Di-tert.-butylberyllium and Beryllium Hydride.

By G. E. Coates and F. Glockling.

Di-*tert.*-butylberyllium, prepared from *tert.*-butylmagnesium chloride and beryllium chloride, decomposes rapidly above 100° to give mainly beryllium hydride, BeH_2, and *iso*butene. The hydride, whichis stable up to 240°, forms bisdimethylaminoberyllium with dimethylamine, and beryllium borohydride with diborane, and is slowly hydrolysed by water.

DIMETHYLBERYLLIUM decomposes at an appreciable rate only when heated to 190—200° (Coates, Glockling, and Huck, *J.*, 1952, 4496). Progressive replacement of the hydrogen atoms by methyl groups profoundly affects the thermal stability. Thus diethylberyllium decomposes above about 85° in a complex reaction giving a variety of products (Goubeau and Rodewald, *Z. anorg. Chem.*, 1949, **258**, 162). Replacement of another hydrogen results in still lower thermal stability, since di*iso*propylberyllium (Coates and Glockling, *J.*, 1954, 22) decomposes above 50° in a much cleaner reaction in which *iso*propylberyllium hydride and propene are the main products obtained at 200°. The further pyrolysis of this hydride is complex and results in no well-defined solid products.

The present work describes the final member of this series, di-*tert.*-butylberyllium, which was prepared from *tert.*-butylmagnesium chloride and beryllium chloride in ether. Complete separation from ether was not achieved but, even when combined with 45 mole % of ether, it begins to decompose at about 50°. Material of this composition formed coloured colloidal solutions, from which metallic beryllium slowly separated, when allowed to stand at room temperature for several weeks. Rather surprisingly this was not observed when the ether content had been reduced to 37%, but decomposition was still observed at 40—50°.

Substitution of hydrogen by methyl groups thus causes a progressive decrease in thermal stability in the order : $Me_2Be > (MeCH_2)_2Be > (Me_2CH)_2Be > (Me_3C)_2Be$. In contrast with results obtained with di*iso*propylberyllium no half-hydride ($Me_3C \cdot BeH$) was isolated from the thermal decomposition of di-*tert.*-butylberyllium, and the reaction proceeded smoothly to give mainly *iso*butene and beryllium hydride which, however, retained some *tert.*-butyl groups as shown by its formation of a little *iso*butane on hydrolysis : $(Me_3C)_2Be \longrightarrow BeH_2 + 2Me_2C{=}CH_2$. The proportion of *tert.*-butyl groups to hydrogen atoms in the product diminished as the temperature of the pyrolysis was increased. After pyrolysis at 150° the product contained 89 mole % of beryllium hydride and 96% at 210°. Pyrolysis at 240—290° caused increasing liberation of hydrogen which became very rapid at about 300°.

Several properties of beryllium hydride as prepared in this way are in marked contrast to those recorded by Schlesinger *et al.* (*J. Amer. Chem. Soc.*, 1951, **73**, 4585) who obtained it from dimethylberyllium and lithium aluminium hydride in ether. Their product apparently differed from ours mainly in its ether content (89 mole % of beryllium hydride; the remainder was assumed to be ether), and decomposed quite rapidly at 125° giving hydrogen, ether, and ethane. This great difference in thermal stability is very surprising, and we cannot account for it unless it is due to attack on the ether in the manner of organolithium compounds. A further remarkable difference is the behaviour on hydrolysis. Water vapour reacted vigorously with Schlesinger's material even at −196°, but our hydride reacted slowly and incompletely with water at room temperature or 50°, and addition of hydrochloric acid was necessary to complete the hydrolysis. This inertness towards water was most marked with the purest (96 mole %) beryllium hydride.

