllium hydroxide.

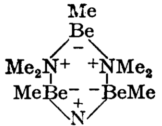
Reaction with Methanethiol.—Methanethiol (22·9 N-c.c.) was condensed on dimethylberyllium (22·7 N-c.c.) at $-183°$. When the mixture was allowed to warm to room temperature, reaction became rapid at about $-10°$ but was much less vigorous than that with methyl alcohol. Methane (23·5 N-c.c.) was collected and the white solid residue heated to 100° to promote any rearrangement which might occur. No change was apparent and on cooling white needles suggestive of dimethylberyllium were visible. In a repetition of this experiment the volatile material formed by heating the primary product to 140° was sublimed out of the reaction vessel. This material absorbed trimethylamine, to give a volatile crystalline solid, m. p. 36°, and was therefore dimethylberyllium (dimethylberyllium–trimethylamine has m. p. 36°; Part II).

Methylberyllium Chloride.—Hydrogen chloride (26·8 N-c.c.) was condensed on dimethylberyllium (27·1 N-c.c.) at $-183°$; on warming, no reaction occurred below $-5°$ since below this temperature the contents of the reaction vessel were always completely condensable in liquid oxygen. The reaction appeared to be complete after 1 hour's heating at 120—130°, and, on cooling, 26·7 N-c.c. of methane, containing no hydrogen chloride, were collected. The white residue therefore had the composition MeBeCl. The vapour pressure of this material, from 120° to 190°, is given by $\log_{10} p_{mm} = 6{\cdot}52—2614/T$ (p = 1 mm. at 128°).

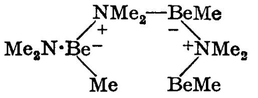
DISCUSSION

The 1 : 1 co-ordination compound between dimethylberyllium and dimethylamine is probably very similar to the compound $\mathrm{Me_2\overset{-}{Be},\overset{+}{N}Me_3}$ described in Part II; the presence of a reactive hydrogen atom in the secondary amine renders it unstable, in contrast to the trimethylamine compound, and vigorous elimination of methane occurs at the low melting point (44°). The trimeric decomposition product very probably has a cyclic structure (I) like those assigned to some similar compounds of aluminium (Brown and Davidson, *loc. cit.*) and gallium (Coates, *loc. cit.*). The alternative, open-chain structure (II) is rejected since it contains a bicovalent beryllium atom and would be expected to co-ordinate with trimethylamine, which it does not. Further, no other example of a solid or liquid compound containing bicovalent beryllium is known.

The reaction between (I) and hydrogen chloride, in which only one mole of methane is formed from a mole of (I) with absorption of between 7 and 8 moles of hydrogen chloride, is



(I)



(II)

evidently much more complex than the reaction of the analogous aluminium compound (Brown and Davidson, *loc. cit.*)

$$(\mathrm{Me_2Al{\cdot}NMe_2})_2 + 8\mathrm{HCl} = 2\mathrm{Me_2\overset{+}{N}H_2\}\overset{-}{Al}Cl_4} + 4\mathrm{CH_4}$$

Dimethylphosphine is much less reactive than dimethylamine towards dimethylberyllium and, unlike both dimethylamine and trimethylphosphine, does not appear even to form a co-ordination compound. Heating equimolar quantities to 190° for 5 hours resulted in the formation of about 0·5 mole of methane and non-volatile, evidently polymeric material, insoluble in benzene.

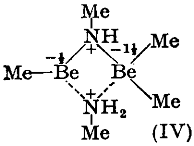
The complex four-stage reaction between dimethylberyllium and methylamine well illustrates the complications due to the presence of two reactive groups instead of one. The initial formation of a 1 : 1 co-ordination compound

$$\mathrm{Me_2Be} + \mathrm{NH_2Me} \longrightarrow \mathrm{Me_2\overset{-}{Be}{\cdot}\overset{+}{N}H_2Me}\ \text{(III)}$$

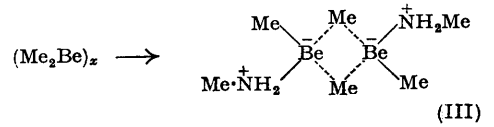
is followed by three successive decompositions at increasing temperatures :

$$\begin{aligned} 2\mathrm{Me_2\overset{-}{Be}{\cdot}\overset{+}{N}H_2Me} &\longrightarrow (\mathrm{Me_2\overset{-}{Be}{\cdot}\overset{+}{N}H_2Me};\ \mathrm{MeBe{\cdot}NHMe})\ \text{(IV)} + \mathrm{CH_4} \\ \text{(IV)} &\longrightarrow 2(\mathrm{MeBe{\cdot}NHMe})_x\ \text{(V)} + \mathrm{CH_4} \\ 2\text{(V)} &\longrightarrow (\mathrm{MeBe{\cdot}NHMe};\ \mathrm{Be{:}NMe})_y\ \text{(VI)} + \mathrm{CH_4} \end{aligned}$$

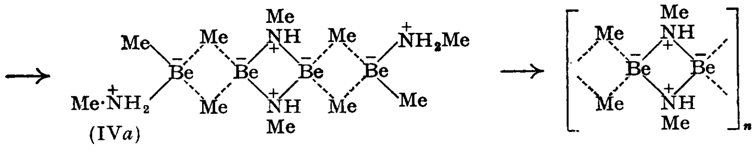
With the exception of the unstable compound (IV) which melts with decomposition at 10°, all these substances are solid and amorphous and are doubtless polymeric. Although (IV) may be a lattice compound between $\mathrm{Me_2\overset{-}{Be}{\cdot}\overset{+}{N}H_2Me}$ and MeBe·NHMe, this seems unlikely since the latter component is itself likely to be to some degree polymeric (*e.g.*, it was non-volatile at 80°). A fairly simple constitution is indicated by the observation that it melts



(IV)



(III)



(IVa)

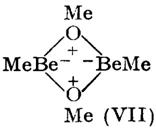
(V)

relatively sharply, though with decomposition, at a low temperature; the structure (IV) is suggested (broken lines represent half bonds, as in Part II). Another possibility is that the beryllium atoms are bridged by methyl groups (see (IV*a* and V) as in dimethylberyllium itself, the methyl bridge persisting to quite a late stage in the decomposition. However, the simpler alternative, which is similar to the structure given for $(Me_2Be)_2(NMe_3)_3$ in Part II, is preferred.

Since the hydrogen of alcohols is more easily replaced than that of amines it was not surprising to find that dimethylberyllium reacts violently with methanol, even at the melting point of the latter (−98°). The formation of a mixture of liquid and solid during the preparation of methylberyllium methoxide is no doubt due to its further reaction with methyl alcohol, followed, during the heating at 80—90°, by reaction between dimethylberyllium and beryllium dimethoxide :

(*a*) $Me_2Be + Me{\cdot}OH \longrightarrow MeBe{\cdot}OMe + CH_4$
(*b*) $MeBe{\cdot}OMe + MeOH \longrightarrow Be(OMe)_2 + CH_4$
(*c*) $Me_2Be + Be(OMe)_2 \longrightarrow 2MeBe{\cdot}OMe$

A similar observation was made during the preparation of dimethylaluminium methoxide (Brown and Davidson, *loc. cit.*) since trimethylaluminium readily loses all three methyl groups on reaction with alcohols; the reaction between trimethylgallium and methyl alcohol, however, proceeds straight to the final product dimethylgallium methoxide (Coates, unpublished observation) since the remaining methyl groups are relatively unreactive. Methylberyllium methoxide is sufficiently volatile to be distilled in a high vacuum, but on heating, particularly above 120°, disproportionates to a white solid and a colourless liquid, becoming homogeneous again on slow cooling. At temperatures above 120° the vapour pressure of the mixture of solid and liquid is somewhat less than that of dimethylberyllium itself, which is in accordance with a reversal of reaction (*c*). In boiling benzene the substance is dimeric, like dimethylaluminium methoxide and dimethylgallium methoxide, and is similarly assigned a cyclic structure (VII).


(VII)

Although in hydroxylic solvents methanethiol is more acidic than methyl alcohol, the former reacts with dimethylberyllium much less energetically than the latter, methane evolution becoming rapid only at about −10° instead of at −100°. Similarly, Coates (unpublished observations) has observed that trimethylgallium reacts with methanethiol more slowly than with methanol, and with thiophenol more slowly than with phenol.

Anhydrous hydrogen chloride reacts much more slowly with dimethylberyllium than any of the other compounds investigated. Evidence has been given for the view that amines containing reactive hydrogen combine with dimethylberyllium first by the formation of a co-ordination compound. It is not improbable that compounds containing hydroxy- and thiol groups react by a similar mechanism. Now there is no reason why the formation of co-ordination compounds of this type should require an activation energy, unless ligands already present have to be displaced. Consequently the interaction of dimethylberyllium (or, for example, trimethylboron) with donor molecules should be rapid and determined only by the free-energy change. Methyl chloride has been shown by Brown and Davidson (*loc. cit.*) not to react with trimethylaluminium, which is a very strong acceptor, and can thus be considered devoid of donor properties. By the well-known influence of electronegativity of substituents on donor properties, hydrogen chloride must be a still weaker donor; therefore any reaction with dimethylberyllium must involve the breaking of at least one covalent bond, and therefore requires a significant activation energy. As a result the reaction is relatively slow. The product, methylberyllium chloride, is a white solid, less volatile than dimethylberyllium, and evidently highly polymerised. The formation of a layer of relatively non-volatile product covering the dimethylberyllium may also account in part for the low reaction rate.

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