Beryllium hydride reacted slowly and quantitatively at 155° with dimethylamine, forming hydrogen and the known compound, bisdimethylaminoberyllium $\{Be(NMe_2)_2\}_3$ (Coates and Glockling, *loc. cit.*). Conversion of beryllium hydride into the volatile beryllium borohydride BeB_2H_8 (Burg and Schlesinger, *J. Amer. Chem. Soc.*, 1940, **62**, 3425 (by reaction with diborane at 95° was slow and incomplete, and was complicated by

partial decomposition of the diborane, although sufficient crystalline material was obtained for identification. The thermal stability of beryllium hydride prepared from di-*tert.*-butylberyllium, appears to be only a little less than that of magnesium hydride prepared by the pyrolysis of primary magnesium alkyls (Wiberg and Bauer, *Chem. Ber.*, 1952, **85**, 593). Magnesium hydride is also quite involatile and forms a borohydride with diborane, but in contrast to (our) beryllium hydride it is vigorously hydrolysed by water or methanol. There was no evidence of reaction between trimethylamine and beryllium hydride, even after 6 hrs. with an excess of amine at 210°. The heat of polymerisation of the hydride is apparently too great to allow the depolymerisation which must necessarily precede co-ordination to trimethylamine. Only strong donors like trimethylamine are able to depolymerise dimethylberyllium (Coates and Huck, *J.*, 1952, 4501), and since metal hydrides tend to be more strongly polymerised than metal alkyls (see Coates and Glockling, *loc. cit.*) the failure of trimethylamine to react with beryllium hydride is not very surprising. It is interesting that dimethylmagnesium takes up trimethylamine reversibly, the dissociation pressure being given by $\log_{10} p$ (mm.) $= 11\cdot66 - 3316/T$; $\Delta H = 15\cdot2$ kcal./mole. Even though combination occurs in this case, no monomeric or volatile compound is formed. Aluminium affords two volatile compounds AlH_3,NMe_3 and $AlH_3,2NMe_3$ (Wiberg, Graf, and Uson, *Z. anorg. Chem.*, 1953, **272**, 221; Stecher and Wiberg, *Ber.*, 1942, **75**, 2002).

Trimethylamine displaces ether from di-*tert.*-butylberyllium, though not completely under the conditions employed. The major product is a crystalline compound, readily volatile and solid at room temperature, which is almost certainly the highly symmetrical di-*tert.*-butylberyllium–trimethylamine $(Me_3C)_2\overset{-}{Be}\cdot\overset{+}{N}Me_3$.

<div align="center">EXPERIMENTAL</div>

Di-tert.-*butylberyllium.*—Anhydrous beryllium chloride (8·0 g.) in ether (150 c.c.) was added slowly to a well-stirred solution under nitrogen of *tert.*-butylmagnesium chloride prepared from magnesium (19·2 g.) and *tert.*-butyl chloride (74 g.) in ether (500 c.c.). Stirring was continued for 2 hr. after addition of the beryllium chloride, then most of the ether was removed by pumping at room temperature. High-vacuum distillation of the di-*tert.*-butylberyllium and much ether was accomplished by heating with continuous pumping at 60° for 2 days, then at 75° for 1 day. The product was transferred to a special reflux-distillation flask (Coates and Glockling, *loc. cit.*) by heating at 50° with continuous pumping, leaving a dark residue of metallic appearance. Reflux distillation was carried out for 4 hr. at 35—40°, followed by 4 hr. at room temperature with the condenser cooled to −40°. The material was then distributed between a series of sample tubes as described previously (*idem, ibid.*). It decomposed slowly at room temperature, giving what appeared to be a colloidal solution of beryllium varying in colour from reddish-blue to light brown. Specimens were therefore stored in a vacuum-flask containing some solid carbon dioxide. The residue from the final distillation was a colourless, highly viscous oil (∼0·5 c.c.), involatile at room temperature, and unaffected by short exposure to air. It was not investigated further.

Analysis of Di-tert.-*butylberyllium by Hydrolysis.*—The contents of a sample tube (0·1578 g.) were distilled at room temperature (3 hr.) into an evacuated trap cooled in liquid air. After the distillate had been exposed to water vapour for several hours, a large excess of water was condensed in the trap, and the reaction allowed to proceed gently, the trap being cooled occasionally. Finally the water was boiled and an excess of dilute hydrochloric acid condensed on the mixture to complete the hydrolysis. No hydrogen was formed. The gaseous hydrolysis products and excess of water were fractionally condensed in two traps cooled in solid carbon dioxide (−78·5°) in series with two in methylene chloride slush baths (−96°) and a liquid-air trap. Ice in the first trap was melted twice to remove dissolved gases. After 90 min. *iso*-butane (formed by hydrolysis of di-*tert.*-butylberyllium), which had mostly condensed in the ampoule cooled in liquid air, was refractionated in the same manner, as were the contents of the ampoules cooled to −96°, containing mainly ether. The final quantities were: ether (15·8 N-c.c.; v. p. at 0°, 184 mm.) and *iso*butane (39·2 N-c.c., v. p. at −78·5°, 20 mm.), unaffected by dilute aqueous potassium permanganate. Thus the material has the average composition; $(Me_3C)_2Be$, 0·806Et_2O, *i.e.*, 55·4 mole % of di-*tert.*-butylberyllium. A further

analysis, by the same procedure, gave the composition as 57·2 mole % of di-*tert.*-butylberyllium. The beryllium chloride formed by hydrolysis was shown to be free from magnesium by chromatographic absorption of the acetate on Whatman No. 1 paper. Pure magnesium and beryllium acetates were used for comparison, the detecting agent being 8-hydroxyquinoline. The solvent used was acetone (80 parts), acetic acid (2 parts), and water (10 parts, all by volume). The R_F value (0·51—0·69) agreed well with that for pure beryllium acetate (0·53—0·70). The R_F value for magnesium acetate was 0·27—0·38.

Part of the material containing 55·4 mole % of di-*tert.*-butylberyllium was again introduced into the reflux still and analysed after 24 hr.' continuous pumping at room temperature (condenser at −20°). The product then contained 63·3 mole % if di-*tert.*-butylberyllium, the remainder being ether. This preparation remained clear after two months at room temperature.

Beryllium Hydride.—*Pyrolysis of di-*tert.-*butylberyllium.* (a) *At* 150° : Di-*tert.*-butylberyllium (0·3137 g., consisting of 31·4 N-c.c. of ether + 39·0 N-c.c. di-*tert.*-butylberyllium) was introduced into the high-temperature bulb (Schlesinger and Burg, *J. Amer. Chem. Soc.*, 1937, **59**, 780) and slowly heated. Decomposition became quite rapid at 100°, and at 150° a white apparently non-crystalline solid formed. After 5 hr. at 150° the gaseous products (96·5 N-c.c.), which were completely condensable in liquid air, were separated and the residue was re-heated at 150° for 5 hr. with continuous pumping through a liquid-air trap. The entire gaseous products (100·8 N-c.c.) were fractionally condensed, using the same sequence of traps as in the hydrolysis experiments, giving ether (32·8 N-c.c.; v. p. at 0°, 186 mm.) and *iso*butene (66·8 N-c.c.; v. p. at −78·5°, 23 mm.). The latter was incompletely absorbed when shaken with excess of aqueous potassium permanganate (residual vol., 5 N-c.c.). The two ampoules, cooled to −78·5°, contained 1 N-c.c. of unidentified gas.

The residue was remarkably resistant to hydrolysis; keeping it overnight with excess of water produced only 43 N-c.c. of hydrogen. With dilute hydrochloric acid the total volume of hydrogen produced was 61·5 N-c.c. (completely oxidised by copper oxide at 300°). Fractionation of the condensable gases in the usual manner gave *iso*butane (7·7 N-c.c.) (not absorbed by aqueous potassium permanganate) and ether (∼0·4 N-c.c.). The hydrogen and *iso*butane values obtained by hydrolysis thus correspond to 89 mole % of beryllium hydride.

(b) *At* 210° : Di-*tert.*-butylberyllium (0·8114 g. consisting of 81·2 N-c.c. of ether + 101 N-c.c. of di-*tert.*-butylberyllium) was heated at 150° in the high-temperature bulb until no further increase of pressure occurred. Ether and *iso*butene were removed and the temperature was raised slowly. Hydrogen produced was removed at intervals with a Töpler pump. A slight white deposit was formed on the upper parts of the bulb and after 1 hr. at 210° only 1·8 N-c.c. of hydrogen were formed. Hydrolysis of the white residue with water proceeded to only a small extent even on boiling; with excess of 0·1N-hydrochloric acid hydrogen was evolved quite briskly, but without apparent heat evolution. Even in acid solution evolution of hydrogen continued for some hours at room temperature before the solution became quite clear. The volume of hydrogen obtained was 183·4 N-c.c. Fractional condensation of the condensable hydrolysis products gave *iso*butane (5·2 N-c.c.; not absorbed by potassium permanganate) and ether (1·1N-c.c.). The composition thus corresponds to 96·3 mole % of beryllium hydride.

Reaction of Beryllium Hydride with Dimethylamine : Formation of Bisdimethylaminoberyllium. Di-*tert.*-butylberyllium (0·1532 g., consisting of 12·0 N-c.c. of ether + 20·6 N-c.c. of di-*tert.*-butylberyllium) was heated to 150° in the high-temperature bulb, and the gaseous products were separated. The residue was then heated at 200° for 2 hr. with continuous pumping. The total gaseous products (52·6 N-c.c.) were separated by methods already described, giving ether (12·9N-c.c.), *iso*butene (35·9 N-c.c.), and saturated hydrocarbons (3·3N-c.c.). Dimethylamine (75·5N-c.c.) was added to the beryllium hydride and the mixture heated at 160° for 4 hr. The hydrogen formed (23·5 N-c.c.) was separated, and heating continued at 155° for a further 6 hr., the white solid beryllium hydride having then entirely disappeared. The total volume of hydrogen was 33·8 N-c.c., and of condensable gases (excess of dimethylamine and a little *iso*butane) 42·0 N-c.c. The residue in the high-temperature bulb formed colourless well-defined crystals of bisdimethylaminoberyllium, m. p. 94° (cf. Coates and Glockling, *loc. cit.*, who prepared and characterised this compound).

Reaction of Beryllium Hydride with Diborane : Formation of Beryllium Borohydride.—Di-*tert.*-butylberyllium (0·2294 g. containing 18 N-c.c. of ether + 30·9 N-c.c. of di-*tert.*-butylberyllium) was pyrolysed first at 150° and then for 2 hr. at 200°. Diborane (31·1 N-c.c.) was condensed on the hydride, and the mixture heated at 95° for 6 hr. Hydrogen (6·4 N-c.c.), presumably formed by thermal decomposition of diborane, was separated. Beryllium boro-

hydride (~2 N-c.c.; v. p. at 20°, 5 mm.) was isolated by passing the condensable volatile components through a trap at −78°.

Reaction of Ethereal Di-tert.-*butylberyllium with Trimethylamine.*—Di-*tert.*-butylberyllium (20·8 N-c.c. of ether + 35·7 N-c.c. of di-*tert.*-butylberyllium) was allowed to stand overnight with trimethylamine (108·5 N-c.c.). Volatile products were separated with the container cooled to −20°. Ether was separated from the gaseous mixture by passing it through traps cooled to −95°, and the trimethylamine returned to the reaction vessel. This procedure was twice repeated with heating at 40° for 4 hr. Fractional condensation and absorption of excess of trimethylamine in acid gave ether (18·4 N-c.c.), *iso*butene (3·5 N-c.c.), and excess of trimethylamine (90·1 N-c.c.). Hence 18·4 c.c. of trimethylamine were combined. The inhomogeneous residue consisted of a colourless liquid (probably unused di-*tert.*-butylberyllium and its ether complex) and a colourless crystalline solid of m. p. 42—47°, which is considered to be di-*tert.*-butylberyllium–trimethylamine. Both the solid and the liquid component were fairly volatile at room temperature and could not be separated. Hydrolysis of the mixture with dilute hydrochloric acid gave ether (3·1 N-c.c.) and *iso*butane (63·9 N-c.c.). In spite of various attempts this reaction could not be made to go to completion with displacement of all the ether.

UNIVERSITY OF BRISTOL.
Present addresses : (G. E. C.)UNIVERSITY OF DURHAM ;
          (F. G.) UNIVERSITY OF LIVERPOOL.